Statistical Methods and Thermodynamics

Chem 530b: Lecture Notes

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Room: Sterling Chemistry Laboratories (SCL) 21
Tuesday and Thursday 11:35 – 12:50 am
Yale University - Department of Chemistry
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1 Syllabus

Statistics, data science and quantum behavior are likely to be key themes that will dominate the way science and engineering develop over the next few decades. This course highlights their impact on molecules and materials. Only an approach combining theoretical and computational methods can be expected to succeed in the face of problems of such difficulty hence the hands on structure of the course. The goal is to introduce the fundamental concepts and ideas of quantum statistical mechanics to elucidate gas phase and condensed phase behavior, as well as to establish a microscopic derivation of statistical thermodynamics. Classical results are obtained according to the classical limit of the quantum mechanical expressions. Topics include ensembles, Fermi, Bose and Boltzmann statistics, density matrices, mean field theories, phase transitions, chemical reaction dynamics, time-correlation functions, Monte Carlo simulations and Molecular Dynamics simulations.

The official textbook for this class is:
R1: ”Introduction to Modern Statistical Mechanics” by David Chandler (Oxford University Press). Ch. 3-8.

Additional textbooks on reserve and the Kline Science and Engineering library include:
R2: ”Introduction to Statistical Thermodynamics” by T.L. Hill (Addison Wesley),
R3: ”Statistical Mechanics” by D. McQuarrie (Harper & Row),
R4: ”Fundamentals of Statistical and Thermal Physics” by F. Reif (McGraw Hill),
R5: ”Statistical Mechanics” by R. Kubo (Noth-Holland Publishing Company),
R6: ”A course in Statistical Mechanics” by H.L. Friedman (Prentice-Hall),
R7: ”Statistical Mechanics: Theory and Molecular Simulation” by Mark E. Tuckerman (Oxford University Press)

All these references are on reserve at the Kline library (KBT) to allow everyone equal usage. References to specific pages of the textbooks listed above are indicated in the notes as follows: R1(190) indicates “for more information see Reference 1, Page 190”.

The lecture notes are online at http://ursula.chem.yale.edu/ batista/classes/vaa/index.html
A useful search engine for mathematical and physical concepts can be found at http://scienceworld.wolfram.com/physics/

Grading
The final exam for this class will be on Tuesday December 17, 9 am (SCL 21).
Grading evaluation is the same for both undergraduate and graduate students. The intended population of the course includes first year graduate students and senior undergraduates.
homework and assignments (30%),
two mid-terms (50%) on 9/17 and 10/22.
final exam (20%).
Lectures on Dec 10 and Dec 12 will make up for lectures not offered on Oct 29 and Nov 19.
Homework will be assigned through Yale canvas.
Tentative Distribution of Topics
1. Aug. 29 - Sept. 12: The Statistical Method and Ensembles (Chapter 3)
2. Exam 1: Sept 17.
3. Sept. 19 - Oct. 3: Ideal Systems (Chapter 4, and refs)
4. Oct. 8 - Oct. 15 Theory of Phase Transitions (Chapter 5, and refs)
9. Oct 31- Nov 7: Monte Carlo Methods in Statistical Mechanics (Chapter 6, and refs)
10. Nov. 12 - Nov. 21: Classical Fluids and Solvation (Chapter 7, and refs)
12. Dec. 3, 5, 10, 12: Non-Equilibrium and Molecular Dynamics (Chapter 8 and refs)
13. Dec. 17: Final exam (9:00am, SCL 21).

Contact Information
Office hours will be held at SCL 162 by appointment at your convenience.
You can send me email to victor.batista@yale.edu if you have any question.
2 Introduction

Statistical Mechanics is a theory that establishes the connection between the observed properties of systems with many degrees of freedom and the microscopic quantum mechanical properties of the elementary constituents of the systems (e.g., electrons, atoms and molecules). Such a theory builds upon the description of matter provided by quantum mechanics and provides the molecular foundation of Thermodynamics. Contrary to evaluating the precise N-particle dynamics of macroscopic systems, Statistical Mechanics describes the properties of systems in terms of the statistics of possible microscopic states. The description of measurements is, therefore, given in terms of the ensemble average of expectation values associated with the quantum states that constitute such an ensemble.

Macroscopic systems consist of an enormously large number of degrees of freedom (e.g., $\sim 10^{23}$ electrons, atoms or molecules), so many degrees of freedom that in practice it is impossible to prepare such systems in a well defined microscopic quantum state (i.e., in a pure quantum state). Instead, they are usually prepared in thermodynamic states (i.e., in a statistical mixtures of quantum states) characterized by a few physical quantities (e.g., the temperature, the pressure, the volume and the number of particles).

To describe macroscopic systems in terms of quantum mechanics it is, therefore, necessary to incorporate into the formalism the incomplete information about the state of the system. The most natural approach is provided by appealing to the concept of probability. This can be accomplished by introducing the density operator, a very useful mathematical tool which facilitates the simultaneous application of the postulates of quantum mechanics and the results of probability calculations.

3 Pure States

A pure state is defined as a state that can be described by a ket vector $|\psi >$. Such state evolves in time according to the time dependent Schrödinger equation,

$$i\hbar \frac{\partial |\psi >}{\partial t} = \hat{H}|\psi >,$$

where $H$ is the Hamiltonian operator. Note that Eq. (1) is a deterministic equation of motion that allows one to determine the state vector at any time, once the initial conditions are provided. The state vector $|\psi >$ provides the maximum possible information of the system. It can be expanded in the basis set of eigenstates $|\phi_k >$ of an arbitrary Hermitian operator $\hat{o}$ that represents an observable of the system,

$$|\psi > = \sum_k a_k |\phi_k >,$$

$^1$If you are starting to get the hang of the bra-ket notation, you can go through the notes recommended by Jonah Pearl.
where \(|\phi_k >\) are the eigenstates of \(\hat{o}\), with eigenvalues \(o_k\),

\[
\hat{o}|\phi_k > = o_k|\phi_k >.
\]

The expansion coefficients \(a_k\), introduced by Eq. (2), are complex numbers that can be written in terms of real amplitudes \(p_k\) and phases \(\theta_k\) as follows,

\[
a_k = \sqrt{p_k}e^{i\theta_k}.
\]

The coefficients \(p_k\) determine the probability of observing the eigenvalue \(o_k\) when the system is in state \(|\psi >\). The expectation value of \(\hat{o}\) is

\[
<\psi|\hat{o}|\psi> = \sum_k p_k o_k,
\]

i.e., the average of expectation values associated with states \(|\phi_k >\).

The expectation value of any arbitrary operator \(\hat{A}\), which does not share a common set of eigenstates with \(\hat{o}\), can be computed in the basis set of eigenstates of \(\hat{o}\) as follows,

\[
<\psi|\hat{A}|\psi> = \sum_k p_k <\phi_k|\hat{A}|\phi_k> + \sum_k \sum_{j \neq k} \sqrt{p_k p_j}e^{i(\theta_j - \theta_k)} <\phi_k|\hat{A}|\phi_j>.
\]

Note that such an expectation value is not only determined by the average of expectation values associated with states \(k\) (i.e., the first term in the r.h.s of Eq. (6)), but also by the second term in that equation. Such second term is responsible for interferences, or coherences, between states \(|\phi_k >\) and \(|\phi_j >\) as determined by the phases \(\theta_k\) and \(\theta_j\).

Consider a large number of \(N\) replicas of the system, all of them described by the same state vector \(|\psi >\). Note that such collection of \(N\) replica systems is also described by a pure state. Therefore, the ensemble averages associated with the observables \(\hat{o}\) and \(\hat{A}\) of such a pure state will coincide with the expectation values given by the equations Eq. (5) and Eq. (6), respectively.

## 4 Statistical Mixture of States

The collection of a large number \(N\) of independently prepared replicas of the system is called an ensemble. An ensemble of \(N\) replicas of systems is in a statistical mixture of states \(|\phi_k >\), with probabilities \(p_k\), when \(n_k\) members of the ensemble are in state \(|\phi_k >\), with \(p_k = n_k/N\). Note that each member of the ensemble is in a specific state \(|\phi_k >\), not in a coherent superposition of states as described by Eq. (2). Therefore, the ensemble averages associated with the observables \(\hat{o}\) and \(\hat{A}\) are

\[
A = \sum_k p_k <\phi_k|\hat{A}|\phi_k>.
\]

and

\[
o = \sum_k p_k <\phi_k|\hat{o}|\phi_k> = \sum_k p_k o_k.
\]
respectively. Note that the ensemble average \( o \), introduced by Eq. (8), coincides with the ensemble average of the pure state described by Eq.(5). However, the ensemble average \( A \), introduced by Eq. (7), does not coincide with the corresponding ensemble average of the pure state, introduced by Eq. (6). As a matter of fact, it coincides only with the first term of Eq. (6) since the second term of the r.h.s. of Eq. (6) is missing in Eq. (7). Therefore, in a statistical mixture there are no contributions to the ensemble average coming from interferences between different states (e.g., interferences between states \( |\psi_k\rangle \) and \( |\psi_j\rangle \)).

The statistical mixture introduced in this section, is also equivalent to an ensemble of N replicas of the system in incoherent superposition of states represented as follows,

\[
|\psi(\xi)\rangle = \sum_k \sqrt{p_k} e^{i\theta_k(\xi)} |\phi_k\rangle,
\]

where the phases \( \theta_k(\xi) \) are distributed among the different members \( \xi \) of the ensemble according to a uniform and random distribution.

In the remaining of this section we introduce the most important types of ensembles by considering systems with only one species of molecules. Additional details for multicomponent systems are considered later.

In the **canonical ensemble** all of the replica systems are in thermal equilibrium with a heat reservoir whose temperature is \( T \). This ensemble is useful for comparisons of the ensemble averages with measurements on systems with specified number of particles \( N \), volume \( V \) and temperature \( T \). It is central to *Monte Carlo simulations*, an important approximation method of Statistical Mechanics.

In the **microcanonical ensemble** all of the replica systems have the same energy \( E \) and number of particles \( N \). This ensemble is no very simply applicable to comparisons with systems we usually study in the laboratory, since those are in thermal equilibrium with their surroundings. However, the microcanonical ensemble is centrally involved in *Molecular Dynamics simulations* which is one of the most important approximation methods of Statistical Mechanics.

In the **grand canonical ensemble** all of the replica systems are in thermal equilibrium with a heat reservoir whose temperature is \( T \) and they are also in equilibrium with respect to exchange of particles with a “particle” reservoir where the temperature is \( T \) and the chemical potential of the particles is \( \mu \). This ensemble is useful for comparisons to measurements on systems with specified \( \mu, T \) and \( V \).

**Exercise 1**: Compute the ensemble average \( \bar{A} \) associated with the incoherent superposition of states introduced by Eq. (9) and verify that such an average coincides with Eq. (7).

## 5 Density Operator

In this section we show that ensemble averages for both pure and mixed states can be computed as follows,

\[
A = Tr \{ \hat{\rho} \hat{A} \},
\]

(10)
where $\rho$ is the density operator

$$\hat{\rho} = \sum_k p_k |\phi_k><\phi_k|.$$  

(11)

Note that, in particular, the density operator of an ensemble where all of the replica systems are described by the same state vector $|\psi\rangle$ (i.e., a pure state) is

$$\hat{\rho} = |\psi><\psi|.$$  

(12)

Eq. (10) can be proved first for a pure state $|\psi\rangle = \sum_k a_k |\phi_k\rangle$, where $|\phi_k\rangle$ constitute a complete basis set of orthonormal states (i.e., $<\phi_k|\phi_k'> = \delta_{kk'}$), by computing the Tr{$\hat{\rho}\hat{A}$} in such representation as follows,

$$A = \sum_{k'} <\phi_{k'}|\psi><\psi|\hat{A}|\phi_{k'}>.$$  

(13)

Substituting the expansion of $|\psi\rangle$ into Eq. (13) we obtain,

$$A = \sum_{k'} \sum_j \sum_k <\phi_{k'}|\phi_k > a_k a_j^* <\phi_j|\hat{A}|\phi_{k'} >,$$

(14)

and since $<\phi_{k'}|\phi_k > = \delta_{kk'}$,

$$A = \sum_k p_k <\phi_k|\hat{A}|\phi_k > + \sum_k \sum_{j\neq k} \sqrt{p_k p_j} e^{i(\theta_k - \theta_j)} <\phi_j|\hat{A}|\phi_k >,$$

(15)

where we have substituted the expansion coefficients $a_j$ in accord with Eq. (4). Equation (15) is identical to Eq. (6) and, therefore, Eq. (10) is identical to Eq. (6) which defines an ensemble average for a pure state.

Eq. (10) can also be proved for an arbitrary mixed state defined by the density operator introduced by Eq. (11), by computing the Tr{$\hat{\rho}\hat{A}$} as follows,

$$A = \sum_{k'} \sum_k p_k <\phi_{k'}|\phi_k > <\phi_k|\hat{A}|\phi_{k'} > = \sum_k p_k <\phi_k|\hat{A}|\phi_k >,$$

(16)

which is identical to Eq. (7).

**Exercise 2:**

(A) Show that Tr{$\hat{\rho}$}=1 for both mixed and pure states.

(B) Show that Tr{$\hat{\rho}^2$}=1 for pure states.

(C) Show that Tr{$\hat{\rho}^2$} $\leq$ 1 for mixed states.

Note that the Tr{$\hat{\rho}^2$} is, therefore, a measurement of decoherence (i.e., lost of interference between the various different states in the ensemble). When the system is in a coherent superposition state, such as the one described by Eq. (2), Tr{$\hat{\rho}^2$}=1. However, Tr{$\hat{\rho}^2$} $\leq$ 1 when the system is in an incoherent superposition of states such as the one described by Eq. (9).
6  Time-Evolution of Ensembles

The evolution of systems in both pure and mixed states can be described according to the following equation:

\[ \frac{\partial \hat{\rho}}{\partial t} = -[\hat{\rho}, \hat{H}] / \hbar. \]  

(17)

**Exercise 3**: Using the equation of motion for a state vector \(|\psi\rangle\) (i.e., Eq. (1)), show that Eq. (17) describes the time evolution of \(\hat{\rho}\) for a pure state.

**Exercise 4**: Using the linearity of Eq. (1), show that Eq. (17) also describes the time evolution of \(\hat{\rho}\) for a mixed state.

7  Classical Analogue

**Microscopic states**: Quantum statistical mechanics defines a microscopic state of a system in Hilbert space according to a well defined set of quantum numbers. Classical statistical mechanics, however, describes the microscopic state in phase space according to a well defined set of coordinates \((x_1, \ldots, x_f)\) and momenta \((p_1, \ldots, p_f)\).

**Ensembles**: Quantum statistical mechanics describes an ensemble according to the density operator \(\hat{\rho}\), introduced by Eq. (11). Classical statistical mechanics, however, describes an ensemble according to the density of states \(\rho = \rho(x_1, \ldots, x_f, p_1, \ldots, p_f)\).

**Time-Evolution of Ensembles**: Quantum statistical mechanics describes the time-evolution of ensembles according to Eq. (17), which can be regarded as the quantum mechanical analogue of the *Liouville’s theorem* of classical statistical mechanics,

\[ \frac{\partial \rho}{\partial t} = -\rho (H) , \]  

(18)

Eq. (18) is the equation of motion for the classical density of states \(\rho = \rho(x_1, \ldots, x_f, p_1, \ldots, p_f)\). Thus the name *density* operator for \(\rho\) appearing in Eq. (17).

Note that the classical analog of the commutator \([G, F] / \hbar\) is the *Poisson bracket* of \(G\) and \(F\),

\[ (G, F) \equiv \sum_{j=1}^f \frac{\partial G}{\partial x_j} \frac{\partial F}{\partial p_j} - \frac{\partial G}{\partial p_j} \frac{\partial F}{\partial x_j}, \]  

(19)

**Exercise 5**: Prove Eq. (18) by using the fact that the state of a classical system is defined by the coordinates \((x_1, \ldots, x_f)\) and momenta \((p_1, \ldots, p_f)\) which evolve in time according to Hamilton’s equations, i.e.,

\[ \frac{dp_j}{dt} = -\frac{\partial H}{\partial x_j}, \quad \frac{dx_j}{dt} = \frac{\partial H}{\partial p_j}, \]  

(20)

where \(H = \sum_{j=1}^f p_j^2 / (2m_j) + V(x_1, \ldots, x_f)\) is the classical Hamiltonian.
Ensemble Averages: Quantum statistical mechanics describes ensemble averages according to Eq. (10). Classical statistical mechanics, however, describes ensemble averages according to the classical analog of Eq. (10),

\[
\bar{A} = \frac{\int dx \int dp \rho(x_1, \ldots, x_f, p_1, \ldots, p_f)A}{\int dx \int dp \rho(x_1, \ldots, x_f, p_1, \ldots, p_f)},
\]

where \(dx dp\) stands for a volume element in phase space.

8 Entropy

The entropy \(\bar{S}\) of an ensemble can be defined in terms of the density operator \(\hat{\rho}\) as follows,

\[
S \equiv -k Tr\{\hat{\rho} \ln \hat{\rho}\},
\]

where \(k\) is the Botzmann constant. Equation (22) is the Von Neumann definition of entropy. This is the most fundamental definition of \(S\) because it is given in terms of the density operator \(\hat{\rho}\), which provides the most complete description of an ensemble. In particular, the Gibbs entropy formula,

\[
S = -k \sum_k p_k \ln p_k,
\]

(23)

can be obtained from Eq. (22) by substituting \(\hat{\rho}\) in accord with Eq. (11).

From Eq. (23) one can see that the entropy of a pure state is zero, while the entropy of a statistical mixture is always positive. Therefore,

\[
S \geq 0,
\]

(24)

which is the fourth law of Thermodynamics.

9 Maximum-Entropy Density Operator

The goal of this section is to obtain the density operator \(\hat{\rho}\), with \(Tr\{\hat{\rho}\} = 1\), that maximizes the entropy \(S = -k Tr\{\hat{\rho} \ln \hat{\rho}\}\) of a system characterized by an ensemble average internal energy

\[
E = Tr\{\hat{\rho} \hat{H}\},
\]

(25)

and fix extensive properties \(X\) such as \(X = (V, N)\) (i.e., canonical and microcanonical ensembles). This is accomplished by implementing the method of Lagrange Multipliers to maximize the function

\[
f(\hat{\rho}) \equiv -k Tr\{\hat{\rho} \ln \hat{\rho}\} + \gamma(E - Tr\{\hat{\rho} \hat{H}\}) + \gamma'(1 - Tr\{\hat{\rho}\}),
\]

(26)

where \(\gamma\) and \(\gamma'\) are Lagrange Multipliers. We, therefore, solve for \(\hat{\rho}\) from the following equation

\[
\frac{\partial f}{\partial \hat{\rho}} \bigg|_X = 0,
\]

(27)
and we obtain that the density operator that satisfies Eq. (27) must satisfy the following equation:

\[ Tr\{-k\ln\hat{\rho} - k - \gamma \hat{H} - \gamma'\} = 0. \]  

(28)

Therefore,

\[ -\ln\hat{\rho} = 1 + \frac{\gamma'}{k} \hat{H} + \frac{\gamma'}{k}. \]  

(29)

Exponentiating both sides of Eq. (29) we obtain

\[ \hat{\rho} = \exp(-(1 + \frac{\gamma'}{k}))\exp(-\frac{\gamma}{k}\hat{H}), \]  

(30)

and, since \( \text{Tr}\{\hat{\rho}\} = 1 \),

\[ \exp(-(1 + \frac{\gamma'}{k})) = \frac{1}{Z}, \]  

(31)

where \( Z \) is the partition function

\[ Z \equiv \text{Tr}\{\exp(-\beta \hat{H})\}, \]  

(32)

with \( \beta \equiv \gamma/k \).

Substituting Eqs. (32) and (31) into Eq. (30), we obtain that the density operator that maximizes the entropy of the ensemble, subject to the contraint of average ensemble energy \( \bar{E} \), is

\[ \hat{\rho} = Z^{-1}\exp(-\beta \hat{H}). \]  

(33)

Note that

\[ \frac{\partial \hat{\rho}}{\partial t} = 0, \]  

(34)

when \( \hat{\rho} \) is defined according to Eq. (33) and, therefore, the system is at equilibrium.

**Exercise 6:** Use Eqs. (17) and (33) to prove Eq. (34).

## 10 Internal Energy and Helmholtz Free Energy

Substituting Eqs. (32) and (31) into Eq. (25) we obtain that the internal energy \( E \) can be computed from the partition function \( Z \) as follows,

\[ E = -\left. \frac{\partial \ln Z}{\partial \beta} \right|_\beta. \]  

(35)

Furthermore, substituting Eqs. (32) and (31) into Eq. (22) we obtain

\[ S = -k\text{Tr}\{\hat{\rho}(-\beta \hat{H} - \ln Z)\} = k\beta E + k\ln Z. \]  

(36)

In the next section we prove that the parameter \( T \equiv (k\beta)^{-1} \) can be identified with the temperature of the ensemble. Therefore,

\[ A = E - TS = -kT\ln Z, \]  

(37)
is the Helmholtz free energy, that according to Eq. (35) satisfies the following thermodynamic equation,

\[ E = \frac{\partial (\beta A)}{\partial \beta} \bigg|_N. \]

(38)

11 Temperature

The parameter \( T \equiv 1/k \beta = 1/\gamma \) has been defined so far as nothing but the inverse of the Lagrange Multiplier \( \gamma \). Note that according to Eq. (36), however, \( T \) can be defined as follows:

\[ \frac{1}{T} = \frac{\partial S}{\partial E} \bigg|_N. \]

(39)

The goal of this section is to show that \( T \) can be identified with the temperature of the system because it is the same throughout the system whenever the system is at thermal equilibrium.

Consider a system at equilibrium, with ensemble average internal energy \( E \), in the state of maximum entropy at fixed \( N \). Consider a distribution of \( S \), \( T \), and \( E \) in compartments (1) and (2) as specified by the following diagram:

\[
\begin{array}{c}
(1) \\
S^{(1)} \quad T^{(1)} \quad E^{(1)} \\
N_1
\end{array}
\begin{array}{c}
(2) \\
S^{(2)} \quad T^{(2)} \quad E^{(2)} \\
N_2
\end{array}
\]

Thermal (Heat) Conductor

Consider a small displacement of heat \( \delta E \) from compartment (1) to compartment (2):

\[ \delta E^{(1)} = -\delta E, \quad \text{and} \quad \delta E^{(2)} = \delta E. \]

(40)

Since the system was originally at the state of maximum entropy, such a displacement would produce a change of entropy

\[ \delta S_{E,N} \leq 0, \]

(41)

where

\[
\delta S = \delta S^{(1)} + \delta S^{(2)} = \left( \frac{\partial S^{(1)}}{\partial E^{(1)}} \right)_N \delta E^{(1)} + \left( \frac{\partial S^{(2)}}{\partial E^{(2)}} \right)_N \delta E^{(2)} = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \delta E \leq 0.
\]

(42)

Since the inequality introduced by Eq. (42) has to be valid for any positive or negative \( \delta E \), then \( T_1 = T_2 \).
12 Minimum Energy Principle

The minimum energy principle is a consequence of the maximum entropy principle. This can be shown by considering the system at thermal equilibrium described by the following diagram:

Consider a small displacement of heat $\delta E$ from compartment (2) to compartment (1). Since the system was originally at equilibrium, such a constraint in the distribution of thermal energy produces a constrained system whose entropy is smaller than the entropy of the system at equilibrium. Mathematically,

$$S(E^{(1)} + \delta E, X) + S(E^{(2)} - \delta E, X) < S(E^{(1)}, X) + S(E^{(2)}, X).$$  (43)

Now consider the system at equilibrium (i.e., without any constraints) with entropy $S(E, X)$ such that

$$S(E, X) = S(E^{(1)} + \delta E, X) + S(E^{(2)} - \delta E, X).$$  (44)

Since, according to Eqs. (285) and (286),

$$S(E, X) < S(E^{(1)}, X) + S(E^{(2)}, X),$$  (45)

and according to Eq. (39),

$$\frac{\partial S}{\partial E} = \frac{1}{T} > 0,$$  (46)

then

$$E < E^{(1)} + E^{(2)}.$$  (47)

Eq. (44) thus establishes that by imposing internal constraints at constant entropy the system that was initially at equilibrium with entropy $S(E, X)$ moves away from such equilibrium and its internal energy increases from $E$ to $E^{(1)} + E^{(2)}$. Mathematically,

$$dE \geq 0,$$  (48)

which is the minimum energy principle.
As an example, consider 2 balloons filled with nitrogen at room temperature. The balloons are in contact and at thermal equilibrium. At a lower temperature, the kinetic energy of molecules would be smaller, so the total energy of the system would be smaller. Therefore, the entropy would also be smaller since \(1/T = dS/dE > 0\). Thus, reducing the energy of the system would be one way of reducing the entropy.

Another way would be as follows. Take the 10 slower molecules of one balloon and exchange them by the 10 faster of the other. Then, separate the balloons so they are no longer touching each other. One of the balloons would now be warmer and the other colder because effectively a little bit of heat has been transferred from one to the other. Since the balloons were originally at equilibrium, that transformation also reduced the total entropy of the system of 2 balloons, although the total internal energy remained the same. If now we bring them at equilibrium with each other but we constrain the entropy to remain the same, we see that to reach that lower value of entropy and reach equilibrium they would have to lose some internal energy. Therefore, the equilibrium could be reached by energy minimization. Another way of reaching the equilibrium would be to keep the energy the same and increase the entropy.

13 Canonical and Microcanonical Ensembles

Exercise 7: (A) Use Eqs. (36) and (11) to show that in a canonical ensemble the probability \(p_j\) of observing the system in quantum state \(|j>\), where
\[H|j> = E_j|j>,\]
is the Boltzmann probability distribution
\[p_j = Z^{-1} \exp(-\beta E_j) = \exp(-\beta(E_j - A)),\]
where \(\beta = (kT)^{-1}\), with \(T\) the temperature of the ensemble and \(k\) the Boltzmann constant.

(B) Show that for a microcanonical ensemble, where all of the states \(|j>\) have the same energy \(E_j = E\), the probability of observing the system in state \(|j>\) is
\[p_j = \frac{1}{\Omega},\]
where \(\Omega\) is the total number of states. Note that \(p_j\) is, therefore, independent of the particular state \(|j>\) in a microcanonical ensemble.

Note that according to Eqs. (23) and (51), the entropy of a microcanonical ensemble corresponds to the Boltzmann definition of entropy,
\[S = k\ln\Omega.\]

14 Equivalency of Ensembles

A very important aspect of the description of systems in terms of ensemble averages is that the properties of the systems should be the same as described by one or another type of ensemble.
The equivalence between the description provided by the microcanonical and canonical ensembles can be demonstrated most elegantly as follows. Consider the partition function of the canonical ensemble

\[ Z = \sum_k e^{-\beta E_k} = e^{-\beta A}, \]  

(53)

and partition the sum over states \( k \) into groups of states such that they sum up to the same energy \( E_l \). Rewriting Eq. (53) according to states of equal energy \( E_l \) we obtain

\[ Z = \sum_l \Omega(E_l) e^{-\beta E_l}. \]  

(54)

where \( \Omega(E_l) \) is the number of states with energy \( E_l \).

Taking the continuous limit of Eq. (54) we obtain,

\[ Z = \int_{0}^{\infty} dE \Omega(E) e^{-\beta E}, \]  

(55)

i.e., the partition function \( Z(\beta) \) is the Laplace transform of the total number of states \( \Omega(E) \) of energy \( E \). Since Laplace transforms are unique, there is a one to one correspondence between \( Z(\beta) \) and \( \Omega(E) \) —i.e., both functions have the same information.

### 14.1 Example

As an example of the equivalence between the microcanonical and canonical ensembles, consider the calculation of the internal energy \( E \) in a system of \( N \) two-level particles. The goal of this pedagogical example is to show that the ensemble average internal energy is the same when computed according to the canonical or microcanonical ensembles.

**Microcanonical ensemble:**

In a system of \( N \) two-level particles (e.g., \( N \) spins that can be up or down) each particle can be assumed to be either in the ground state with energy equal to zero, or in the excited state with energy \( \epsilon \). The total internal energy is

\[ E = m\epsilon = \sum_{j=1}^{N} n_j \epsilon, \]  

(56)

where \( n_j = 0, 1 \) and \( m \) is the number of particles with energy \( \epsilon \). The number of possible states \( \Omega(E) \) with energy \( E = m\epsilon \),

\[ \Omega(E) = \binom{N}{m} = \frac{N!}{m!(N-m)!}, \]  

(57)

determines the entropy of the system according to Eq. (52),

\[ S = k\ln\Omega(E), \]  

(58)
and, therefore, the average temperature $T$ of the system according to Eq. (39),

$$
\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{N} = \frac{\partial S}{\partial m} \frac{\partial m}{\partial E} = \frac{k}{\epsilon} \frac{\partial}{\partial m} (\ln N! - \ln m! - \ln (N - m)!),
$$

(59)

since according to the Stirling formula,

$$
\ln N! \approx N \ln N - N,
$$

(60)

$$
\ln m! \approx m \ln m - m, \text{ etc.}
$$

Therefore,

$$
\frac{1}{T} = \frac{k}{\epsilon} (0 - \ln m - 1 + 1 + \ln (N - m) + \frac{(N - m)}{(N - m) - 1}),
$$

(61)

or

$$
\frac{1}{T} = \frac{k}{\epsilon} \ln \left( \frac{N - m}{m} \right) = \frac{k}{\epsilon} \ln \left( \frac{N}{m} - 1 \right).
$$

(62)

Thus,

$$
\beta \epsilon = \ln \left( \frac{N}{m} - 1 \right) \Rightarrow \exp(\beta \epsilon) + 1 = \frac{N}{m},
$$

(63)

and, therefore, the internal energy $E$ is obtained as follows,

$$
\frac{m}{N} = \frac{1}{1 + \exp(\beta \epsilon)} \Rightarrow E = \frac{N \epsilon}{1 + \exp(\beta \epsilon)},
$$

(64)

Canonical Ensemble:
The partition function of the canonical ensemble is

$$
Z = \prod_{j=1}^{N} \sum_{n_{j} = 0}^{1} e^{-\beta n_{j}} = (1 + e^{-\beta \epsilon})^{N},
$$

(65)

Therefore,

$$
\ln Z = N \ln (1 + e^{-\beta \epsilon}),
$$

(66)

and

$$
E = -\left( \frac{\partial \ln Z}{\partial \beta} \right)_{N,V} = \frac{N \epsilon}{1 + e^{\beta \epsilon}},
$$

(67)

which coincides with Eq. (64).
15 Thermal Fluctuations

In the previous section we have demonstrated that the ensemble average internal energy of a system of \( N \) two-level particles is the same when computed according to the canonical or microcanonical ensembles, as long as \( N \) is sufficiently large. Nevertheless, the internal energy fluctuates among different replicas in the canonical ensemble while remains fixed among different members of the microcanonical ensemble. The goal of this section is to demonstrate that such inherent difference between the two representations does not contradict the equivalency of ensembles. The reason for this is that the relative size of the fluctuations becomes vanishingly small in the limit when \( N \) is sufficiently large.

Consider the average squared fluctuation \( (\delta E)^2 \) of the internal energy \( E \) in the canonical ensemble,

\[
(\delta E)^2 = \text{Tr}\{\hat{\rho}(\hat{H}^2 - 2\hat{H}\bar{E} + \bar{E}^2)\}.
\]

Eq. (68) can be simplified according to

\[
(\delta E)^2 = \text{Tr}\{\hat{\rho}\hat{H}^2\} - \bar{E}^2.
\] (69)

Substituting Eq. (11) into Eq. (69) we obtain

\[
(\delta E)^2 = \sum_k p_k E_k^2 - \left(\sum_k p_k E_k\right)^2, \tag{70}
\]

and since \( Z = \text{Tr}\{e^{-\beta \hat{H}}\} \) and \( \hat{\rho} = Z^{-1}e^{-\beta \hat{H}} \),

\[
(\delta E)^2 = \frac{\text{Tr}\{\hat{H}^2 e^{-\beta \hat{H}}\}}{\text{Tr}\{e^{-\beta \hat{H}}\}} - \left(\frac{\text{Tr}\{\hat{H} e^{-\beta \hat{H}}\}}{\text{Tr}\{e^{-\beta \hat{H}}\}}\right)^2. \tag{71}
\]

Therefore,

\[
(\delta E)^2 = \frac{1}{\text{Tr}\{e^{-\beta \hat{H}}\}} \frac{\partial^2 \text{Tr}\{e^{-\beta \hat{H}}\}}{\partial^2 \beta} \bigg|_{N,V} - \left(\frac{1}{\text{Tr}\{e^{-\beta \hat{H}}\}} \frac{\partial \text{Tr}\{e^{-\beta \hat{H}}\}}{\partial \beta} \bigg|_{N,V}\right)^2, \tag{72}
\]

and

\[
(\delta E)^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \bigg|_{N,V} - \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta}\right)^2 \bigg|_{N,V} = \frac{\partial^2 \ln Z}{\partial \beta^2} \bigg|_{N,V} = -\frac{\partial E}{\partial \beta} \bigg|_{N,V}. \tag{73}
\]

Note that these energy fluctuations are vanishingly small, in comparison to the total internal energy \( E \) of the system,

\[
\frac{\sqrt{(\delta E)^2}}{E} = \sqrt{-\frac{\partial E}{\partial \beta}} \bigg|_{N,V} \propto \frac{1}{\sqrt{N}}, \tag{74}
\]

whenever \( N \) is sufficiently large. For instance, when \( N \sim 10^{23} \) the energy fluctuations are extremely small in comparison to \( E \).
Note: As a by-product of this calculation we can obtain a remarkable result. Namely, that the rate at which energy changes due to changes in the temperature is determined by the size of the energy fluctuations \((\delta E)^2\). To obtain this result, consider that according to Eq. (73)

\[
(\delta E)^2 = -\left(\frac{\partial E}{\partial T}\right)_{N,V} \left(\frac{\partial T}{\partial \beta}\right)_{N,V} kT^2.
\]

(75)

Therefore,

\[
(\delta E)^2 = C_v kT^2,
\]

(76)

where

\[
C_v \equiv \left(\frac{\partial E}{\partial T}\right)_{N,V},
\]

(77)

is the heat capacity of the system, i.e., the property of the system that determines the rate of energy change due to changes in the temperature.

16 Grand Canonical Ensemble

The goal of this section is to obtain the density operator

\[
\hat{\rho} = \sum_j p_j |\phi_j><\phi_j|,
\]

(78)

with

\[
1 = \sum_j p_j,
\]

(79)

that maximizes the entropy

\[
S = -k \sum_j p_j \ln p_j,
\]

(80)

subject to the constraints of fixed volume \(V\), average internal energy

\[
E = \sum_j p_j E_j,
\]

(81)

and average number of particles

\[
\bar{N} = \sum_j p_j N_j.
\]

(82)

Such density operator describes the maximum entropy ensemble distribution for a grand canonical ensemble — i.e., a collection of replica systems in thermal equilibrium with a heat reservoir whose temperature is \(T\) as well as in equilibrium with respect to exchange of particles with a “particle”
reservoir where the temperature is $T$ and the chemical potential of the particles is $\mu$. This problem is solved in terms of the Method of Lagrange Multipliers by maximizing the function

$$f(p_1, p_2, ...) \equiv -k \sum_j p_j \ln p_j + \gamma(E - \sum_j p_j E_j) + \gamma'(N - \sum_j p_j N_j) + \gamma''(1 - \sum_j p_j), \quad (83)$$

where $\gamma$, $\gamma'$ and $\gamma''$ are Lagrange Multipliers. Solving for $p_j$ from the following equation

$$\frac{\partial f}{\partial p_j} = -k(\ln p_j + 1) - \gamma E_j - \gamma' N_j - \gamma'', \quad (84)$$

we obtain

$$p_j = \exp(1 - \gamma') \exp(-\frac{\gamma}{k} E_j - \frac{\gamma'}{k} N_j). \quad (85)$$

Introducing the quantities $\beta \equiv \gamma/k$ and $\beta \mu \equiv -\gamma'/k$ we obtain the generalized Boltzmann distribution

$$p_j = \frac{e^{-\beta E_j + \beta \mu N_j}}{\sum_j e^{-\beta E_j + \beta \mu N_j}} = \Xi^{-1} e^{-\beta E_j + \beta \mu N_j}, \quad (86)$$

where

$$\Xi \equiv \sum_j \exp(-\beta E_j + \beta \mu N_j), \quad (87)$$

is the grand canonical partition function.

The goal of the remaining of this section is to find the relation between the canonical and the grand canonical partition functions, $Z$ and $\Xi$, respectively.

Substituting Eq. (86) into Eq. (80) we obtain

$$S = -k \sum_j p_j(-\beta E_j + \beta \mu N_j - \ln \Xi), \quad (88)$$

and solving for $\ln \Xi$ from Eq. (88) we obtain

$$\ln \Xi = \beta(-E + ST + \mu \bar{N}). \quad (89)$$

Therefore,

$$\ln \Xi = \beta(-A + \mu \bar{N}), \quad (90)$$

and

$$\ln \Xi = \ln Z + \beta \mu \bar{N}. \quad (91)$$

### 17 Density Fluctuations

The goal of this section is to show that the fluctuations in the number of particles in the system at constant $V$ and $T$ can be computed from the grand canonical partition function and that the size of the fluctuations in the number of particles $\sqrt{(\delta N)^2}$ decays as $1/\sqrt{N}$. 


The ensemble average squared fluctuation in the number of particles

\[
\langle (\delta N)^2 \rangle = (N - \overline{N})^2 = N^2 - \overline{N}^2,
\]

(92)

(where the overline indicates an ensemble average), can be computed as follows

\[
\langle (\delta N)^2 \rangle = \sum_j p_j N_j^2 - (\sum_j p_j N_j)^2.
\]

(93)

Substituting Eq. (86) into Eq. (93) we obtain

\[
\langle (\delta N)^2 \rangle = \Xi^{-1} \sum_j N_j^2 e^{-\beta E_j + \beta \mu N_j} - \left( \Xi^{-1} \sum_j N_j e^{-\beta E_j + \beta \mu N_j} \right)^2.
\]

(94)

Therefore,

\[
\langle (\delta N)^2 \rangle = \frac{\partial^2 \ln \Xi}{\partial (\beta \mu)^2} \bigg|_V = \frac{\partial N}{\partial (\beta \mu)} \bigg|_V.
\]

(95)

17.1 Example

Consider a system of uncorrelated particles distributed among \( m \) boxes. Assume that the average number of particles per box \( \overline{n}_j \ll 1 \), so that there is either one or none particle per box —i.e., \( n_j \equiv 1, 0 \) with \( n_j \) the number of particles associated with box \( j \). The goal of this section is to compute the size of the fluctuations in the total number of particles in the system and to show that the size of such fluctuations is much smaller than the average number of particles \( \overline{N} \), when \( \overline{N} \) is sufficiently large.

The ensemble average squared fluctuation in the number of particles

\[
\langle (\delta N)^2 \rangle = (N - \overline{N})^2 = N^2 - \overline{N}^2,
\]

(96)

can be computed as follows

\[
\langle (\delta N)^2 \rangle = \sum_{j=1}^{m} \sum_{k=1}^{m} < n_j n_k > - (\sum_{j=1}^{m} < n_j >)^2.
\]

(97)

Factorizing the sums we obtain,

\[
\langle (\delta N)^2 \rangle = \sum_j < n_j^2 > + \sum_{j=1}^{m} \sum_{k \neq j} < n_j n_k > - \sum_{j=1}^{m} < n_j >^2 - \sum_{j=1}^{m} \sum_{k \neq j} < n_j > < n_k >.
\]

(98)

Note that since \( n_j = 0, 1, < n_j^2 > = < n_j > \). Furthermore, \( < n_j n_i > = < n_j > < n_i > \) when \( j \neq i \) simply because the particles are uncorrelated. Therefore,

\[
\langle (\delta N)^2 \rangle = \sum_{j=1}^{m} < n_j > - \sum_{j=1}^{m} < n_j >^2 = \sum_{j=1}^{m} < n_j > (1 - < n_j >).
\]

(99)
Considering that $<n_j><n_1> = \overline{N}$, 

$$\overline{(\delta N)^2} = m <n_1> = \overline{N}. \quad (100)$$

Therefore, 

$$\sqrt{\overline{(\delta N)^2}} \overline{N} = \frac{1}{\sqrt{\overline{N}}}, \quad (101)$$

i.e., the size of the fluctuations in the number of particles in the system becomes negligible small when $\overline{N} \sim 10^{23}$.

As a by-product of this derivation we can obtain the thermodynamic equation that establishes the relationship between the number of particles, the temperature and the chemical potential. Substituting Eq. (95) into Eq. (100) we obtain,

$$\frac{\partial^2 \ln \Xi}{\partial (\beta \mu)^2} V = \frac{\partial \overline{N}}{\partial (\beta \mu)}, \quad (102)$$

Therefore,

$$\frac{\partial \ln \overline{N}}{\partial (\beta \mu)} V = 1, \quad (103)$$

or dividing both sides of Eq. (102) by $V$,

$$\ln \left( \frac{\overline{N} V}{\overline{N}} \right) = \beta \mu + c, \quad (104)$$

where $c$ is a constant.

**Quiz 1**

(10 pts) (A) What is a statistical ensemble and why is it necessary to describe macroscopic systems in terms of ensembles?

(20 pts) (B) How do you describe an ensemble and its time evolution?

   (B.1) In classical statistical mechanics (CSM).
   (B.2) In quantum statistical mechanics (QSM).

(10 pts) (C) How do you describe a microscopic state?

   (C.1) In classical statistical mechanics (CSM).
   (C.2) In quantum statistical mechanics (QSM).

(20 pts) (D) How do you compute an ensemble average?

   (D.1) In classical statistical mechanics (CSM).
   (D.2) In quantum statistical mechanics (QSM).

(20 pts) (E) How do you describe the maximum entropy ensemble of a system with a fixed number of particles and fixed volume?
(20 pts) (F) Prove that

\[ E = \frac{\partial(\beta A)}{\partial \beta} \bigg|_{V,N} \]  

when \( A = E - TS \).

**Solution**

(A) The collection of a large number of independently prepared replicas of the system is called an **ensemble**. An ensemble of \( N \) replicas of systems is in a statistical mixture of states \( |\phi_k> \), with probabilities \( p_k \), when \( n_k \) members of the ensemble are in state \( |\phi_k> \), with \( p_k = n_k/N \). (See page 6 of the lecture notes)

Measurements on macroscopic systems must be described in terms of ensemble averages simply because, in practice, macroscopic systems can only be prepared in thermodynamic states (i.e., in a statistical mixtures of quantum states) characterized by a few physical quantities (e.g., the temperature, the pressure, the volume and the number of particles). (See pages 3 and 4 of the lecture notes)

(B.1) An ensemble is described in classical statistical mechanics by the density of states \( \rho = \rho(x_1,...,x_f,p_1,...,p_f) \), where \( (x_1,...,x_f) \) and \( (p_1,...,p_f) \) are the coordinates and momenta. The density of states evolves in time according to the following equation of motion:

\[ \frac{\partial \rho}{\partial t} = - \{ \rho, H \}, \]  

where \( H = \sum_{j=1}^f p_j^2/(2m_j) + V(x_1,...x_f) \) is the classical Hamiltonian and \( \{ \rho, H \} \) represents the Poisson bracket of \( \rho \) and \( H \). (See page 10 of the lecture notes)

(B.2) An ensemble is described in quantum statistical mechanics by the density operator \( \hat{\rho} = \sum_k p_k |\phi_k><\phi_k| \),

where \( |\phi_k> \) are the possible quantum states that the system can populate and \( p_k \) is the probability of populating state \( |\phi_k> \). (See page 10 of the lecture notes) The density operator evolves in time according to the following equation:

\[ \frac{\partial \hat{\rho}}{\partial t} = -\frac{[\hat{\rho}, \hat{H}]}{i\hbar}, \]  

where \([\hat{\rho}, \hat{H}]\) is the commutator of \( \hat{\rho} \) and \( \hat{H} \). (See page 9 of the lecture notes)

(C.1) A microscopic state is described in classical statistical mechanics by a point in phase-space defined by a set of coordinates \((x_1,...x_f)\) and momenta \((p_1,...,p_f)\). (See page 9 of the lecture notes)

(C.2) A microscopic state is described in quantum statistical mechanics by a quantum state in Hilbert space, defined in terms of a set quantum numbers associated with a ket-vector. (See page 9 of the lecture notes)
(D.1) An ensemble average is computed in classical statistical mechanics according to the following equation:
\[
\bar{A} = \frac{\int d\mathbf{x} \int d\mathbf{p} \rho(x_1, \ldots, x_f, p_1, \ldots, p_f) A}{\int d\mathbf{x} \int d\mathbf{p} \rho(x_1, \ldots, x_f, p_1, \ldots, p_f)},
\]
where \(d\mathbf{x}d\mathbf{p}\) stands for a volume element in phase space and \(A\) is the quantity of interest. (See page 10 of the lecture notes)

(D.2) An ensemble average is computed in quantum statistical mechanics according to the following equation:
\[
A = Tr\{\hat{\rho} \hat{A}\},
\]
where \(\hat{\rho}\) is the density operator and \(A\) is the quantity of interest. (See page 7 of the lecture notes)

(E) The maximum entropy ensemble of a system with a fixed number of particles and fixed volume is described by the density operator
\[
\hat{\rho} = Z^{-1} \exp(-\beta \hat{H}),
\]
where \(Z\) is the partition function
\[
Z \equiv Tr\{\exp(-\beta \hat{H})\},
\]
and \(\beta = (kT)^{-1}\). (See page 12 of the lecture notes)

(F)
\[
E \equiv Tr\{\hat{\rho} \hat{H}\} = -\frac{\partial \ln Z}{\partial \beta} \bigg|_x,
\]
\[
S \equiv -kTr\{\hat{\rho} \ln \hat{\rho}\} = k\beta E + k\ln Z.
\]
Therefore,
\[
A \equiv E - TS = -kT \ln Z,
\]
and
\[
E = \frac{\partial (\beta A)}{\partial \beta} \bigg|_x.
\]

19 Postulates of Statistical Mechanics

Once again we remark that in statistical mechanics we build on the description of matter provided by quantum mechanics in terms of the eigenstates, or the Hamiltonian. The theory of ensembles enables us to express measurable quantities of macroscopic systems in terms of the underlying quantum mechanical principles inspite of having incomplete information about the preparation of the system and the interactions with its surroundings. If we look carefully we can see that the ensemble-average technique depends on two postulates and then builds an enormous structure on them to do the characteristic work of the theory.
**First Postulate:** The experimental result of a measurement of an observable in a macroscopic system is the ensemble average of such observable.

**Second Postulate:** Any macroscopic system at equilibrium is described by the maximum entropy ensemble, subject to contraints that define the macroscopic system.

The first postulate is needed to equate the ensemble average to a more elementary description of what is begin observed. To analyze this aspect, consider a variable that depends on the quantum state (or otherwise classically, on the locations and velocities of the particles that constitute the system). With a sufficiently delicate measuring device one could measure a fluctuating observable $O(t)$, but the measured value of the observable $O$ is usually taken to be a time average

$$
\overline{O} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau O(t) dt,
$$

(117)
due to the slow response of the measuring system when compared to the rapid changes in quantum states, or locations and velocities of the particles that make up the system.

According to the dynamical picture described above, the time dependence of $O(t)$ is due to the fact that the system changes its microscopic state in time. To compute the time average, introduced by Eq. (117), it is necessary to know the sequence of quantum states through which the system passes in time and this is determined by the initial conditions as well as by the interactions between the system and its surroundings. Due to the large number of degrees of freedom in a macroscopic systems, it is therefore impossible to know the sequence of quantum states since neither the initial conditions nor the detailed description of the interactions are ready available. The first postulate thus introduces an alternative way of computing the average over microscopic states. The alternative approach thus involves constructing a large number of replicas of the system of interest, compute $O$ for each replica and average the results

$$
\overline{O} = \sum_j p_j O(j),
$$

(118)
where $p_j$ is the probability of state $j$. Note that by implementing this alternative approach there is no need to follow the sequence of quantum states as described above as long as there is an alternative way to find how many of the replica systems of the ensemble are in each quantum state $j$.

The second postulate is needed to connect the attributes of a quantum state to its probability (i.e., to the fraction of the replica systems in an ensemble that will be found in that state). We found that the maximum entropy postulate established the connection between $p_j$ and the attributes of $j$ such as its energy $E_j$ and the number of particles $N_j$. For a canonical ensemble $p_j$ is determined by the Boltzmann distribution, introduced by Eq. (50); for a microcanonical ensemble $p_j$ is independent of $j$ and is determined by inverse of the total number of states (see Eq. (51)); and for the grand canonical ensemble $p_j$ is determined by the generalized Boltzmann distribution, introduced by Eq. (86). Therefore, the second postulate established through Eqs. (50), (51) and (86) that all quantum states with the same energy and the same number of particles are equally probable.

Going back to the dynamical picture, one can analyze the implications of the second postulate with regards to how much time the system lives in each microscopic state during the measurement.
of $O$. In the dynamical picture the second postulate establishes that the system is observed for the same fraction time in all microscopic states with the same energy and the same number of particles. Therefore, the ensemble average, introduced by Eq. (118), is equal to the average over time, introduced by Eq. (117). When formulated in such terms, the second postulate is known as the ergodic hypothesis of statistical mechanics and a system that satisfies such hypothesis is called ergodic.

### 19.1 Example: Ensemble Averages

Consider a system with two spins with magnetic moments $\mu_1$ and $\mu_2$, respectively, at thermal equilibrium with a bath at temperature $T$. There is an external magnetic field $B$ that interacts with each spin according to $E(i, \pm) = \pm \mu_i B$. Assuming that the spins do not interact with each other, compute:

(A) The average value of the total internal energy of the system.

(B) The mean squared fluctuation of the total energy of the system.

(C) The entropy of the system.

(D) The Helmholtz free energy.

(E) Assuming that the contributions to the total magnetization $M$ are $m_i(\pm) = \pm \mu_i$, compute the average value of the magnetization of the system at temperature $T$.

Note: The spins can only be "up" (+) or "down" (-) relative to the magnetic field. When a spin is "up" its interaction with the external field is $E(i, +) = \mu_i B$ and when the spin is "down" its interaction with the external field is $E(i, -) = -\mu_i H$.

### Solution

(A) To compute the internal energy as an ensemble average we first compute the partition function

$$Z = e^{-\beta B(-\mu_1-\mu_2)} + e^{-\beta B(-\mu_1+\mu_2)} + e^{-\beta B(\mu_1-\mu_2)} + e^{-\beta B(\mu_1+\mu_2)},$$

which is

$$Z = 4\cosh(\beta B \mu_2)\cosh(\beta B \mu_1).$$

According to Eq. (35),

$$E = -\frac{\partial \ln Z}{\partial \beta} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{4B}{Z} (\mu_2 \sinh(\beta B \mu_2) \cosh(\beta B \mu_1) + \mu_1 \cosh(\beta B \mu_2) \sinh(\beta B \mu_1)),$$

which gives

$$E = -B \mu_2 \tanh(\beta B \mu_2) - B \mu_1 \tanh(\beta B \mu_1).$$

(B) According to Eq. (73),

$$\langle \delta E \rangle^2 = -\frac{\partial \langle E \rangle}{\partial \beta} = \frac{(B \mu_2)^2}{\cosh^2(\beta B \mu_2)} + \frac{(B \mu_1)^2}{\cosh^2(\beta B \mu_1)}.$$
(C) According to Eq. (37),
\[ S = k \beta \bar{E} + k \ln Z. \]  
(124)

Therefore,
\[ S = -k \beta B \mu_2 \tanh(\beta B \mu_2) - k \beta B \mu_1 \tanh(\beta B \mu_1) + k \ln(4 \cosh(\beta B \mu_2) \cosh(\beta B \mu_1)). \]  
(125)

(D) According to Eq. (37),
\[ A = -k T \ln Z = -k T \ln(4 \cosh(\beta B \mu_2) \cosh(\beta B \mu_1)), \]  
(126)

(D) The ensemble average magnetization is
\[ M = \sum_j p_j m_j, \]  
(127)

where, according to Eq. (50),
\[ p_j = Z^{-1} \exp(-\beta E_j) = \exp(-\beta (E_j - A)). \]  
(128)

Therefore,
\[ M = \left( (-\mu_1 - \mu_2) e^{-\beta B(-\mu_1 - \mu_2)} + (-\mu_1 + \mu_2) e^{-\beta B(-\mu_1 + \mu_2)} \\
+ (\mu_1 - \mu_2) e^{-\beta B(\mu_1 - \mu_2)} + (\mu_1 + \mu_2) e^{-\beta B(\mu_1 + \mu_2)} \right) / (4 \cosh(\beta B \mu_2) \cosh(\beta B \mu_1)). \]  
(129)
20 Exam 1

Exam 1 CHEM 430b/530b
Statistical Methods and Thermodynamics

Exercise 1
(20 points) Item (1.1): Explain the fundamental postulates of Statistical Mechanics.
(20 points) Item (1.2): Show that the definitions of entropy given by Gibbs and Boltzmann can be obtained from the Von Neumann definition of entropy.
(20 points) Item (1.3): Prove that
\[
S = -k\beta \frac{\partial \ln Z}{\partial \beta} \bigg|_{V,N} + k \ln Z.
\] (130)

Exercise 2
Consider a system of \( N \) non-interacting spins in a magnetic field \( B \), in thermal equilibrium with a bath at temperature \( T = 1/(k\beta) \). Each spin has a magnetic moment of size \( \mu \) and can point either parallel or anti-parallel to the field.
(10 points) Item (2.1): Determine the internal energy of the system as a function of \( \beta, B \), and \( N \).
(10 points) Item (2.2): Determine the entropy of the system as a function of \( \beta, B \), and \( N \).
(10 points) Item (2.3): Determine the average total magnetization of the system as a function of \( \beta, B \), and \( N \).
(10 points) Item (2.4): Determine the average squared fluctuation of the total magnetization of the system \( (\delta M)^2 \) as a function of \( \beta, B \), and \( N \).

Solution:
Item (1.1):
First Postulate: The experimental result of a measurement of an observable in a macroscopic system is the ensemble average of such observable.
Second Postulate: Any macroscopic system at equilibrium is described by the maximum entropy ensemble, subject to constraints that define the macroscopic system.

The first postulate is needed to equate the ensemble average to a more elementary description of what is being observed. The second postulate is needed to connect the attributes of a quantum state to its probability. We found that the maximum entropy postulate established the connection between \( p_j \) and the attributes of \( j \) as follows. For a canonical ensemble \( p_j \) is determined by the Boltzmann distribution; for a microcanonical ensemble \( p_j \) is independent of \( j \) and is determined by inverse of the total number of states and for the grand canonical ensemble \( p_j \) is determined by the

29
generalized Boltzmann distribution. Therefore, the second postulate established that all quantum states with the same energy and the same number of particles are equally probable.

**Item (1.2):** According to Eq. (22), the Von Neumann definition of entropy is:

\[ S \equiv -k \text{Tr}\{\hat{\rho} \ln \hat{\rho}\}, \]  

(131)

which according to the definition \( \hat{\rho} = \sum_k p_k |\phi_k\rangle \langle \phi_k| \) becomes,

\[ S \equiv -k \sum_j \langle \phi_j| \sum_k p_k |\phi_k\rangle \langle \phi_k| \ln(\sum_k p_k |\phi_k\rangle \langle \phi_k|) |\phi_j\rangle. \]  

(132)

Expanding \( \ln \hat{\rho} = 0 + (\hat{\rho} - 1) - (\hat{\rho} - 1)^2/2! + \ldots \) we obtain

\[ S \equiv -k \sum_j p_j \ln p_j, \]  

(133)

which is the Gibbs definition of entropy.

According to Eq. (51), \( p_j = 1/\Omega \) for a microcanonical ensemble. Therefore,

\[ S = k \ln \Omega, \]  

(134)

which is the Boltzmann definition of entropy.

**Item (1.3):** According to Eq. (50), the probability \( p_j \) of observing a system in quantum state \( |j\rangle \) is

\[ p_j = Z^{-1} \exp(-\beta E_j) = \exp(-\beta(E_j - A)), \]  

(135)

where \( Z = \sum_j \exp(-\beta E_j) \). Substituting this expression in the Gibbs definition of entropy, introduced in Item (1.2), we obtain

\[ S = k\beta Z^{-1} \sum_j E_j \exp(-\beta E_j) + k\ln Z = -k\beta \frac{\partial \ln Z}{\partial \beta} \bigg|_{V,N} + k\ln Z. \]  

(136)

**Item (2.1):**

According to Eq. (65), the canonical partition function for a system of \( N \) two-level particles \( j \) with energies \( E_j = \pm \mu B \) is

\[ Z = \prod_{j=1}^{N} (e^{-\beta \mu B} + e^{\beta \mu B}) = (2\cosh(\beta \mu B))^N. \]  

(137)

Therefore,

\[ E = -\frac{\partial \ln Z}{\partial \beta} \bigg|_{N,V} = -\mu BN \tanh(\beta \mu B). \]  

(138)

**Item (2.2):** According to Eq. (50),

\[ S = k \ln Z + \frac{E}{T} = kN \ln(2\cosh(\beta \mu B)) - \beta k \mu BN \tanh(\beta \mu B). \]  

(139)
Item (2.3): According to Eq. (127), the ensemble average magnetization is

\[ M = \sum_j p_j m_j, \]  

(140)

where \( m_j = \pm \mu \) and

\[ p_j = Z^{-1} \exp(-\beta B m_j) = \exp(-\beta (B m_j - A)). \]  

(141)

Therefore,

\[ \overline{M} = -\frac{\partial \ln Z}{\partial (B \beta)} \bigg|_{N,V} = N \mu \tanh(\beta B \mu). \]  

(142)

Item (2.4):

\[ \overline{(\delta M)^2} = \frac{\partial^2 \ln Z}{\partial (B \beta)^2} = N \mu^2 \text{sech}^2(\beta B \mu). \]  

(143)
21 Notes for the Inquisitive Mind: Measures of Information

21.1 Shannon Entropy

The goal of this section is to show that the Shannon entropy,

\[ S = - \sum_j P_j \log_2 P_j, \]  

(144)

is a measure of an amount of information (i.e., information = data). In fact, in this section, we show that if we consider a message composed of symbols \( x_j \) with probability \( P_j \) (as obtained when transmitted through a noisy communication channel), then \( S \) gives the average number of bits necessary to store each one of the symbols of that message. Such fundamental observation has given birth to the field of information theory and is known as the Shannon’s source coding theorem, as follows: It is impossible to compress the data of a long stream of a random variable such that the average number of bits per symbol is less than the Shannon entropy of the source without losing information.

As an example, consider that the 'message' is a set of \( n \) snapshots reporting the position of a fluctuating particle. Storing each symbol \( x_j \) requires specifying \( K \) bits (e.g., an array of \( K \) elements that can be either 1 or 0, indicating for example which box is occupied by the particle when the coordinate range is discretized into \( K \) boxes). The more snapshots (i.e., 'symbols'), the more information the message has with regards to the particle whereabouts. Therefore, the amount of information \( S \) scales with the number \( n \) of symbols: \( S = Kn \).

The number of bits required to store a symbol (i.e., \( K \)) can be given in terms of the total number of possible symbols \( \Omega = 2^K \), as follows: \( K = -\log_2(1/\Omega) \), where \( 1/\Omega \) is the probability of a symbol when randomly picked out of \( \Omega \) equally probable choices. More generally, when considering two messages, one with \( n_1 \) symbols from a library of \( \Omega_1 = 2^{K_1} \) possibilities, and the other one with \( n_2 \) symbols chosen from \( \Omega_2 = 2^{K_2} \) possibilities, the amount of information in the two messages is the same when the number of possibilities for the two messages is equal, so \( \Omega_1^{n_1} = \Omega_2^{n_2} \), since then \( n_1 \log_2 \Omega_1 = n_2 \log_2 \Omega_2 \) as pointed out by Hartley in the [The Bell System Technical Journal, July 1928, p. 535] so the total number of bits required to store the two messages is the same: \( K_1 n_1 = K_2 n_2 \) and \( K_1 / \log_2 \Omega_1 = K_2 / \log_2 \Omega_2 \). This relation holds for all values of \( \Omega \) only when \( K = K_0 \log \Omega \), where the arbitrary constant \( K_0 \) can be omitted since the logarithmic base is also arbitrary. The particular base of the log fixes the size of the unit of information. With the base 2, the resulting units are called binary digits, or more briefly bits as suggested by [J.W. Tukey]. If the base 10 is used, the units may be called decimal digits, with \( \log_2 \Omega = \log_{10} \Omega / \log_{10} 2 \).

The amount of information (i.e., the number of bits) of each symbol is therefore equal to the logarithm of the number of possible symbols. The amount of information of a message is the number of possible messages (which is the number of symbols times the number of possible symbols: \( S = n \log_2 \Omega \)). It is, therefore, clear that for a message composed of symbols with probability \( P_j \), the average number of bits necessary to store one of its symbols is given by Eq. (144), as discussed by Claude E. Shannon in his seminal work on communication theory published in [The Bell System Technical Journal 27: 379-423, 1948], with symbols drawn with probability \( P_j \) as randomly picked from \( \Omega_j = 1/P_j \) equally probable choices.
21.2 Majorization

When comparing the entropies of two sources with probabilities $p = (p_1, p_2, ..., p_n)$ with $p_{j+1} < p_j$ and $q = (q_1, q_2, ..., q_n)$ with $q_{j+1} < q_j$, it is possible to show that $S(p) < S(q)$ when $p$ majorizes $q$, as follows:

$$\sum_{i=1}^{j} p_i > \sum_{i=1}^{j} q_i, \quad (145)$$

for any $j < n$ with

$$\sum_{i=1}^{n} q_i = \sum_{i=1}^{n} p_i = 1. \quad (146)$$

This can be shown by subtracting Eq. (145) from Eq. (146) to obtain:

$$\sum_{i=j+1}^{n} q_i > \sum_{i=j+1}^{n} p_i. \quad (147)$$

Therefore,

$$\sum_{j=1}^{n} \left[ \sum_{i=j+1}^{n} q_i \right] \log \left( \frac{q(i)}{q(j+1)} \right) > \sum_{j=1}^{n} \left[ \sum_{i=j+1}^{n} p_i \right] \log \left( \frac{q(i)}{q(j+1)} \right). \quad (148)$$

Changing the order of the sums in Eq. (148), we obtain:

$$\sum_{i=1}^{n} \left[ \sum_{j=1}^{i-1} q_i \right] \log \left( \frac{q(i)}{q(j+1)} \right) > \sum_{i=1}^{n} \left[ \sum_{j=1}^{i-1} p_i \right] \log \left( \frac{q(i)}{q(j+1)} \right), \quad (149)$$

and canceling equal terms within the sums over $j$, we obtain:

$$\sum_{i=1}^{n} q_i \log \left( \frac{q(1)}{q(i)} \right) > \sum_{i=1}^{n} p_i \log \left( \frac{q(1)}{q(i)} \right),$$

$$\log(q(1)) - \sum_{i=1}^{n} q_i \log(q(i)) > \log(q(1)) - \sum_{i=1}^{n} p_i \log(q(i)), \quad (150)$$

$$- \sum_{i=1}^{n} q_i \log(q(i)) > - \sum_{i=1}^{n} p_i \log(q(i)).$$
Furthermore, since \( \log(x) < x - 1 \), we obtain:

\[
\log \left( \frac{q(i)}{p(i)} \right) < \frac{q(i)}{p(i)} - 1,
\]

\[
p(i) \log \left( \frac{q(i)}{p(i)} \right) < q(i) - p(i),
\]

\[
\sum_{i=1}^{n} p(i) \log \left( \frac{q(i)}{p(i)} \right) < 0,
\]

(151)

\[
\sum_{i=1}^{n} p(i) \log (q(i)) < \sum_{i=1}^{n} p(i) \log (p(i)),
\]

\[- \sum_{i=1}^{n} p(i) \log (q(i)) > - \sum_{i=1}^{n} p(i) \log (p(i)).
\]

Therefore, according to Eqs. (150) and (151), we obtain:

\[- \sum_{i=1}^{n} q(i) \log (q(i)) > - \sum_{i=1}^{n} p(i) \log (p(i)).
\]

(152)

### 21.3 Maximum Entropy Image Reconstruction

Maximum entropy reconstruction is a widely applicable technique for generating images with maximum information, from noisy data, as discussed by Skillin and Bryan [Mon. Not. R. Astr. Soc. (1984) 211, 111-124]. The image is regarded as a set of positive numbers \( f_1, \ldots, f_N \) giving the intensity of pixels which are to be determined for image reconstruction (e.g., the image of a galaxy, or cell culture). The observational constraints on permitted reconstructions come from data points \( D_k \) that are related to the actual image in some known way by means of the measuring device, and subject to some form of noise due to interference with the background. In a linear experiment, \( D_k = \sum R_{kj} f_j + n_k \sigma_k \), where \( R \) is the instrument response, \( \sigma_k \) is the standard error on the data and \( n_k \) is a random variable of zero mean and unit variance. Naively, one may attempt to recover the image \( P \) from the data \( D \) by applying \( R^{-1} \) but this usually fails whenever the data are incomplete since \( R^{-1} \) is not uniquely defined, or when \( R^{-1} \) is badly conditioned as in most deconvolution problems.

The reconstruction is set up by comparing the noisy data \( D_k \) with the simulated data \( F_k \) which would be obtained in the absence of noise: \( F_k = \sum R_{kj} f_j \). A reconstruction is said to be feasible if the simulated data agree with the actual data to within the noise. The misfit is usually measured by the chi-squared value: \( \chi^2 = \sum_k (F_k - D_k)^2 / \sigma_k^2 \), where the summation is over the observed data points \( k \).

According to the maximum entropy criteria, one selects the feasible image with greatest entropy: \( S = -\sum_k P_k \log_2 P_k \), where \( P_k = f_k / \sum_j f_j \), by maximizing \( S \) subject to minimum \( \chi^2 \). Using the Lagrange multiplier method for \( Q = S - \lambda \chi^2 - \mu (1 - \sum_k P_k) \), with some value of the Lagrange multipliers \( \lambda \) and \( \mu \), we make \( \partial Q / \partial f_j = 0 \) to obtain \( f_j \).
As pointed out by Skilling and Bryan, the resulting maximum entropy fitting provides a unique approach to reconstruct an image without introducing correlations beyond those which are required by the data. Maximizing the entropy can also be justified in terms of information. Given an image radiating with intensity pattern \( f_j \), the entropy measures the average number of bits needed to define (or store) the position \( j \) of a single radiated photon coming from the image. Maximizing \( S \), subject to observational constraints, involves seeking a maximally non-biased answer to the fundamental question 'Where would the next photon come from?'. The practical merit of maximizing entropy is that the resulting image has minimum configurational information, so that there must be evidence in the data for any structure which is seen, and the displayed structure is uniquely easy to comprehend.

### 21.4 Fisher Index

Another measure of information is the Fisher index \( I \), defined as follows:

\[
I = \int_{-\infty}^{\infty} dx P(x) \left( \frac{1}{P(x)} \frac{\partial P(x)}{\partial x} \right)^2,
\]

\[
= \int_{-\infty}^{\infty} dx P(x) \left( \frac{\partial \log[P(x)]}{\partial x} \right)^2.
\]  

(153)

For an ergodic system, \( P(x) \) is determined by the time the variable is found at \( x \) over the total observation time, so the total probability is normalized:

\[
1 = \int_{-\infty}^{\infty} dx P,
\]

\[
= \lim_{t_f \to \infty} \frac{1}{t_f} \int_{-t_f/2}^{t_f/2} dt,
\]

\[
= \lim_{t_f \to \infty} \frac{1}{t_f} \int_{-\infty}^{\infty} dx \left| \frac{\partial t}{\partial x} \right|,
\]

\[
= \lim_{t_f \to \infty} \frac{1}{t_f} \int_{-\infty}^{\infty} dx \frac{1}{\sqrt{v^2}},
\]

(154)

from where we identify \( 1/P = t_f \sqrt{v^2} \), with \( t_f \to \infty \). Therefore,

\[
I = \lim_{t_f \to \infty} t_f \int_{-\infty}^{\infty} dx \sqrt{v^2} \left( \frac{\partial P}{\partial x} \right)^2,
\]

\[
= \lim_{t_f \to \infty} t_f \int_{-\infty}^{\infty} dx v^2 \left| \frac{\partial t}{\partial x} \right| \left( \frac{\partial P}{\partial x} \right)^2,
\]

\[
= \lim_{t_f \to \infty} t_f \int_{-\infty}^{\infty} dx \left| \frac{\partial t}{\partial x} \right| \left( \frac{\partial P}{\partial t} \right)^2,
\]

\[
= \lim_{t_f \to \infty} t_f \int_{-\infty}^{\infty} dt \left( \frac{\partial P}{\partial t} \right)^2,
\]

(155)
In the third row of Eq. (155), we have used that \( \frac{\partial P}{\partial x} = -\frac{1}{v} \frac{\partial P}{\partial t} \), since according to the continuity equation \( \frac{dP}{dt} = \frac{\partial P}{\partial t} + v \frac{\partial P}{\partial x} \) and \( dP/dt = 0 \) for the system at equilibrium. Furthermore,

\[
\frac{\partial P}{\partial t} = \frac{1}{t_f} \frac{\partial}{\partial t} (v^2)^{-1/2},
\]

\[
= \frac{1}{t_f} \left( -\frac{1}{2} \right) (v^2)^{-3/2} 2v \frac{\partial v}{\partial t}
\]

\[
= -\frac{1}{t_f} \frac{1}{v^2} \frac{\partial v}{\partial t} = -\frac{1}{t_f} \frac{a}{v^2} = -\frac{1}{t_f} \frac{F}{mv^2}.
\]  \hspace{1cm} (156)

Therefore,

\[
I = \lim_{t_f \to \infty} \frac{1}{t_f} \int_{t_f/2}^{t_f/2} dt \frac{F^2}{(mv^2)^2},
\]

\[
= \left\langle \frac{F^2}{(mv^2)^2} \right\rangle ,
\]  \hspace{1cm} (157)

### 21.5 Mutual Information

The goal of this section is to introduce measures of mutual information (or uncertainty) shared by variables \( x_1 \) and \( x_2 \). Such measures estimate the amount of uncertainty about a variable \( x_1 \) reduced by measuring a variable \( x_2 \). In particular, when \( x_1 \) and \( x_2 \) are completely uncorrelated, knowing one of the two variables does not provide any information about the other and the joint probability distribution \( P(x_1, x_2) \) is equal to the product of the marginal probability distributions \( P_1(x_1) = \int dx_2 P(x_1, x_2) \) and \( P_2(x_2) = \int dx_1 P(x_1, x_2) \).

The most common measure of mutual information is the index \( I_{x_1, x_2} \), defined as follows:

\[
I_{x_1, x_2} = \int dx_1 dx_2 P(x_1, x_2) \left( \log[P(x_1, x_2)] - \log[P_1(x_1)P_2(x_2)] \right).
\]  \hspace{1cm} (158)

Note that in the particular case of uncorrelated variables, \( I_{x_1, x_2} = 0 \).

Analogously, another measure of mutual information can be defined, as follows:

\[
\tilde{I}_{x_1, x_2} = \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 P \left( \frac{1}{P_1^2} \left( \frac{\partial P}{\partial x_1} \right)^2 + \frac{1}{P_2^2} \left( \frac{\partial P}{\partial x_2} \right)^2 - \frac{1}{P_1^2} \left( \frac{\partial P_1}{\partial x_1} \right)^2 - \frac{1}{P_2^2} \left( \frac{\partial P_2}{\partial x_2} \right)^2 \right).
\]  \hspace{1cm} (159)
Bose-Einstein and Fermi-Dirac Distributions

Consider a system consisting of $N$ quantum particles of a certain kind (e.g., bosons, or fermions with a certain spin). If the interaction of the particles is weak enough, each particle has its own motion which is independent of all others and the system is an ideal gas of quantum particles. The quantum states allowed for this individual motion are the one-particle states $|j\rangle$ that satisfy the eigenvalue problem

$$H|j\rangle = \epsilon_j |j\rangle,$$

where $\epsilon_j$ are the eigenvalues. Since identical particles are indistinguishable in quantum mechanics, each quantum state $|\xi\rangle$ for the complete system is completely specified when the number of particles occupying each one-particle state is specified —i.e., the quantum numbers $\xi$ of the whole system are determined by the set of occupation numbers $n_1, n_2, \ldots$. The total energy of each quantum state $|\xi\rangle$ is, therefore,

$$E_\xi = \sum_j n_j \epsilon_j.$$

Furthermore, since the quantum particles are indistinguishable,

$$\hat{P}_{jk}|\xi(1, 2, 3, \ldots, j, j + 1, \ldots, k, k + 1, \ldots)\rangle = \pm|\xi(1, 2, 3, \ldots, k, j + 1, \ldots, j, j + 1, \ldots)\rangle,$$

where $\hat{P}_{jk}$ is the operator that permutes particles $j$ and $k$. The plus sign, in Eq. (162), corresponds to a system of bosons (i.e., integer spin particles) and the minus sign corresponds to a system of fermions (i.e., half-integer spin particles). The Pauli Exclusion Principle is a consequence of the symmetry requirement introduced by Eq. (162). Such principle establishes that in a system of fermions with the same spin there cannot be two particles occupying the same spatial state, and, therefore, $n_j = 0, 1$. In a system of bosons, however, $n_j = 0, 1, 2, \ldots$ —i.e., there can be an arbitrary large number of particles in each state $j$.

The grand canonical partition function for a system of indistinguishable particles is defined, according to Eq. (87),

$$\Xi = \sum_\xi e^{-\beta E_\xi + \beta \mu n_\xi},$$

or in terms of occupation numbers $n_j$,

$$\Xi = \sum_{n_1, n_2, \ldots} e^{-\beta \sum_k \epsilon_k n_k + \beta \mu \sum_k n_k}.$$

The grand canonical partition function for a system of fermions is

$$\Xi = \prod_k \sum_{n_k=0}^{1} e^{-\beta \epsilon_k n_k + \beta \mu n_k} = \prod_k (1 + e^{\beta (\mu - \epsilon_k)}),$$

due to the Pauli Exclusion Principle and Eq. (164). Therefore, the average occupation number

$$\bar{n}_k = \Xi^{-1} \sum_{n_1, n_2, \ldots} n_k e^{-\beta \sum_k \epsilon_k n_k + \beta \mu \sum_k n_k} = \partial \ln \Xi / \partial (-\beta \epsilon_j),$$
is given by the following expression

\[ n_k = \frac{e^{\beta(\mu - \epsilon_k)}}{e^{\beta(\mu - \epsilon_k)} + 1} = \frac{1}{1 + e^{\beta(\epsilon_k - \mu)}}, \]  

(167)

which is the \textit{Fermi-Dirac distribution}.

Analogously, the grand canonical partition function for a system of bosons is

\[ \Xi = \prod_k \sum_{n_k=0}^{\infty} e^{-\beta(\epsilon_k - \mu)n_k} = \prod_k \frac{1}{1 - e^{\beta(\epsilon_k - \mu)}}, \]  

(168)

Therefore, the average occupation number is given by the following expression

\[ \overline{n}_k = \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1}, \]  

(169)

which is the \textit{Bose-Einstein distribution}.

23 Classical limit of Quantum Statistical Distributions

According to Eqs. (167) and (169), the average number \( n_j \) of noninteracting quantum particles in state \( j \) is

\[ \overline{n}_j = \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1}, \]  

(170)

where the minus sign corresponds to the Bose-Einstein distribution and the plus sign corresponds to the Fermi-Dirac distribution.

In the limit when \( \overline{n}_j \to 0 \) the system is very "dilute", since there are much more energetically accessible states than particles. This limit is achieved for all states of energy \( \epsilon_j \) when

\[ e^{\beta(\epsilon_j - \mu)} \gg 1. \]  

(171)

Therefore, in the limit when \( \overline{n}_j \to 0 \),

\[ \overline{n}_j \approx e^{-\beta(\epsilon_j - \mu)}, \]  

(172)

and the average number of particles is

\[ \overline{N} = \sum_j \overline{n}_j \approx \sum_j e^{-\beta(\epsilon_j - \mu)}, \]  

(173)

so that

\[ \beta \mu = \ln \overline{N} - \ln \sum_j e^{-\beta\epsilon_j}. \]  

(174)
Moreover, according to Eqs. (172) and (173),
\[
\frac{\bar{n}_j}{N} = \frac{e^{-\beta \epsilon_j}}{\sum_j e^{-\beta \epsilon_j}},
\] (175)
which is the classical Boltzmann distribution. Therefore, in the limit when \( \bar{n}_j \to 0 \) both the Fermi-Dirac and the Bose-Einstein distributions converge to the classical Boltzmann distribution.

Furthermore, according to Eqs. (165) and (168),
\[
\ln \Xi = \pm \sum_j \ln (1 \mp e^{-\beta (\epsilon_j - \mu)}),
\] (176)
and in the limit when \( e^{\beta (\epsilon_j - \mu)} \gg 1 \),
\[
\ln \Xi \approx \sum_j e^{-\beta (\epsilon_j - \mu)},
\] (177)
since
\[
\lim_{x \to 0} \ln (1 + x) = x.
\] (178)
Therefore, according to Eqs. (173) and (177),
\[
\ln \Xi \approx N,
\] (179)
and according to Eqs. (179) and (91),
\[
N \approx \ln Z + \beta \mu N.
\] (180)
Substituting Eq. (174) into Eq. (179), we obtain
\[
N \approx \ln Z + N \ln N - N \ln \sum_j e^{-\beta \epsilon_j},
\] (181)
and according to the Stirling formula, introduced by Eq. (60),
\[
Z = \left( \frac{\sum_j e^{-\beta \epsilon_j}}{N!} \right)^N,
\] (182)
where the \( 1/N! \) factor, in Eq. (182), indicates that quantum particles remain indistinguishable even in the classical limit!
24 Gibbs Paradox

The factor $1/N!$, in Eq. (182), is essential to resolve the paradox formulated by Gibbs before the discovery of Quantum Mechanics, stating that the entropy of a gas of $N$ particles in a volume $V$ at temperature $T$ decreases by a factor of $N$ $k \ln(2)$ when the system is divided in 2 by an internal membrane, although the thermodynamic quantities that define the state (i.e., $N$, $T$, $V$) remain constant.

To explain the paradox and its solution, consider a monatomic gas of $N$ non-interacting molecules at temperature $T$ and volume $V$, with internal energy $E = \frac{3}{2}NkT$ and entropy $S = \frac{E}{T} + k\ln(Z)$.

If we ignore the factor $1/N!$, in Eq. (182), we obtain:

$$Z = \left( \sum_j e^{-\beta \epsilon_j} \right)^N$$

$$= \left( \int dr \int dpe^{-\frac{p^2}{2m}} \right)^N$$

$$= V^N \left( \frac{\pi m}{\beta} \right)^{3N/2}$$

(183)

Therefore, $\ln(Z) = N\ln(V) + \frac{3}{2}N\ln\left( \frac{\pi m}{\beta} \right)$ and the entropy is:

$$S = \frac{3}{2}Nk + Nk\ln(V) + \frac{3}{2}Nk\ln\left( \frac{\pi m}{\beta} \right).$$

(184)

Equation (184) leads to the Gibbs paradox when we consider twice the entropy $S_{1/2}$ of half of the system (e.g., with half the number of particles $N/2$ and volume $V/2$):

$$2 \times S_{1/2} = \frac{3}{2}Nk + Nk\ln(V) + \frac{3}{2}Nk\ln\left( \frac{\pi m}{\beta} \right) - Nk\ln(2),$$

(185)

since $2 \times S_{1/2} \neq S$ and the sum of the entropies of the halves should be equal to the total entropy.

In contrast, correcting Eq. (184) with the factor $1/N!$, using the Sterling approximation $\ln(N!) \approx N\ln(N) - N$, we obtain:

$$S = \frac{3}{2}Nk + Nk\ln(V) + \frac{3Nk}{2} \ln\left( \frac{\pi m}{\beta} \right) - Nk\ln(N) + Nk$$

(186)

and

$$2 \times S_{1/2} = \frac{3}{2}Nk + Nk\ln(V) + \frac{3Nk}{2} \ln\left( \frac{\pi m}{\beta} \right) - Nk\ln(2) - Nk\ln(N) + Nk + Nk\ln(2).$$

(187)

showing that $S = 2 \times S_{1/2}$.

The origin of the paradox is thus the misleading assumption that particles are distinguishable. However, that would require a method to determine whether a specific molecule is on one side of the dividing membrane or the other.
### 25 Example 1: Ideal Gas of Structureless Quantum Particles

An ideal gas of \( N \) non-interacting structureless particles of mass \( m \) is described by the \( N \)-particle Hamiltonian

\[
\hat{H} = \sum_{j=1}^{N} \hat{h}_j,
\]

where \( \hat{h}_j \) is the one-particle Hamiltonian

\[
\hat{h}_j = -\frac{\hbar^2}{2m} \nabla^2_{R_j} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x_j^2} + \frac{\partial^2}{\partial y_j^2} + \frac{\partial^2}{\partial z_j^2} \right),
\]

with \( R_j = (x_j, y_j, z_j) \). The eigenstates of \( \hat{h}_j \) are the free-particle states

\[
\phi_j(x, y, z) = A e^{i k_j \cdot R_j},
\]

where \( k_j = (k_x, k_y, k_z) \), and \( A \) is a normalization constant determined by the volume of the box that contains the gas. The one-particle eigenstates satisfy the eigenvalue problem

\[
\hat{h}_j |\phi_j> = \epsilon_j |\phi_j>,
\]

with \( \epsilon_j = (\hbar k_j)^2/(2m) \). Note that since the volume of the box is \( V = L_x \times L_y \times L_z \), and \( |\phi_j> \) are stationary states, then \( Kx Lx = nx \pi, Ky Ly = ny \pi \) and \( Kz Lz = nz \pi \), with \( nx, ny, nz = 1, 2, \ldots \)

Therefore,

\[
\sum_{nx,ny,nz} = \sum_{Kx,Ky,Kz} V \frac{1}{\pi^3} \ldots
\]

and

\[
Z = \frac{1}{N!} \left( \sum_j e^{-\beta \epsilon_j} \right)^N = \frac{1}{N! \pi^{3N}} \left( V \int_0^\infty dK_x \int_0^\infty dK_y \int_0^\infty dK_z e^{-\frac{\beta k^2}{2m}(K_x^2 + K_y^2 + K_z^2)} \right)^N.
\]

Computing the Gaussian integrals analytically, we obtain

\[
Z = \frac{1}{N! \pi^{3N}} \left( V \int_0^\infty dK_x \int_0^\infty dK_y \int_0^\infty dK_z e^{-\frac{\beta k^2}{2m}(K_x^2 + K_y^2 + K_z^2)} \right)^N = \frac{V^N}{2^{3N} N! \pi^{3N}} \left( \frac{2\pi m}{\beta \hbar^2} \right)^{3N/2},
\]

since \( \int_0^\infty e^{-ax^2} dx = \frac{\sqrt{\pi}}{\alpha} \). Therefore,

\[
Z = \frac{V^N}{N! \hbar^{3N}} \left( \frac{2\pi m}{\beta} \right)^{3N/2} \Rightarrow E = -\frac{\partial \ln Z}{\partial \beta} \bigg|_{V,N} = \frac{3}{2} NkT.
\]
In addition, defining the pressure \( p \) according to

\[
\beta p \equiv \frac{\partial \ln Z}{\partial V} \bigg|_{T,N}
\]

we obtain

\[
\beta p = \frac{N}{V} \Rightarrow pV = NkT,
\]

which is the equation of state for an ideal gas of structureless particles.

### 26 Example 2: Dilute Gas of Diatomic Molecules

In the previous example, we showed that the state of a structureless particle is completely defined by the vector \( \mathbf{K} = (K_x, K_y, K_z) \) that specifies the momentum \( \mathbf{K} \hbar \) of the center of mass. Specifying the state of a molecule, however, requires the specification of its internal state besides specifying the translation of the molecule as a whole, since the molecule can vibrate, rotate, or undergo electronic excitations while translating as specified by the vector \( \mathbf{K} \).

Contrary to structureless particles, molecules are described by the Hamiltonian

\[
\hat{H} = -\frac{\hbar^2}{2m} \nabla_\mathbf{R}^2 + \hat{H}_{el}(\mathbf{R}, \mathbf{r}),
\]

where, \( \mathbf{R} \) and \( \mathbf{r} \) are the nuclear and electronic coordinates.

A simple expression for the canonical partition function of an ideal gas of diatomic molecules in the ground electronic state can be obtained by factorizing the total energy into translational, rotational and vibrational modes (i.e., assuming that these modes are uncoupled from each other) and then modeling vibrations according to the harmonic approximation and rotations according to the rigid rotor approximation. The resulting partition function is

\[
Z = \left( \frac{\sum_j e^{-\beta E_j}}{N!} \right)^N,
\]

Here, \( E_j = E_{rot}(J(j)) + E_{transl}(n(i)) + E_{vib}(\nu(j)) \), where \( J(j) \) specifies the rotational quantum number, \( \nu(j) \) the vibrational quantum number and \( n(j) \) the translational modes of particle \( j \).

Therefore,

\[
Z = \left( \frac{q_{transl} \cdot q_{int}}{N!} \right)^N, \quad \text{where} \quad q_{int} = q_{rot} \cdot q_{vib},
\]

with

\[
q_{rot} = \sum_{J=0}^{\infty} (2J + 1) e^{-\beta \omega_0^2 J(J+1)},
\]

and

\[
q_{vib} = \sum_{\nu=0}^{\infty} e^{-\beta \omega_0(1/2+\nu)} = \frac{e^{-\beta \omega_0/2}}{1 - e^{-\beta \omega_0/2}},
\]
and according to Eq. (194),
\[ q_{\text{transl}} = \frac{V}{\hbar^3} \left( \frac{2\pi m}{\beta} \right)^{3/2}. \] (202)

Note that for simplicity we have ignored the internal structure of nuclei and the degeneracy factor associated with the permutation of indistinguishable nuclei.

27 Example 3: Phonons in a Solid Lattice

Having computed the partition function of a harmonic oscillator, we now compute the partition function of the normal modes of a solid at low temperature. According to the harmonic approximation, the Hamiltonian of the system is
\[ \hat{H} = \sum_{\alpha=1}^{DN} \hat{h}_\alpha, \] (203)
where DN is the number of normal modes, with D the dimensionality of the lattice and \( \hat{h}_\alpha \) is the Hamiltonian of a harmonic oscillator with a frequency \( \omega_\alpha \) and eigenvalues
\[ E_{n}(\alpha) = \hbar \omega_\alpha \left( \frac{1}{2} + n_\alpha \right), \] (204)
with \( n_\alpha = 1, 2... \)

An arbitrary vibrational state \( \xi \) of the lattice can be specified by the DN normal mode frequencies \( \omega_\alpha \) and vibrational quantum numbers \( n_\alpha \). The energy of such state is
\[ E_\xi = \sum_{\alpha=1}^{DN} [n_\alpha \hbar \omega_\alpha + \frac{\hbar}{2} \omega_\alpha]. \] (205)

The canonical partition function for the lattice is
\[ Z(\beta, N) = \sum_{n_1} \sum_{n_2} \sum_{n_3} ... \exp \left( -\beta \sum_{\alpha=1}^{DN} n_\alpha \hbar \omega_\alpha + \frac{\hbar}{2} \omega_\alpha \right), \] (206)
which according to Eq.(174) becomes,
\[ Z(\beta, N) = \prod_{\alpha=1}^{DN} \frac{e^{-\beta \hbar \omega_\alpha}}{1 - e^{-\beta \hbar \omega_\alpha}} = \prod_{\alpha=1}^{DN} (e^{\frac{\beta \hbar \omega_\alpha}{2}} - e^{-\beta \frac{\hbar \omega_\alpha}{2}})^{-1}, \] (207)
and
\[ \ln Z = -\sum_{\alpha=1}^{DN} \ln (e^{\frac{\beta \hbar \omega_\alpha}{2}} - e^{-\beta \frac{\hbar \omega_\alpha}{2}}), \] (208)
or in the continuous representation,

\[
\ln Z = - \int_0^\infty d\omega g(\omega) \ln\left( e^{\beta \frac{\hbar \omega}{2}} - e^{-\beta \frac{\hbar \omega}{2}} \right)
\]  

(209)

where \( g(\omega) \) is the density of states — i.e., the number of vibrational states with frequencies between \( \omega \) and \( \omega + d\omega \).

### 27.1 Einstein Model

The Einstein model assumes that all vibrational modes in a solid lattice have the same frequency \( \omega_E \) and, therefore,

\[
g(\omega) = DN\delta(\omega - \omega_E).
\]

(210)

Substituting Eq. (210) into Eq. (209) we obtain

\[
\ln Z = - ND \ln\left( e^{+\beta \hbar \omega_E/2} - e^{-\beta \hbar \omega_E/2} \right).
\]

(211)

The average internal energy of the lattice can be computed from Eq. (211) as follows,

\[
E = \frac{\partial \ln Z}{\partial (-\beta)} = +DN \frac{\hbar \omega_E}{2} \coth(\beta \hbar \omega_E/2).
\]

(212)

Note that in the high temperature limit,

\[
\lim_{\beta \to 0} E = \frac{DN}{\beta} = DNkT.
\]

(213)

The heat capacity at constant volume \( C_v \) can also be obtained from Eq. (211) as follows,

\[
C_v = \left( \frac{\partial E}{\partial T} \right)_v = -N D \frac{\hbar \omega_E}{2kT^2} \left( e^{\beta \hbar \omega_E/2} - e^{-\beta \hbar \omega_E/2} \right)^2
\]

\[
\times \left( e^{+\beta \hbar \omega_E/2} - e^{-\beta \hbar \omega_E/2} \right)^2.
\]

(214)

The expression introduced by Eq. (214) can be simplified to obtain

\[
C_v = \frac{\theta}{T} \left( \frac{DNk}{e^{\theta/T} - 1} \right)^2 = NDk \frac{\theta}{T} \left( \frac{e^\theta}{e^{\theta/T} - 1} \right)^2.
\]

(215)

with \( \theta \equiv \frac{\hbar \omega_E}{2k} \).
Limiting cases
(i) At high temperature, \( \theta << T \) and \( e^\frac{\theta}{T} \approx 1 + \frac{\theta}{T} \). Therefore,

\[
C_v = NDK \left( \frac{\theta}{T} \right)^2 \frac{1 + \frac{\theta}{T} + \ldots}{(1 + \frac{\theta}{T} - 1 + \ldots)^2} = NDK. \tag{216}
\]

Eq. (216) is the Dulong-Petit’s law —i.e., the experimental limit for \( C_v \) at high temperature.
(ii). At low temperature, \( \theta >> T \). Therefore,

\[
C_v = NDK \left( \frac{\theta}{T} \right)^2 e^{-\frac{\theta}{T}}. \tag{217}
\]

It is important to note that Eq. (217) does not predict the correct limit for \( C_v \) at low temperature, since \( C_v \) should be proportional to \( T^3 \) when \( T \rightarrow 0 \).

27.2 Debye Model
Debye approximated the normal vibrations with the elastic vibrations of an isotropic continuous body where the number of vibrational modes with frequencies between \( \omega \) and \( \omega + d\omega \) is

\[
g(\omega) = \begin{cases} 
\xi \omega^2, & \text{when } \omega < \omega_0, \\
0, & \text{otherwise},
\end{cases} \tag{218}
\]

where \( \xi \equiv 3V/(2\pi^2c^3) \) and

\[
\int_0^{\omega_0} d\omega g(\omega) = 3N = \frac{V\omega_0^3}{2\pi^2c^3}. \tag{219}
\]

Therefore,

\[
\xi = 9N2\pi^2c^3/(\omega_0^32\pi^2c^3). \tag{220}
\]

According to Eqs. (219) and (209),

\[
\ln Z = -\int_0^{\omega_0} d\omega \xi \omega^2 \ln \left( e^{\beta h\omega} - e^{-\beta h\omega} \right). \tag{221}
\]

Therefore,

\[
\ln Z = -\int_0^{\omega_0} d\omega \xi \omega^2 \ln e^{\beta h\omega} - \int_0^{\omega_0} d\omega \xi \omega^2 \ln(1 - e^{\beta h\omega}), \tag{222}
\]

and

\[
\ln Z = -\frac{\beta h}{2} \xi \frac{\omega_0^4}{4} - \int_0^{\omega_0} d\omega \xi \omega^2 \ln(1 - e^{\beta h\omega}). \tag{223}
\]

The internal energy \( E \) is computed from Eqs. (223) and (220) as follows,

\[
E = \frac{\partial \ln Z}{\partial (-\beta)} = \frac{\hbar}{2} \frac{9N\omega_0^4}{\omega_0^44} + \int_0^{\omega_0} d\omega \xi \omega^3 \hbar \frac{e^{-\beta h\omega}}{1 - e^{-\beta h\omega}}, \tag{224}
\]
and introducing the change of variables $\gamma \equiv \beta \hbar \omega$,

$$E = \frac{\hbar}{2} \frac{9N\omega_0}{4} + \frac{1}{\beta \hbar} \int_0^{\beta \hbar \omega_0} d\gamma \xi \frac{\gamma^3}{(\beta \hbar)^3} \hbar \frac{1}{(e^\gamma - 1)^{\frac{1}{3}}}.$$  \hspace{1cm} (225)

Considering that

$$f(x) = \frac{3}{x^3} \int_0^x d\gamma \frac{\gamma^3}{e^\gamma - 1} = \begin{cases} 1 - \frac{3}{8}x + \ldots & x << 1, \\ \frac{\pi}{5x^3} + \ldots & x >> 1, \end{cases}$$ \hspace{1cm} (226)

we obtain, according to Eqs. (225) and (226),

$$\tilde{E} = E - \frac{\hbar}{2} \frac{9N\omega_0}{4} = \frac{\omega_0^3 3N}{\beta \omega_0^3} \times \begin{cases} 1 - \ldots = 3NkT & \text{when } T \to \infty, \\ \frac{\pi}{5(\beta \hbar \omega_0)^\frac{3}{5}} = \frac{(kT)^3}{5(\hbar \omega_0)^3} & \text{when } T \to 0. \end{cases}$$ \hspace{1cm} (227)

Therefore the Debye model predicts the following limits for the heat capacity of a solid lattice,

$$C_v = \begin{cases} 3Nk & \text{when } T \to \infty, \\ 3Nk^4 \frac{\pi^4}{5(\hbar \omega_0)^3} T^3 & \text{when } T \to 0. \end{cases}$$ \hspace{1cm} (228)

which are the correct high and low temperature limits, represented by the following diagram:

28 Example 4: Electrons in Metals

The goal of this section is to show that even at room temperature, the conducting electrons in metals can be modeled as an ideal gas of fermions contained in a box of volume $V = L^3$, where $L$ defines the dimensions of the piece of metal. Such a goal is accomplished by comparing the kinetic energy of conducting electrons, modeled as an ideal gas of fermions, with typical energy fluctuations due to thermal motion.

The average number of electrons occupying the $j$-th energy state is

$$n_j = \frac{1}{e^{\beta (\epsilon_j - \mu)} + 1},$$ \hspace{1cm} (229)
where
\[ \epsilon_j = \frac{\hbar^2 K_j^2}{2m}, \quad (230) \]
and
\[ K_j = (n_x(j), n_y(j), n_z(j)) \pi / L \quad (231) \]
with \( n_x(j), n_y(j), n_z(j) = 1, 2, \ldots \) Therefore, the average number of electrons is
\[ \overline{N} = \sum_j n_j, \quad (232) \]
\[ \overline{N} = 2 \sum_{n_x} \sum_{n_y} \sum_{n_z} \frac{1}{e^{\beta(\epsilon(n_x,n_y,n_z)-\mu)} + 1}, \quad (233) \]
or,
\[ \overline{N} = 2 \int_{-\infty}^{\infty} dk_x \int_{-\infty}^{\infty} dk_y \int_{-\infty}^{\infty} dk_z \left( \frac{L}{\pi} \right)^3 \frac{1}{e^{\beta(\epsilon(n_x,n_y,n_z)-\mu)} + 1}. \quad (234) \]
In particular, at \( T = 0 \),
\[ \frac{1}{1 + e^{\beta(\epsilon(n_x,n_y,n_z)-\mu)}} = \begin{cases} 1, & \frac{\hbar^2 K_j^2}{2m} < \mu, \\ 0, & \frac{\hbar^2 K_j^2}{2m} > \mu, \end{cases} \quad (235) \]
therefore,
\[ \overline{N} = 8\pi \int_0^{K_f} dK K^2 \left( \frac{L}{2\pi} \right)^3 = 8\pi \left( \frac{L}{2\pi} \right)^3 \frac{K_f^3}{3} = \frac{2V}{(2\pi)^3} \frac{4}{3} \pi K_f^3, \quad (236) \]
where \( K_f \) is the Fermi momentum defined as follows
\[ \frac{\hbar^2 K_f^2}{2m} = \mu. \quad (237) \]
The value of \( K_f \) for a specific metal can be found, according to Eq. (236) and using the values of the density and atomic weight of the corresponding metal, assuming that each atom in the metal donates an electron to the conducting electron gas. Such value of \( K_f \), can be used to compute the chemical potential according to Eq. (237). The calculation for Cu, with a density of 9 g/cm\(^3\) and atomic weight of 63.5 g/mol gives
\[ \mu/k \approx 80,000K, \quad (238) \]
which indicates that even at room temperature the ideal gas approximation is accurate.

**Thermal Energy and Heat Capacity**

The remaining of this section proves that at low temperature \( T \) the heat capacity \( C_v \) of electrons in metals is proportional \( T \).

The thermal energy \( E \) of electrons in metals is
\[ E = \sum_j 2\overline{n}_j \epsilon_j, \quad (239) \]
where index $j$ specifies a one-electron quantum state with energy $\epsilon_j$ and $n_j$ is the average number of electrons with one kind of spin in such state. The factor 2, introduced by Eq. (239) counts for the spin degeneracy. Substituting $n_j$ according to Eq. (229) and changing the sum over $j$ by a sum over energy levels we obtain

$$E = 2 \int_0^\infty d\epsilon \frac{\rho(\epsilon)\epsilon}{e^{\beta(\epsilon-\mu)} + 1},$$  

where $\rho(\epsilon)$ is the degeneracy of the energy level. Eq. (240) can be integrated by parts, according to

$$\int_a^b ud\phi = u \phi \bigg|_a^b - \int_a^b \phi du,$$

defining $d\phi = \epsilon \rho(\epsilon)d\epsilon$ and $u(\epsilon) = 1/(exp(\beta(\epsilon-\mu)) + 1)$. Note that according to this choice of variables $\phi(\epsilon) = \int_0^\epsilon d\bar{\epsilon}\rho(\bar{\epsilon})\bar{\epsilon}$. We obtain

$$E = \lim_{\epsilon \to \infty} \frac{2\int_0^\epsilon d\epsilon' \rho(\epsilon')\epsilon'}{e^{\beta(\epsilon-\mu)} + 1} - \lim_{\epsilon \to 0} \frac{2\int_0^\epsilon d\epsilon' \rho(\epsilon')\epsilon'}{e^{\beta(\epsilon-\mu)} + 1} - 2 \int_0^\infty d\epsilon \int_0^\epsilon d\epsilon' \rho(\epsilon')\epsilon' \frac{(-e^{\beta(\epsilon' - \mu)})}{(e^{\beta(\epsilon' - \mu)} + 1)^2}.$$  

(242)

Note that the first term, introduced by Eq. (242) is equal to 0 since in the limit when $\epsilon \to \infty$ the denominator becomes extremely large. The second term introduced by Eq. (242) is also equal 0 since in the limit when $\epsilon \to 0$ the numerator is equal to 0. Therefore, introducing the definition

$$F(\epsilon) \equiv \frac{1}{e^{\beta(\epsilon-\mu)} + 1},$$  

(243)

we obtain that Eq. (242) can be rewritten as follows,

$$E = -2 \int_0^\infty d\epsilon \rho(\epsilon) \frac{\partial F}{\partial \epsilon}.$$  

(244)

At this point, it is important to note that $\partial F/\partial \epsilon$ is a function peaked at $\epsilon = \mu$, as represented by the following diagram,
Therefore we can approximate \( \phi(\epsilon) \), in Eq. (244), by its expansion around \( \epsilon = \mu \),

\[
\phi(\epsilon) = \phi(\mu + x) \approx \sum_{n=0}^{\infty} \left. \frac{\partial^n \phi}{\partial \epsilon^n} \right|_{\epsilon=\mu} (\epsilon - \mu)^n \frac{n!}{n!},
\]

(245)

where \( x \equiv \epsilon - \mu \). Substituting Eq. (245) into Eq. (244) for a given spin, we obtain,

\[
E = - \int_{0}^{\infty} d\epsilon \sum_{n=0}^{\infty} \left. \frac{\partial^n \phi}{\partial \epsilon^n} \right|_{\epsilon=\mu} (\epsilon - \mu)^n \frac{n!}{n!} \frac{\partial F}{\partial \epsilon}.
\]

(246)

Considering the first few terms of Eq. (246) we obtain,

\[
E = \phi(\mu) \left( - \int_{0}^{\infty} d\epsilon \frac{\partial F}{\partial \epsilon} \right) + \frac{\partial \phi}{\partial \epsilon} \left( - \int_{0}^{\infty} d\epsilon (\epsilon - \mu) \frac{e^{\beta(\epsilon - \mu)}}{e^{2\beta(\epsilon - \mu) + 1}} \right) + \frac{(kT)^2}{2} \frac{\partial^2 \phi}{\partial \epsilon^2} \left( - \int_{0}^{\infty} d\epsilon \frac{(\epsilon - \mu)^2}{e^{2\beta(\epsilon - \mu) + 1}} \right) + \ldots,
\]

(247)

where the first term is equal to \( \phi(\mu) \) because \( F(\infty) = 0 \) and \( F(0) = 1 \). To show that the second term in Eq. (247) is equal to 0 we rewrite Eq. (247) in terms of the variable \( \bar{x} = \beta x \),

\[
E = \phi(\mu) \left( - \int_{-\infty}^{\infty} d\bar{x} \frac{\partial F}{\partial \bar{x}} \right) + \frac{\partial \phi}{\partial \bar{x}} \left( - \int_{-\infty}^{\infty} d\bar{x} (\bar{x} - \mu) \frac{1}{e^{2\beta(\bar{x} - \mu) + 1}} \right) + \frac{(kT)^2}{2} \frac{\partial^2 \phi}{\partial \bar{x}^2} \left( - \int_{-\infty}^{\infty} d\bar{x} \frac{\bar{x}^2}{e^{2\beta(\bar{x} - \mu) + 1}} \right) + \ldots,
\]

(248)

where the lower integration limit has been changed from 0 to \( -\infty \) since the integrand is approximately equal to zero whenever \( \text{abs}(\epsilon - \mu) \) is large. Note that the integral introduced by the second
term of Eq. (248) is equal to 0 because the integrand is odd. In addition,

\[ \int_{-\infty}^{\infty} d\bar{x} \frac{\bar{x}^2}{e^\bar{x} + e^{-\bar{x}} + 2} = \frac{\pi^2}{3}, \]

therefore,

\[ E = \phi(\mu) + \frac{(kT)^2}{2} \frac{\partial^2 \phi}{\partial \epsilon^2} \left( -\frac{\pi^2}{3} \right) + ..., \]

At sufficiently low T, higher order terms in Eq. (250) are negligible. Therefore, at low T

\[ C_v \propto T, \]

as observed in experiments.

### 28.1 Continuous Approximation

The goal of this subsection is to show that the error introduced by approximating Eq. (233) according to Eq. (234) is negligible when L_y sufficiently large. For simplicity, we show this for a 1-dimensional problem, where

\[ \sum_{K_x = \pi/L}^{\infty} \frac{1}{e^{\beta \left( \frac{\hbar^2}{2m} K_x^2 - \mu \right)} + 1} = \sum_{K_x} f(K_x) \Delta K, \]

with

\[ f(K_x) = \frac{1}{e^{\beta(\epsilon(K_x) - \mu)} + 1} \frac{L_x}{\pi}, \]

a decreasing function of K_x and

\[ \Delta K = \frac{\pi}{L_x}, \]

Remember, that \( K_x = K_x(n_x) \) is a function of the quantum number n_x, as defined by Eq. (231), where n_x = 1, 2, ..., with \( K_x = n_x \pi/L \).

The discrete sum, introduced by Eq. (252), can be represented by the following diagram,
The diagram shows that,
\[
\sum_{n_x=1}^{\infty} f(K_x(n_x)) \Delta K \leq \int_0^{\infty} dK f(K) \leq \sum_{n_x=0}^{\infty} f(K_x(n_x)) \Delta K = \sum_{n_x=1}^{\infty} f(K_x(n_x)) \Delta K + f(K_x(0)) \Delta K,
\]
(255)
since \(f(K_x(n_x))\) is a decreasing function of \(K_x\). So,
\[
0 \leq \int_0^{\infty} dK f(K) - \sum_{n_x=1}^{\infty} f(K_x(n_x)) \Delta K \leq f(K_x(0)) \Delta K \leq 1.
\]
(256)
Therefore, Eq. (256) shows that the discrete sum and the integral become equal to each other when \(L_x\) is very large since
\[
0 \leq \int_0^{\infty} dK_x e^{\beta(\epsilon(K_x)-\mu)} + 1 - \sum_{K_x=\pi/L}^{\infty} \Delta K_x e^{\beta(\epsilon(K_x(\pi))-\mu)} + 1 \leq \frac{\pi}{L_x},
\]
(257)
so
\[
\lim_{L_x \to \infty} \frac{L_x}{\pi} \int_0^{\infty} dK_x e^{\beta(\epsilon(K_x)-\mu)} + 1 = \sum_{n_x=1}^{\infty} e^{\beta(\epsilon(K_x(n_x))-\mu)} + 1.
\]
(258)

### 28.2 Joint Probabilities

The goal of this section is to show that the joint probability \(g_{ij}\) that an electron is in state \(i\) and another electron of the same spin is in state \(j\) is
\[
g_{ij} = \bar{n}_i \bar{n}_j - \delta_{ij} \bar{n}_i,
\]
(259)
where \(\bar{n}_i\) is the average population of state \(i\). Note that the average \(\bar{n}_i \bar{n}_j\) thus provides information about correlations between different particles.

Consider the population of state \(i, n_i,\) in terms of the sum of occupation variables \(n_i^{(\alpha)}\) over all electrons \(\alpha,\)
\[
n_i = \sum_{\alpha} n_i^{(\alpha)},
\]
(260)
where \(n_i^{(\alpha)} = 1, 0.\) Therefore, the probability that states \(i\) and \(j\) are populated is
\[
\bar{n}_i \bar{n}_j = \sum_{\beta} \sum_{\alpha} n_i^{(\alpha)} n_j^{(\beta)} = \sum_{\alpha} n_i^{(\alpha)} n_j^{(\alpha)} + \sum_{\alpha, \beta \neq \alpha} n_i^{(\alpha)} n_j^{(\beta)},
\]
(261)
Note that
\[
\sum_{\alpha} n_i^{(\alpha)} n_j^{(\alpha)} = \sum_{\alpha} (n_i^{(\alpha)})^2 \delta_{ij},
\]
(262)
and that
\[
\overrightarrow{n_i^2} = \sum_{\alpha} \sum_{\beta} \overrightarrow{n_i^{(\alpha)}} \overrightarrow{n_i^{(\beta)}} = \sum_{\alpha} (\overrightarrow{n_i^{(\alpha)}})^2 + \sum_{\alpha} \sum_{\beta \neq \alpha} \overrightarrow{n_i^{(\alpha)}} \overrightarrow{n_i^{(\beta)}},
\]
(263)
where the double sum with \( \beta \neq \alpha \) in Eq. (263) is equal to 0 because it corresponds to the joint probability that both particles \( \alpha \) and \( \beta \) are in state \( i \).

Substituting Eqs. (262) and (263) into Eq. (261), we obtain
\[
\overrightarrow{n_i n_j} = \overrightarrow{n_i^2} \delta_{ij} + g_{ij}.
\]
(264)
Eq. (264) is identical to Eq. (259) because \( \overrightarrow{n_i^2} = \overrightarrow{n_i} \) when \( n_i = 0, 1 \).

Finally, note that according to Eq. (165),
\[
\overrightarrow{n_j n_i} = \frac{1}{\Xi} \frac{\partial^2 \Xi}{\partial(-\beta \epsilon_i) \partial(-\beta \epsilon_j)} \bigg|_{V,T} = \overrightarrow{n_i} \delta_{ij} + g_{ij}.
\]
(265)

Therefore,
\[
g_{ij} = \left( \delta_{ij} \frac{\partial}{\partial(-\beta \epsilon_i)} \bigg|_{V,T} \right) \overrightarrow{n_i} + \left( \overrightarrow{n_j} - \delta_{ij} \right) \overrightarrow{n_i}.
\]
(266)

29 Chemical Equilibrium

The goal of this section is to derive the law of mass action and to obtain an expression of the equilibrium constant for a chemical reaction in the gas phase in terms of the canonical partition function of the molecular constituents. To achieve these goals, we first obtain an expression of the chemical potential for the constituent molecules in terms of their canonical partition functions and then we derive the law of mass action by using the minimum energy principle. Finally, we combine both results and we obtain an expression of the equilibrium constant in terms of the molecular canonical partition functions.

The grand canonical ensemble of a multicomponent system is described by the density operator, introduced by Eq. (78) but where
\[
p_j = \frac{e^{-\beta E_j + \beta \sum_k \mu_k N_j(k)}}{\sum_j e^{-\beta E_j + \beta \sum_k \mu_k N_j(k)}} = \Xi^{-1} e^{-\beta E_j + \beta \sum_k \mu_k N_j(k)},
\]
(267)
with $\mu_k$ the chemical potential of species $k$ and $N_j(k)$ the number of particles of species $k$ in quantum state $j$. Eq. (267) is obtained by maximizing the entropy of the system, introduced by Eq. (23), subject to the constraints of constant volume, average internal energy $E_j$ and average number of particles $N_j(k)$ for all the different species $k$ in the system.

Substituting Eq. (267) into Eq. (80), we obtain

$$S = \frac{E}{T} - \frac{1}{T} \sum_k \mu_k N(k) + k\ln \Xi. \quad (268)$$

Therefore,

$$G \equiv \sum_k \mu_k N(k) = E - TS + T k\ln \Xi, \quad (269)$$

and since $G = H - TS = E + PV - TS$,

$$PV = kT \ln \Xi. \quad (270)$$

Eqs. (268)—(270) provide an expression for the change in internal energy $dE$ due to changes in the extensive properties of the system such as changes of volume $dV$, number of particles $dN(k)$ and entropy $dS$,

$$dE = T dS - P dV + \sum_k \mu_k dN(k). \quad (271)$$

According to Eq. (271), $\mu_k$ can be computed as follows,

$$\mu_k = \left( \frac{\partial E}{\partial N(k)} \right)_{S,V}, \quad (272)$$

and since $A = E - TS$ and $dA = dE - T dS - S dT$,

$$\mu_k = \left( \frac{\partial A}{\partial N(k)} \right)_{T,V}. \quad (273)$$

Furthermore, according to Eqs. (273) and (53),

$$\beta \mu_k = - \left( \frac{\partial \ln Z}{\partial N(k)} \right)_{T,V}. \quad (274)$$

The canonical partition function,

$$Z = \prod_k \frac{(q_t(k) * q_{int}(k))^{N(k)}}{N(k)!}, \quad (275)$$

is computed according to Eq. (199), where $q_t(j) = V(2\pi m_j kT)^{3/2}/h^3$ and $q_{int}$ are the translational and internal canonical partition functions of species $j$, respectively. The underlying assumption,
when computing $Z$ according to Eq. (275), is that the constituents of the systems in the gas phase do not interact with each other except when they undergo reactive collisions. Substituting Eq. (275) into Eq. (274) and using the Stirling Formula, introduced by Eq. (60), we obtain

$$
\beta \mu_k = -\ln \left( \frac{q_t(k) * q_{\text{int}}(k)}{N(k)} \right).
$$

(276)

To derive the law of mass action, we consider the following chemical reaction,

$$
aA + bB \rightleftharpoons cC + dD,
$$

(277)

where the stoichiometric coefficients ($c_k = a, b, c$ and $d$) determine the relative changes in the number of moles of the molecular constituents due to the chemical reaction, as follows:

$$
dN(A)_a = dN(B)_b = -dN(C)_c = -dN(D)_d.
$$

(278)

Substituting Eq. (278) into Eq. (271) we obtain an expression for the change in internal energy at constant entropy $S$ and volume $V$,

$$
dE_{s,V} = \sum_j \mu_j dN(j) = d\bar{N}(A) \sum_j \mu_j \nu_j,
$$

(279)

where $\nu_j = c_j / a$.

The minimum energy principle establishes that

$$
dE_{s,V} \geq 0,
$$

(280)

for all arbitrary changes $d\bar{N}(A)$ in a system that was initially at equilibrium. Therefore, according to Eqs. (279) and (280),

$$
\sum_j \beta \mu_j \nu_j = 0.
$$

(281)

Substituting Eq. (276) into Eq. (281), we obtain

$$
\sum_j \ln \left( \frac{q_{\text{int}} * (2\pi m_j kT)^{3/2}}{\hbar^3} \right)^{\nu_j} \left[ \frac{V}{N(j)} \right]^{\nu_j} = 0,
$$

(282)

and

$$
\ln \prod_j \left[ \frac{q_{\text{int}} * (2 \pi m_j k T)^{3/2}}{\hbar^3} \right]^{\nu_j} \left[ \frac{V}{N(j)} \right]^{\nu_j} = 0.
$$

(283)
Therefore,
\[
K(T) \equiv \prod_j \left( \frac{q_{\text{int}} \ast (2 \pi m_j k T)^{3/2}}{h^3} \right)^{-\nu_j} = \prod_j \left( \frac{V}{N(j)} \right)^{\nu_j},
\] (284)

which is the law of mass action. Such law establishes that the concentrations of the constituent molecules in chemical equilibrium define an equilibrium constant \( K(T) \) that depends only on the temperature of the system and on the nature of the chemical species. The first equality, in Eq. (284), provides a molecular expression of such equilibrium constant in terms of the canonical partition functions of the molecular constituents and \( T \).

### 29.1 Minimum Energy Principle

The minimum energy principle, introduced by Eq. (280), is a consequence of the maximum entropy principle. This can be shown by considering the system at thermal equilibrium described by the following diagram:

![Diagram of system at thermal equilibrium](image)

Consider a small displacement of heat \( \delta E \) from compartment (2) to compartment (1). Since the system was originally at equilibrium, such a constraint in the distribution of thermal energy produces a constrained system whose entropy is smaller than the entropy of the system at equilibrium. Mathematically,
\[
S(E^{(1)} + \delta E, X) + S(E^{(2)} - \delta E, X) < S(E^{(1)}, X) + S(E^{(2)}, X).
\] (285)

Now consider the system at equilibrium (i.e., without any constraints) with entropy \( S(E, X) \) such that
\[
S(E, X) = S(E^{(1)} + \delta E, X) + S(E^{(2)} - \delta E, X).
\] (286)

Since, according to Eqs. (286) and (285),
\[
S(E, X) < S(E^{(1)}, X) + S(E^{(2)}, X),
\] (287)

and according to Eq. (39),
\[
\frac{\partial S}{\partial E} \bigg|_{V,N} = \frac{1}{T} > 0,
\] (288)
then
\[ E < E^{(1)} + E^{(2)}. \]  
(289)

Eq. (286) thus establishes that by imposing internal constraints at constant entropy the system that was initially at equilibrium with entropy \( S(E, X) \) moves away from such equilibrium and its internal energy increases from \( E \) to \( E^{(1)} + E^{(2)} \). Mathematically,
\[ dE \geq 0, \]  
(290)

which is the minimum energy principle.

30 Exam 2

Exam 2 CHEM 430b/530b
Statistical Methods and Thermodynamics

Exercise 1
(20 points) Item (1.1): Consider an ideal gas of bosons with \( \mu = 0 \) at temperature \( T = 1/(\beta k) \).
Show that
\[ \delta_{n_k} \delta_{n_j} = \delta_{kj} \frac{\partial \overline{n_k}}{\partial (\beta \epsilon_k)} \bigg|_{V, T}, \]  
(291)

where \( \delta_{n_k} = n_k - \overline{n}_k \) and \( \overline{n}_k \) is the average occupation of the one-boson energy level \( k \).

(20 points) Item (1.2): Explain the minimum energy principle and show that such principle is a consequence of the maximum entropy principle.

(20 points) Item (1.3): Explain the classical limit of the quantum statistical distributions.

Exercise 2
Consider an ideal gas of \( O_2 \) molecules adsorbed on a surface of area \( S \) in thermal equilibrium at temperature \( T = 1/(k \beta) \). Assume that each \( O_2 \) molecule in the gas can freely translate, vibrate and rotate but only on the 2-dimensional surface. Assume that the rotational motion of \( O_2 \) molecules can be described by a rigid rotor model where the rotational eigenstates have degeneracy \( g(J) = 2 \) for all values of \( J \) except for \( J=0 \) for which \( g(J)=1 \). Assume that the rotational states have eigenvalues \( E_J = \frac{\hbar^2 J^2}{2I_0} \), with \( J=0, 1, 2, ..., \), where \( I_0 \) is the moment of inertia of the \( O_2 \) molecule.

(10 points) Item (2.1): Compute the rotational canonical partition function of an \( O_2 \) molecule as a function of its moment of inertia \( I_0 \) and \( \beta \).

(10 points) Item (2.2): Compute the vibrational canonical partition function of an \( O_2 \) molecule as a function of its vibrational frequency \( \omega_0 \) and \( \beta \).

(10 points) Item (2.3): Compute the translational canonical partition function of an \( O_2 \) molecule as a function of its total mass \( m \), \( \beta \) and the surface area \( S \).
(10 points) Item (2.4): Compute the average internal energy $E$ of the $O_2$ gas as a function of $\beta$, the $O_2$ mass $m$, the area of the surface $S$, the $O_2$ moment of inertia $I_0$ and the total number $N$ of $O_2$ molecules on the surface.

Solution:

Exercise 1:

Item (1.1): Since $\delta_{nk} = n_k - \overline{n}_k$,

$$\delta_{nk}\delta_{nj} = n_k n_j - \overline{n}_k \overline{n}_j,$$

where

$$\overline{n}_j = \frac{1}{e^{\beta \epsilon_j} - 1},$$

because $\mu = 0$. Therefore,

$$\overline{n}_k \overline{n}_j = \frac{1}{\Xi} \frac{\partial^2 \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots e^{-\beta (\epsilon_1 n_1 + \epsilon_2 n_2 + \cdots)}}{\partial (\beta \epsilon_j) \partial (\beta \epsilon_k)},$$

or

$$\overline{n}_k \overline{n}_j = \frac{1}{\Xi} \frac{\partial^2}{\partial (\beta \epsilon_k) \partial (\beta \epsilon_j)} \prod_j \frac{1}{1 - e^{-\beta \epsilon_j}}.$$

Computing the first partial derivative we obtain

$$\overline{n}_k \overline{n}_j = \frac{1}{\Xi} \frac{\partial}{\partial (-\beta \epsilon_j)} \left( e^{-\beta \epsilon_k} \prod_{l \neq k} \frac{1}{1 - e^{-\beta \epsilon_l}} \right),$$

and computing the second partial derivative we obtain

$$\overline{n}_k \overline{n}_j = \frac{1}{\Xi} \frac{\partial}{\partial (-\beta \epsilon_k)} \left( e^{-\beta \epsilon_k} \prod_{l \neq k} \frac{1}{1 - e^{-\beta \epsilon_l}} \right) \left( e^{-\beta \epsilon_j} \prod_{l \neq j, l \neq k} \frac{1}{1 - e^{-\beta \epsilon_l}} \right),$$

where,

$$\Xi = \prod_j \frac{1}{1 - e^{-\beta \epsilon_j}}.$$

Therefore,

$$\overline{n}_k \overline{n}_j = \delta_{kj} \frac{e^{-\beta \epsilon_k}}{(1 - e^{-\beta \epsilon_k})^2} + \frac{e^{-\beta \epsilon_k}}{(1 - e^{-\beta \epsilon_k})} \frac{e^{-\beta \epsilon_j}}{(1 - e^{-\beta \epsilon_j})},$$

and

$$\delta_{nk}\delta_{nj} = \delta_{kj} \frac{e^{-\beta \epsilon_k}}{(1 - e^{-\beta \epsilon_k})^2} = \delta_{kj} \frac{\partial}{\partial (-\beta \epsilon_k)} \frac{1}{e^{\beta \epsilon_k} - 1}.$$
which, according to Eq (264), gives
\[
\delta_{nk} \delta_{nj} = \delta_{kj} \frac{\partial \tilde{n}_k}{\partial (-\beta \epsilon_k)}.
\] (301)

Item (1.2): See topic “Minimum Energy Principle” on page 55 of the lecture notes.
Item (1.3): See topic “Classical limit of Quantum Statistical Distributions” on page 36 of the lecture notes.

Exercise 2:
Item (2.1): The rotational canonical partition function of an \(O_2\) molecule is
\[
q_{\text{rot}} = \sum_{J=0}^{\infty} g(J) e^{-\beta \epsilon_J}.
\] (302)

Taking the continuous limit we obtain,
\[
q_{\text{rot}} \approx \lim_{\epsilon \to 0} \int_{\epsilon}^{\infty} dJ g(J) e^{-\beta \epsilon_J} = \sqrt{\frac{\pi 2I_0}{\beta \hbar^2}}.
\] (303)

Item (2.2): The vibrational canonical partition function of an \(O_2\) molecule is
\[
q_{\text{vib}} = \sum_{\nu=0}^{\infty} e^{-\beta \epsilon_\nu} = \frac{e^{-\beta \hbar \omega_0 / 2}}{1 - e^{-\beta \hbar \omega_0}}.
\] (304)

Item (2.3): The translational canonical partition function of an \(O_2\) molecule is
\[
q_{\text{transl}} = \frac{S}{n^2} \sum_{k_x} \sum_{k_y} e^{-\beta \left(\frac{k_x^2 + k_y^2}{2m}\right) \hbar^2} \approx \frac{S}{n^2} \int dk_x e^{-\beta k_x^2 \hbar^2 / 2m} \int dk_y e^{-\beta k_y^2 \hbar^2 / 2m}.
\] (305)

Therefore,
\[
q_{\text{transl}} \approx \frac{S \pi 2m}{\beta \hbar^2},
\] (306)

where \(S = L_x \times L_y\), with \(L_x\) and \(L_y\) the lengths of the surface along the x and y directions, respectively.

Item (2.4): The total canonical partition function of the system is
\[
Q = \frac{1}{N!} \prod_{j=1}^{N} q_{\text{rot}} q_{\text{vib}} q_{\text{transl}}.
\] (307)
Substituting the expressions for $q_{\text{rot}}$, $q_{\text{vib}}$ and $q_{\text{trans}}$ computed in items (2.1)—(2.3) we obtain,

$$Q = \frac{1}{N!} \prod_{j=1}^{N} S \frac{2\pi m}{\beta \hbar^2} (e^{\beta \hbar \omega_0/2} - e^{-\beta \hbar \omega_0/2})^{-1} \sqrt{\frac{2\pi I_0}{\beta \hbar^2}} = \frac{1}{N!} \prod_{j=1}^{N} \frac{\pi x}{\beta^{3/2}(e^{\beta y} - e^{-\beta y})},$$

(308)

Therefore, the average internal energy of the $O_2$ gas is

$$\bar{E} = \sum_{j=1}^{N} \frac{\partial \ln Q}{\partial \beta} = \frac{N}{Q} \frac{\partial Q}{\partial (-\beta)} = \frac{\beta^{3/2}(e^{\beta y} - e^{-\beta y}) N}{x} \frac{x (3/2 \beta^{1/2} (e^{\beta y} - e^{-\beta y}) + \beta^{3/2} y (e^{\beta y} + e^{-\beta y}))}{\beta^{3/2}(e^{\beta y} - e^{-\beta y})^2},$$

(309)

which gives

$$\bar{E} = \sum_{j=1}^{N} \frac{3/2 (e^{\beta y} - e^{-\beta y}) + \beta y (e^{\beta y} + e^{-\beta y})}{\beta (e^{\beta y} - e^{-\beta y})} = \left( \frac{3}{2\beta} + \frac{3y (e^{\beta y} + e^{-\beta y})}{2 \beta (e^{\beta y} - e^{-\beta y})} \right) * N,$$

(310)

where $x = \frac{S^2 m \pi}{\hbar^2} \sqrt{\frac{2\pi I_0}{\hbar^2}}$ and $y = \frac{\hbar \omega_0}{2}$.

### 31 Quiz 2

**Quiz 2** CHEM 430b/530b  
**Statistical Methods and Thermodynamics**

**30 points** Exercise 1: Derive the Fermi-Dirac distribution.

**30 points** Exercise 2: Derive the Bose-Einstein distribution.

**40 points** Exercise 3: Derive an expression for the average density of electrons $\bar{N}/V$ in a metal at $T = 0$ K, as a function of the Fermi energy $\mu$ and the electron mass $m$.

**Solution:**

Exercise 1: See topic “Bose-Einstein and Fermi-Dirac distributions” on pages 34 and 35 of the lecture notes.

Exercise 2: See topic “Bose-Einstein and Fermi-Dirac distributions” on pages 34 and 35 of the lecture notes.

Exercise 3: According to Eq. (236),

$$\bar{N} = 8\pi \int_{0}^{K_f} dK K^2 \left( \frac{L}{2\pi} \right)^3 = 8\pi \left( \frac{L}{2\pi} \right)^3 K_f^3 = \frac{2V}{(2\pi)^3} \frac{4}{3} \pi K_f^3,$$

(311)
where $K_f$ is the Fermi momentum defined as follows

$$\frac{\hbar^2 K_f^2}{2m} = \mu.$$  

(312)

Therefore,

$$\frac{N}{V} = 2^2 4 \pi \frac{4}{3} \pi \left(\frac{2m\mu}{\hbar^2}\right)^{(3/2)}.$$  

(313)

### 32 Ising Model

The goal of this section is to introduce the Ising model which is a simple model of systems with *interparticle interactions* and to compute its canonical partition function according to both the macroscopic approximation and the rigorous transfer matrix technique.

The 1-dimensional Ising model is described by a system of $N$ spins arranged in a ring as represented in the following diagram:

![Diagram of the Ising model](image)

The Hamiltonian of the system is

$$H = -\bar{\mu} B \sum_j S_j - J \sum_{jk} S_j S_k,$$

(314)

where $\bar{\mu}$ is the magnetic dipole moment, $B$ is an external magnetic field and $J$ is the coupling constant between spins. The sum of products $S_j S_k$ defines the interaction between spins, including only nearest neighbors.

In the absence of an external magnetic field, the canonical partition function of the system is

$$Z = \sum_{S_1=-1}^{1} \sum_{S_2=-1}^{1} \cdots \sum_{S_N=-1}^{1} e^{\beta J S_1 S_2} e^{\beta J S_2 S_3} \cdots e^{\beta J S_N S_1},$$

(315)
The partition function, introduced by Eq. (315), is approximately equal to

$$Z \approx \sum_{b_1=\pm 1} \ldots \sum_{b_N=\pm 1} e^{\beta J \sum_{j=1}^N b_j} = [2\cosh(\beta J)]^N,$$

(316)

where we have replaced the products of interaction $S_k S_j$ by bonds $b_j = \pm 1$ and we have assumed that all bonds are linearly independent. Note, however, that such approximation consists in assuming that $N$ is sufficiently large (i.e., $N \gg 1$) as to neglect the energy of one bond relative to the total energy of the system, since only $N-1$ bonds are actually linearly independent.

To perform a rigorous calculation of the canonical partition function introduced by Eq. (315), we define the transfer function $T(S_i, S_{i+1}) \equiv \exp(\beta J S_i S_{i+1})$.

(317)

Substituting Eq. (317) into Eq. (315) we obtain

$$Z = \sum_{S_1=-1}^1 \sum_{S_2=-1}^1 \ldots \sum_{S_N=-1}^1 T(S_1, S_2) T(S_2, S_3) \ldots T(S_N, S_1).$$

(318)

This expression corresponds to the trace of a product of $N$ identical $2 \times 2$ matrices. To show this we introduce the transfer matrix,

$$T \equiv \begin{pmatrix} T(1,1) & T(1,-1) \\ T(-1,1) & T(-1,-1) \end{pmatrix}.$$

(319)

Note that the element $(j,k)$ of $T^2$ is

$$T^2(j,k) = \sum_{S_2=-1}^1 T(j, S_2) T(S_2, k),$$

(320)

and therefore

$$Z = \sum_{S_1=-1}^1 T^N(S_1, S_1) = \text{Tr}\{T^N\}.$$

(321)

Thus the calculation of the canonical partition function for the 1-dimensional Ising model has been reduced to that of computing the trace of the $N$th power of the transfer matrix.

We note that $T = \Gamma^\dagger T_d \Gamma$, with $T_d$ the diagonal matrix of eigenvalues of $T$, and $\Gamma$ the matrix of eigenvectors of $T$ with $\Gamma \Gamma^\dagger = 1$, so $T^N = \Gamma^\dagger T_d^N \Gamma$. Furthermore, the $\text{Tr}\{T^N\} = \text{Tr}\{\Gamma^\dagger T_d^N \Gamma\} = \text{Tr}\{\Gamma^\dagger T_d^N \Gamma\} = \text{Tr}\{T_d^N\}$ since the trace is invariant under cyclic permutations (i.e., $\text{Tr}(ABC) = \text{Tr}(CAB)$ since $\sum_{j,k} (AB)_{jk} C_{kj} = \sum_{j,k} C_{kj} (AB)_{jk}$).

Now, the trace of a matrix is the sum of its eigenvalues and the eigenvalues of $T^N$ are $\lambda_\pm^N$, where $\lambda_\pm$ are the eigenvalues of $T$ determined by the equation

$$\begin{vmatrix} e^{\beta J} - \lambda & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J} - \lambda \end{vmatrix} = 0,$$

(322)
with solutions
\[ \lambda_\pm = e^{\beta J} \pm e^{-\beta J}. \] (323)

Hence, the partition function is simply,
\[ Z = \lambda_+^N + \lambda_-^N = 2^N (\cosh^N(\beta J) + \sinh^N(\beta J)). \] (324)

Note that when \( N \) is sufficiently large, \( \sinh^N(\beta J) \ll \cosh^N(\beta J) \) and Eq. (324) coincides with Eq. (316).

In the presence of a magnetic field, however,
\[ Z = \sum_{S_1=-1}^1 \sum_{S_2=-1}^1 ... \sum_{S_N=-1}^1 e^{\beta JS_1 S_2 + \beta \mu B (S_1 + S_2)/2} e^{\beta JS_2 S_3 + \beta \mu B (S_2 + S_3)/2} ... e^{\beta JS_N S_1 + \beta \mu B (S_N + S_1)/2}, \] (325)

Exercise: 1-dimensional Ising Model
Compute the canonical partition function introduced by Eq. (325) by implementing the transfer matrix approach.

33 Lattice Gas

The goal of this section is to show that with a simple change of variables, the Ising model can be mapped into the lattice gas which is a simple model of density fluctuations and liquid-gas transformations. The 1-dimensional lattice gas model is described by the following diagram:

```
The lattice divides space into cells \( c_1, c_2, ..., c_N \). Each cell has an occupation number \( n_j = 0, 1 \). The interaction between particles occupying the cells is modeled by assuming that the energy associated with a pair of occupied nearest neighbor cells is \( -\epsilon n_j n_k \), and the total energy of the system is
```
\[ E = -\mu \sum_j n_j - \epsilon \sum_j \sum_k n_j n_k, \] (326)
where $j$ is the index of the cell and $\mu$ is the chemical potential of a particle. The partition function of the lattice model is

$$
\Xi = \sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \cdots \sum_{n_N=0}^{1} e^{\beta \mu \sum_{j=1}^{N} n_j + \beta \epsilon \sum_{j,k} n_j n_k}.
$$

(327)

To show the correspondence between the lattice gas and the Ising model, we make the variable transformation $n_j \equiv (S_j + 1)/2$ and we obtain

$$
\Xi = \sum_{S_1=-1}^{1} \sum_{S_2=-1}^{1} \cdots \sum_{S_N=-1}^{1} e^{\beta \frac{\mu}{2} \sum_{j} (S_j+1) + \beta \epsilon \sum_{j,k} (S_j+1)(S_k+1)},
$$

(328)

Therefore the lattice model is isomorphic with the Ising model: “Spin up” in the Ising model corresponds to an occupied cell in the lattice model, “spin down” corresponds to an empty cell, the magnetic field in the Ising model corresponds (within constants) to the chemical potential in the lattice gas and the coupling constant in the Ising model is $\epsilon/4$ in the lattice gas. The Ising model can also be mapped into many other problems in Chemistry and beyond, ranging from models of population dynamics to models of the brain.

### 34 Mean Field Theory

The goal of this section is to introduce the so-called mean field theory (also known as self consistent field theory) and to illustrate the theory by applying it to the description of the Ising model. The main idea of the mean field theory is to focus on one particle and assume that the most important contribution to the interactions of such particle with its neighboring particles is determined by the mean field due to the neighboring particles. In the 1-dimensional Ising model, for instance, the average force $F_k$ exerted on spin $S_k$ is

$$
F_k \equiv -\frac{\partial H}{\partial S_k} = \bar{\mu} B + J \sum_j S_j,
$$

(329)

where the index $j$ includes all the nearest neighbors of spin $S_k$. Therefore, the average magnetic field $\overline{B}$ acting on spin $S_k$ is

$$
\overline{B} \equiv \frac{F_k}{\bar{\mu}} = B + \Delta B,
$$

(330)

where

$$
\Delta B = J 2 \overline{S}_k / \bar{\mu},
$$

(331)

is the contribution to the mean field due to the nearest neighbors. Note that $\overline{S}_k = \overline{S}_j$ when all spins are identical.

Eq. (330) defines the self consistent aspect of the theory, since according to such equation the mean field $\overline{B}$ acting on spin $S_k$ is determined by its own mean value $\overline{S}_k$. 
The assumption that the interactions of a spin with its neighboring spins can be approximately described by the mean field, introduced by Eq. (331), introduces an enormous simplification. Such mean field approximation simplifies the many body statistical mechanics problem to a one-body problem (i.e., Eq. (330) transforms the problem of N interacting spins influenced by an external magnetic field $B$ to a problem of N non-interacting spins influenced by the mean field $\overline{B}$).

The partition function, under the mean field approximation, is

$$Z \approx \sum_{S_1} \cdots \sum_{S_N} e^{\beta \sum_j S_j (B + \Delta B) \mu} = 2^N \cosh^N (\beta \mu \overline{B}), \quad (332)$$

and the average value of $S_k$ is

$$\overline{S_k} = \frac{1}{N} \sum_j p_j (\sum_l S_l (j)) = \frac{1}{N} Z^{-1} \sum_{S_1} \cdots \sum_{S_N} (\sum_l S_l) e^{\beta \sum_j S_j (B + \Delta B) \mu}, \quad (333)$$

where $p_j$ is the probability of state $j$. The average value of spin is

$$\overline{S_k} = \frac{1}{N} \frac{\partial \ln Z}{\partial (\beta \mu \overline{B})} = \tanh (\beta \mu (B + 2J \overline{S_k} / \mu)). \quad (334)$$

Note that Eq. (334) involves a transcendental equation. Its solution corresponds to the value of $\overline{S_k} = m$ for which the function on the left hand side of Eq. (334) (i.e., $\overline{S_k}$) equals the function on the right hand side of Eq. (334) (i.e., $\tanh (\beta \mu (B + 2J \overline{S_k} / \mu))$).

In the absence of an external magnetic field (i.e., when $B = 0$), Eq. (334) always has the trivial solution $S_k = 0$ and a non-trivial solution $S_k = m$ only when $\beta 2J > 1$. Such solution is represented by the following diagram:

The diagram shows that the mean field theory predicts spontaneous magnetization (i.e., magnetization in the absence of an external magnetic field) for the 1-dimensional Ising model at any
temperature \( T < 2J/k \), since there is a non-trivial solution \( S_k = m \) for which Eq. (334) is satisfied. Unfortunately, however, this result is erroneous! The 1-dimensional Ising model does not undergo spontaneous magnetization at any finite temperature, since each spin has only two nearest neighbors and the stabilization energy due to two nearest neighbors is not enough to overcome the randomization process due to thermal fluctuations. This simple example, however, illustrates the theory including the fact that it is sometimes inaccurate near critical points. The theory works better in higher dimensionality, e.g., in the 2-dimensional Ising model where the theory predicts spontaneous magnetization at a critical temperature \( T_c = 4J/K \) that is close to the experimental value 2.3 J/K.

**Exercise:** Show that there is no spontaneous magnetization in the 1-dimensional Ising model at finite temperature by computing the average magnetization \( \bar{M} = \sum_j \bar{S}_j \) from the exact canonical partition function. Hint: Compute the average magnetization in the presence of an external magnetic field and show that in the limit when \( B \to 0 \) such magnetization becomes negligible.

### 34.1 Variational Mean Field Theory

The goal of this section is to introduce a variational approach for computing the optimum mean field determined by the Gibbs-Bogoliubov-Feynman equation and to illustrate such variational method by applying it to the description of the 1-dimensional Ising model.

Consider the task of computing the canonical partition function \( Z \) of the one-dimensional Ising model,

\[
Z(K, N) = \sum_{S_1} \sum_{S_2} \cdots \sum_{S_N} e^{-\beta E(S_1, S_2, S_3, \ldots S_N)},
\]

where

\[
E(S_1, S_2, S_3, \ldots S_N) = -\bar{\mu} B \sum_j S_j - J \sum_{jk} S_j S_k.
\]

The mean field approximation, introduced by Eq. (332), is

\[
Z_{MF}(K, N) = \sum_{S_1} \sum_{S_2} \cdots \sum_{S_N} e^{-\beta \bar{E}_{MF}(S_1, S_2, S_3, \ldots S_N)} = 2^N \cosh^N(\beta \bar{\mu}(B + \Delta B)),
\]

with

\[
\bar{E}_{MF}(S_1, S_2, S_3, \ldots S_N) = -\bar{\mu}(B + \Delta B) \sum_j S_j,
\]

where \( \Delta B = J2S_k / \bar{\mu} \). Note that the mean field partition function \( Z_{MF} \), introduced by Eq. (337), is an approximation to the actual partition function \( Z(K, N) \), introduced by Eq. (335). The goal of the variational treatment is, therefore, to optimize the expression of the mean field \( \Delta B \) in order for \( Z_{MF} \) to be as similar as possible to \( Z(K, N) \).

To obtain a variational expression that involves both \( Z_{MF}(K, N) \) and \( Z(K, N) \) (i.e., the Gibbs-Bogoliubov-Feynman equation) we note that, according to Eqs. (335) and (337),

\[
Z(K, N) = Z_{MF}(K, N) \frac{\sum_{S_1} \sum_{S_2} \cdots \sum_{S_N} e^{-\beta \Delta E} e^{-\beta \bar{E}_{MF}}}{\sum_{S_1} \sum_{S_2} \cdots \sum_{S_N} e^{-\beta \bar{E}_{MF}}} = Z_{MF}(e^{-\beta \Delta E}),
\]

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where $\Delta E = E - E_{MF}$, and $\langle \rangle$ indicates a mean field ensemble average. Furthermore, we note that

$$\langle e^{-\beta \Delta E} \rangle = \langle e^{-\beta (\Delta E)} e^{-\beta (\Delta E - \langle \Delta E \rangle)} \rangle \geq e^{-\beta \langle \Delta E \rangle},$$  

(340)

since $\langle e^{-\beta (\Delta E)} \rangle = e^{-\beta \langle \Delta E \rangle}$ and $e^x \geq 1 + x$. Therefore,

$$Z(K, N) \geq Z_{MF}(K, N) e^{-\beta \langle \Delta E \rangle},$$

(341)

which is the Gibbs-Bogoliubov-Feynman equation.

Eq. (341) allows us to find the optimum mean field by maximizing the right hand side (r.h.s.) of Eq. (341) with respect to $\Delta B$.

Note that according to Eqs. (337) and (334),

$$\frac{\partial Z_{MF}}{\partial \Delta B} = Z_{MF} N \beta \bar{\mu} \langle s_k \rangle.$$

(342)

and according to Eq. (336) and (338),

$$\langle \Delta E \rangle = -J \sum_{j=1}^{N} \sum_{k} \langle s_j s_k \rangle + \Delta B \bar{\mu} \sum_{j} \langle s_j \rangle = -J \frac{N}{2} \langle s_j \rangle^2 + \Delta B \bar{\mu} N \langle s_j \rangle.$$

(343)

Therefore, computing the derivative of the r.h.s. of Eq. (341) with respect to $\Delta B$ and making such derivative equal to zero we obtain, according to Eqs. (342) and (343),

$$Z_{MF} N \beta \bar{\mu} \langle s_k \rangle e^{-\beta \langle \Delta E \rangle} + Z_{MF} e^{-\beta \langle \Delta E \rangle} (-\beta) (-J \frac{N}{2} \frac{\partial \langle s_j \rangle}{\partial \Delta B} 2 \langle s_j \rangle + \bar{\mu} N \langle s_j \rangle) + \Delta B \bar{\mu} N \frac{\partial \langle s_j \rangle}{\partial \Delta B} = 0.$$

(344)

Therefore, solving for $\Delta B$ in Eq. (344) we obtain

$$\Delta B = 2J \langle s_j \rangle / \bar{\mu},$$

(345)

which is identical to the mean field introduced by Eq. (331). This means that the mean field introduced by Eq. (331) is the optimum field as determined by the Gibbs-Bogoliubov-Feynman equation (i.e., the mean field that maximizes the r.h.s. of Eq. (341)).

### 35 Renormalization Group Theory

The goal of this section is to introduce several concepts of Renormalization Group Theory and to illustrate such concepts with the 1-dimensional Ising model.

Consider the task of computing the canonical partition function $Z$ of the one-dimensional Ising model in the absence of an external magnetic field. According to Eq. (315),

$$Z(K, N) = \sum_{S_1} \sum_{S_2} \cdots \sum_{S_N} e^{K(S_1 S_2 + S_2 S_3 + \cdots + S_N S_1)},$$

(346)

66
where coupling parameter $K \equiv \beta J$ and $N$ is the total number of spins. Note that according to Eq. (346),
\[
\lim_{K \to 0} Z(K, N) = \prod_{j=1}^{N} \sum_{S_j=-1}^{1} 1 = 2^N.
\] (347)

The renormalization group strategy for the 1-dimensional Ising model can be described as follows. Step (1). Sum over the even numbered spins in Eq. (346). Note that summing, e.g., over $S_2$ we obtain
\[
Z(K, N) = \sum_{S_1, S_3, S_4, S_5, S_6, S_7} [e^{K(S_1+S_3)} + e^{-K(S_1+S_3)}] e^{K S_3 S_4} e^{K S_4 S_5} e^{K S_5 S_6} e^{K S_6 S_7} ...,\] (348)
summing over $S_2$ and $S_4$ we obtain,
\[
Z(K, N) = \sum_{S_1, S_3, S_5, S_6, S_7} [e^{K(S_1+S_3)} + e^{-K(S_1+S_3)}] [e^{K(S_3+S_5)} + e^{-K(S_3+S_5)}] e^{K S_3 S_5} e^{K S_5 S_7} ...,\] (349)
and summing over all even numbered spins we obtain
\[
Z(K, N) = \sum_{S_1, S_3, S_5, S_7} [e^{K(S_1+S_3)} + e^{-K(S_1+S_3)}] [e^{K(S_3+S_5)} + e^{-K(S_3+S_5)}] [e^{K(S_5+S_7)} + e^{-K(S_5+S_7)}] ... .\] (350)
Step (2). Rewrite the remaining sum (i.e., the sum over odd numbered spins introduced by Eq. (351) by implementing the Kadanoff transformation
\[
e^{K(S+S')} + e^{-K(S+S')} = f(K) e^{K'S'S'},\] (351)
where both $f(K)$ and $K'$ are functions of $K$. Substituting Eq. (351) into Eq. (350) we obtain
\[
Z(K, N) = f(K)^{N/2} \sum_{S_1, S_3, S_5, S_7} e^{K'S_1 S_3} e^{K'S_3 S_5} e^{K'S_5 S_7} ... = f(K)^{N/2} Z(K', N/2).\] (352)
Note that such transformation allows us to rewrite the partition function $Z(K, N)$ in terms of a renormalized partition function $Z(K', N/2)$ (i.e., a partition function with new parameters that describes an Ising model with half the number of spins and a different coupling parameter $K'$). To determine the renormalization group equations (i.e., $K'$ and $f(K)$ as a function of $K$) and show that $K' < K$, we note that when $S = S' = \pm 1$, Eq. (351) gives
\[
e^{2K} + e^{-2K} = f(K) e^{K'},\] (353)
and when $S = -S' = \pm 1$, Eq. (351) gives
\[
2 = f(K) e^{-K'}.
\] (354)
Therefore, solving for $f(K)$ in Eq. (354) and substituting into Eq. (353) we obtain
\[
K' = \frac{1}{2} \ln(\cosh(2K)),
\] (355)
and substituting Eq. (355) into Eq. (354) we obtain
\[ f(K) = 2\cosh^{1/2}(2K). \] (356)

Eqs. (355) and (356) are called renormalization group equations since they provide the renormalization scheme.

**Step 3.** Go to (1), replacing \( Z(K, N) \) by \( Z(K', N/2) \).

Step (3) is repeated each time on the subsequent (renormalized) partition function (i.e., \( Z(K'', N/4), Z(K''', N/8), Z(K^IV, N/16), Z(K^V, N/32), \ldots \) etc.) until the renormalized parameters become approximately constant (i.e., until the renormalized parameters reach a fixed point and become invariant under the Kadanoff transformation). Note that, according to Eq. (355), \( K > K' > K'' > K''' \), etc., so after a few iterations the coupling parameter becomes negligibly small and the partition function can be approximated by using Eq. (347) as follows:

\[ \ln Z(K, N) \approx \frac{N}{2} \ln 2 + \frac{N}{2} \ln \left[ \cosh^{1/2}(2K) \right] + \frac{N}{8} \ln \left[ \cosh^{1/2}(2K') \right] + \frac{N}{16} \ln \left[ \cosh^{1/2}(2K'') \right] + \frac{N}{32} \ln \left[ \cosh^{1/2}(2K''') \right] + \frac{N}{64} \ln \left[ \cosh^{1/2}(2K^IV) \right] + \frac{N}{128} \ln 2. \] (357)

The renormalization group strategy thus involves computing the total sum, introduced by Eq. (346), step by step. The success of the approach relies on the fact that the sum converges to an expression that can be easily computed, after a few iterations.

Sometimes the partition function is known for a specific value of the coupling parameter (e.g., for \( K' \approx 0 \) in the 1-dimensional Ising model). The renormalization group theory can then be implemented to compute the partition function of the system for a different value \( K \) of the coupling constant. This is accomplished by inverting Eq. (355) as follows:

\[ K = \frac{1}{2} \cosh^{-1}[\exp(2K')]. \] (358)

and computing \( Z(K, N) \) from \( Z(K', N/2) \) according to Eq. (352).

One could also define the function \( g(K) \) as follows

\[ Ng(K) \equiv \ln Z(K, N), \] (359)

and substituting Eq. (358) into Eq. (352) we obtain

\[ Ng(K) = \frac{N}{2} \ln 2 + \frac{N}{2} \ln \left[ \cosh^{1/2}(2K) \right] + \frac{N}{2} g(K'). \] (360)

Therefore, given the partition function \( Z(K', N) \) for a system with coupling constant \( K' \), one can compute \( g(K') \) and \( K \) according to Eqs. (359) and (358), respectively. The partition function \( Z(K, N) = \exp(Ng(K)) \) is then obtained by substituting the values of \( g(K') \) and \( K \) in Eq. (359).

Note that according to this procedure, \( K > K' \) and the subsequent iterations give larger and larger values of \( K \). This indicates that the flow of \( K \) has only two fixed points at \( K = 0 \) (e.g., at infinite temperature) and \( K = \infty \) (e.g., at 0 K). Systems with phase transitions, however, have nontrivial fixed points at intermediate values of \( K \). For instance, following a similar procedure, as the one described in this section, it is possible to show that the 2-dimensional Ising model has an additional fixed point \( K_c \) and that the heat capacity \( C = \frac{\partial^2}{\partial T^2} g(k) \) diverges at \( K_c \). Thus, \( K_c \) determines the critical temperature where the system undergoes a phase transition and spontaneously magnetizes.
The goal of this section is to introduce the Metropolis Monte Carlo Method (J. Chem. Phys. 21, 1087, 1953) and to illustrate the algorithm as applied to the computation of canonical ensemble averages for the Ising model.

The Metropolis Monte Carlo method is a computational approach (i.e., an algorithm) for generating a set of N configurations of the system \( \xi_1, \xi_2, \xi_3, ..., \xi_N \) such that

\[
\lim_{N \to \infty} \frac{N_{\xi}}{N} = P(\xi),
\]

where \( P(\xi) \) is a given probability distribution (e.g., the Boltzmann distribution \( P(\xi) = \frac{Z}{\prod} \exp[-\beta E(\xi)] \)) and \( N_{\xi} \) is the number of configurations \( \xi \) (e.g., the number of configurations generated with a particular arrangement of spins \( S_1(\xi), S_2(\xi), ..., S_N(\xi) \) in the Ising model).

The Metropolis Monte Carlo algorithm can be described as follows:

**Step (1):** Pick a configuration \( \xi_n \) (the initial configuration can be any configuration of the system, e.g., any arrangement of spins in the Ising model).

**Step (2):** Pick a trial configuration \( \xi_t \) (usually a configuration similar to \( \xi_n \)) and compute the probability ratio \( R = \frac{P(\xi_t)}{P(\xi_n)} \). Pick a random number \( p \) with value between 0 and 1. Make \( \xi_{n+1} = \xi_t \) if \( p \leq R \). Otherwise, make \( \xi_{n+1} = \xi_n \).

**Step (3):** Go to (2) replacing \( \xi_n \) by \( \xi_{n+1} \).

Step (3) is repeated \( N \) times, where \( N \) is a sufficiently large number. Note that, according to step (2), the probability of accepting a trial configuration \( \xi_t \) by making \( \xi_{n+1} = \xi_t \) from a configuration \( \xi_n \) is

\[
P_{\xi_n, \xi_t} = \begin{cases} R = \frac{P(\xi_t)}{P(\xi_n)}, & \text{when } P(\xi_t) < P(\xi_n), \\ 1, & \text{otherwise.} \end{cases}
\]

The goal of the remaining of this section is to prove that such an algorithm indeed produces an ensemble of configurations that satisfies Eq. (361).

Consider an ensemble of \( N(\xi) \) configurations with \( N(\xi) \) members of the ensemble in state \( \xi \). Apply the Metropolis Monte Carlo algorithm to each member of the ensemble by setting \( \xi_n = \xi \) and \( \xi_t = \xi' \) in step (2), where \( \xi \) and \( \xi' \) are any two possible states. Note that by applying the algorithm we generate more configurations and we therefore evolve the initial distribution. To show that the algorithm produces an ensemble of configurations that satisfies Eq. (361) we need to show that the any initial distribution \( N(\xi)/N \) evolves towards the distribution \( P(\xi) = \) and once such a distribution is reached it remains at equilibrium.

According to step (2), for any pair of states \( \xi \) and \( \xi' \), the number of configurations generated in state \( \xi' \) by applying the algorithm to the \( N(\xi) \) configurations in state \( \xi \) is \( N(\xi)P_{\xi, \xi'} \), where \( P_{\xi, \xi'} \) is the probability of accepting the trial configuration \( \xi' \) when \( \xi_n = \xi \). In addition, the number of configurations generated in state \( \xi' \) by applying the algorithm to the \( N(\xi') \) configurations in state \( \xi' \)
is \((1 - P_{\xi',\xi}) N(\xi')\). Therefore, the total number \(\overline{N}(\xi')\) of configurations generated in state \(\xi'\) due to any other state \(\xi\) is

\[
\overline{N}(\xi') = N(\xi') + \Delta N(\xi'),
\]

where

\[
\Delta N(\xi') = N(\xi) P_{\xi,\xi'} - N(\xi') P_{\xi',\xi},
\]

is the net change in the number of configurations in state \(\xi'\), relative to \(N(\xi')\).

According to Eqs. (362) and (364),

\[
\Delta N(\xi') = \frac{N(\xi')}{\overline{N}(\xi')} P(\xi') - N(\xi'),
\]

when \(P(\xi') > P(\xi)\) and

\[
\Delta N(\xi') = N(\xi) \frac{P(\xi)}{P(\xi')} - N(\xi'),
\]

when \(P(\xi') < P(\xi)\). Therefore, according to Eqs. (365) and (366), \(\Delta N(\xi') = 0\) when \(N(\xi)/\overline{N} = P(\xi)\) and \(N(\xi')/\overline{N} = P(\xi')\), i.e., the algorithm does not alter the relative population of the states when the ensemble distribution is equal to the equilibrium distribution. In addition, Eqs. (365) and (366) indicate that \(\Delta N(\xi') > 0\) when \(N(\xi')/\overline{N} < P(\xi')\) (and \(\Delta N(\xi') < 0\) when \(N(\xi')/\overline{N} > P(\xi')\)), i.e., the algorithm evolves any arbitrary distribution towards the equilibrium distribution where \(\frac{N(\xi')}{\overline{N}} = P(\xi)\).

Note: The most important aspect of the method is that the algorithm is able generate an ensemble of configurations with the probability distribution \(P(\xi) = Z^{-1} \exp[-\beta E(\xi)]\), simply by computing the probability ratios \(P(\xi')/P(\xi)\). Therefore, the method avoids the need of computing the canonical partition function of the system \(Z\), a computational task that would be computationally intractable for most real applications. This numerical technique is thus extremely useful since it allows one to compute any canonical ensembles without having to compute the canonical partition function of the system as follows,

\[
\langle A \rangle \approx \bar{A} = \frac{1}{N} \sum_{\xi} N_{\xi} A(\xi),
\]

where \(A(\xi)\) is the value of the observable \(A\) for state \(\xi\) and \(\bar{A}\) is the Monte Carlo estimator of \(\langle A \rangle\) associated with the finite number of configurations \(N\).

Exercise:
Implement the Metropolis Monte Carlo Algorithm to generate an ensemble of configurations for a 2-dimensional Ising model with \((20 \times 20\) spins) in the absence of an external field. Compute the average value of the magnetization at various different temperatures and show that the system exhibits spontaneous magnetization when \(T < 2.3J/k\), where \(J\) is the coupling constant between spins.
## 37 Variance-Reducing Techniques

The goal of this section is to introduce a few techniques commonly used for reducting the statistical error in Monte Carlo computations of ensemble averages.

According to the previous section, the Monte Carlo computation of the ensemble average
\[
\langle A \rangle = Z^{-1} \int d\xi A(\xi) e^{-\beta E(\xi)},
\] (368)
entails sampling an ensemble of random configurations \( \xi \) with probability distribution \( P(\xi) = Z^{-1} \exp[-\beta E(\xi)] \), computing \( A(\xi) \) for each configuration and finally averaging all of these values to obtained the unbiased estimator \( \bar{A} \) introduced by Eq. (367). The convergence rate of such computation is determined by the central limit theorem (CLT) (see, e.g., K.L. Chung *A course in Probability Theory*, Academic Press, New York, 1974).

The CLT states that given a sequence of random variables \( A(\xi_1), A(\xi_2), A(\xi_3), \ldots A(\xi_N) \) with expectation \( \langle A \rangle \) and variance
\[
\sigma^2 = \frac{1}{N} \sum_\xi N(\xi)(A(\xi) - \langle A \rangle)^2,
\] (369)
then the distribution of averages \( \bar{A} \) obtained with different sequences of random variables tends to be a Gaussian distribution
\[
G(\bar{A}) = \frac{1}{\sqrt{2\pi\varepsilon}} e^{-\frac{(\bar{A} - \langle A \rangle)^2}{2\varepsilon^2}},
\] (370)
where
\[
\varepsilon = \sigma/\sqrt{N},
\] (371)
regardless of the dimensionality of the integral introduced by Eq. (368) and the nature of the probability function used to generate the sequences of random variables \( A(\xi_1), A(\xi_2), A(\xi_3), \ldots A(\xi_N) \).

The standard deviation \( \varepsilon \) of the distribution of the average is the standard error of the Monte Carlo computation. Therefore, results are reported as follows
\[
\langle A \rangle = \bar{A} \pm \varepsilon.
\] (372)

Note that according to the definitions of the variance and the standard error, introduced by Eqs. (369) and (371), respectively, the standard error is large whenever the random variables \( A(\xi_j) \) spread over a wide range of values. This is one of the main problems in calculations of high dimensional integrals, since the integrand \( A(\xi) \) usually spreads over a very large range of values and the variance \( \sigma^2 \) is thus formidably large. In addition, depending on the observable of interest, the Boltzmann distribution might not sample the configurations of the system that contribute with the most to the ensemble average. These difficulties are sometimes overcome by implementing variance reduction techniques such as importance sampling, correlated sampling, stratified sampling, adaptive sampling, control variates and umbrella sampling. J.M. Hammersley and D.C. Handscomb *Monte Carlo Methods*, Chapter 5, John Wiley & Sons Inc., London, (1964) and J.S. Liu *Monte Carlo Strategies in Scientific Computing*, Chapter 2, Springer New York (2001) are recommended references for these methods. Here we limit our presentation to a concise description of some of them.
37.1 Importance Sampling

The importance sampling technique concentrates the distribution of sampled configurations in the parts of the integration range that are of most importance. Instead of computing the ensemble average
\[ \langle A \rangle = \int d\xi P(\xi) A(\xi), \]  
according to the estimator \( \bar{A} \) introduced by Eq. (367), after sampling configurations \( \xi \) according to the probability distribution \( P(\xi) \), configurations are sampled according to a different probability distribution \( \tilde{P}(\xi) \) and the ensemble average is computed according to the estimator
\[ \langle A \rangle \approx \bar{g} = \frac{1}{N} \sum_{\xi} N(\xi) \frac{g(\xi)}{P(\xi)}, \]  
where \( g(\xi) \equiv P(\xi) A(\xi) \) and \( \tilde{P}(\xi) \) is assumed to be normalized.

The variance of the estimator introduced by Eq. (374) is
\[ \sigma^2 = \frac{1}{N} \sum_{\xi} N(\xi) \left( \frac{g(\xi)}{P(\xi)} - \langle A \rangle \right)^2, \]  
or
\[ \sigma^2 = \frac{1}{N} \sum_{\xi} N(\xi) \frac{g(\xi)^2}{P(\xi)^2} - \left( \frac{1}{N} \sum_{\xi} N(\xi) \frac{g(\xi)}{P(\xi)} \right)^2. \]  
Note that according to Eq. (376), \( \sigma^2 = 0 \) when \( \tilde{P}(\xi) = g(\xi) \). Therefore, the variance can be reduced by choosing \( \tilde{P}(\xi) \) similar to \( |g(\xi)| \). Such choice of \( \tilde{P}(\xi) \) concentrates the distribution of sampled configurations in the parts of the integration range that are of most importance. According to such distribution, the random variables \( g(\xi)/\tilde{P}(\xi) \) spread over a modest range of values close to 1 and therefore the standard error of the Monte Carlo calculation is reduced.

The umbrella sampling technique is a particular form of importance sampling, specially designed to investigate rare events. Configurations are sampled according to the non-Boltzmann distribution \( P(\xi) \propto \exp[-\beta (E(\xi)+W(\xi))] \), where \( W(\xi) \) is zero for the interesting class of configurations that defined the rare event and very large for all others.

37.2 Correlated Sampling

Consider the task of computing the integral
\[ \Delta I = I_1 - I_2, \]  
with
\[ I_1 = \int dx g_1(x)f_1(x), \]  
(377)
(378)
and

\[ I_2 = \int dx g_2(x) f_2(x). \]  \hfill (379)

The procedure for correlated sampling can be described as follows:

Step (1). Sample random configurations \( x_1, \ldots, x_N \) by using the sampling function \( f_1(x) \) and evaluate the function \( g_1 \) for each of these configurations to obtain \( g_1(x_1), g_1(x_2), g_1(x_3) \ldots g_1(x_N) \). In addition, sample random configurations \( y_1, \ldots, y_N \) by using the sampling function \( f_2(y) \) and evaluate the function \( g_2 \) for each of these configurations to obtain \( g_2(y_1), g_2(y_2), g_2(y_3) \ldots g_2(y_N) \).

Step (2) Estimate \( \Delta I \) according to

\[ \Delta I = \frac{1}{N} \sum_{j=1}^{N} g_1(x_j) - g_2(y_j). \]  \hfill (380)

The variance of \( \Delta I \) is

\[ \sigma^2 = \frac{1}{N} \sum_{j=1}^{N} \left( g_1(x_j) - g_2(y_j) - (I_1 - I_2) \right)^2, \]  \hfill (381)

or

\[ \sigma^2 = \frac{1}{N} \sum_{j=1}^{N} \left( g_1(x_j) - I_1 \right)^2 + \frac{1}{N} \sum_{j=1}^{N} \left( g_2(y_j) - I_1 \right)^2 - 2 \frac{1}{N} \sum_{j=1}^{N} \left( g_1(x_j) - I_1 \right) \left( g_2(y_j) - I_2 \right), \]  \hfill (382)

where the first two terms on the r.h.s. of Eq. (382) are the variances \( \sigma_1^2 \) and \( \sigma_2^2 \) of the random variables \( g_1 \) and \( g_2 \), respectively, and the third term is the covariance \( \text{cov}(g_1,g_2) \) of the two random variables. Note that when \( x_j \) and \( y_j \) are statistically independent then the \( \text{cov}(g_1,g_2)=0 \) and

\[ \sigma^2 = \sigma_1^2 + \sigma_2^2. \]  \hfill (383)

However, if the random variables are positively correlated then the \( \text{cov}(g_1,g_2) > 0 \) and the variance \( \sigma^2 \) is reduced. The key to reduce the variance is thus to ensure positive correlation between \( g_1 \) and \( g_2 \). This could be achieved by using the same sequence of random numbers for sampling both sets of random configurations \( x_j \) and \( y_j \).

### 37.3 Control Variates

Consider the Monte Carlo computation of a multidimensional integral (e.g., an ensemble average),

\[ \langle A \rangle = \int d\xi g(\xi), \]  \hfill (384)

and assume that the integral

\[ \int d\xi \bar{g}(\xi) = A, \]  \hfill (385)

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can be analytically computed for an approximate expression of the integrand $\tilde{g}(\xi) \approx g(\xi)$. The function $\tilde{g}(\xi)$ is called the control variate for $g(\xi)$.

The control variates method is an approach that exploits the information provided by Eq. (385) to reduce the variance of the Monte Carlo computation. The integral, introduced by Eq. (384), is written in two parts,

$$\langle A \rangle = A_0 + \int d\xi (g(\xi) - \tilde{g}(\xi)), \quad (386)$$

where the first term on the r.h.s. of Eq. (386) is analytically computed and the second term is computed by correlated sampling Monte Carlo integration. Note that since $\tilde{g}(\xi)$ mimics $g(\xi)$ and usually absorbs most of its variation, the error in the Monte Carlo computation of the second term in the r.h.s. of Eq. (386) is usually appreciably smaller than those of a Monte Carlo evaluation of the integral introduced by Eq. (384).

### 37.4 Stratified Sampling

Consider the task of computing the multidimensional integral (e.g., an ensemble average),

$$\langle A \rangle = \int d\xi f(\xi). \quad (387)$$

The stratified sampling technique breaks the integration range into the union of $k$ disjoint subregions $D_1, D_2, ..., D_k$, so that within each subregion the integrand is relatively constant. Then, we can sample $m_j$ random configurations $\xi_j(1), \xi_j(2), ..., \xi_j(m_j)$ in the subregion $D_j$ and approximate each subregional integral by

$$\int_{D_j} d\xi f(\xi) \approx A_j = \frac{1}{m_j} [f(\xi_j(1)) + f(\xi_j(2)) + ... + f(\xi_j(m_j))]. \quad (388)$$

The overall integral is computed as

$$\langle A \rangle \approx \bar{A} = A_1 + A_2 + ... + A_k, \quad (389)$$

whose variance is

$$\sigma^2 = \frac{\sigma_1^2}{m_1} + \frac{\sigma_2^2}{m_2} + ... + \frac{\sigma_k^2}{m_k}, \quad (390)$$

where $\sigma_j^2$ indicates the variation of the integrand in the subregion $D_j$. Note that only when the integrand is relatively constant within each subregion the variance introduced by Eq. (390) will be smaller than the variance of the estimator obtained by using a single region for the whole integration range, $\bar{\sigma}^2/m$ where $m = m_1 + m_2 + ... + m_k$ and $\bar{\sigma}$ is the overall variation of the integrand in the whole integration range.

If we look carefully we can see that the stratified sampling technique described in this section is a particular version of the importance sampling method.

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37.5 Simulated Annealing

Consider the task of computing a thermodynamic ensemble average for a system with many degrees of freedom at low temperature (e.g., a large cluster, a polymer, or a protein). The challenge presented by these many-body systems is that in addition to their global minimum energy configuration they usually have many local energy minima separated by high energy barriers. A Metropolis Monte Carlo computation at low temperature that starts from a configuration that is far from the minimum energy geometry usually leads to erroneous results. The reason for this is that the configurations that make the most important contributions to an ensemble average are those that are close to the minimum energy configuration and the algorithm is inefficient at sampling configurations that are beyond high potential energy barriers. Reliable Monte Carlo calculations thus require obtaining first the minimum energy configuration of the system.

The simulated annealing algorithm (by S. Kirkpatrick, C.D. Gelatt and M.P. Vecchi Science 220 671-680, 1983) is an efficient technique to find the minimum energy configuration of the system. The algorithm can be described as follows:

Step (1): Initialize an arbitrary configuration $\xi_0$ for the system at temperature $T_0$, where $T_0$ is reasonably large.

Step (2): Starting from the configuration $\xi_0$, sample N configurations $\xi_1, \xi_2, ..., \xi_N$ by implementing the Metropolis Monte Carlo method with $P(\xi) = Z^{-1}\exp(-E(\xi)/(kT_0))$.

Step (3): Go to (2), replacing $\xi_0$ by $\xi_N$ and $T_0$ by a lower temperature. Step (3) is repeated each time on the subsequent configuration $\xi_N$ until the temperature of the system is equal to 0.

It can be shown that the configuration that corresponds to the global minimum of $E(\xi)$ can be reached according to such algorithm whenever the temperature decreases at a logarithmic rate (e.g., see S. Geman and D. Geman IEEE Transactions on Pattern Analysis and Machine Intelligence 6:721-741, 1984). In practice, however, a linear or even exponential temperature decrease schedule can often be implemented.

Exercise:
This computational assignment has been designed and organized by Dr. Jose A. Gascon.

1. Write a program for implementing the simulated annealing procedure and find the minimum energy geometry of a “cluster” of two atoms interacting according to the 12-6 Lennard-Jones potential

$$U(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right], \quad (391)$$

where $\varepsilon = 0.0104$ ev and $\sigma = 3.4$ Å. You can write your own code or modify the Fortran program [mclj.for] attached to the www page for the lecture notes of this course.

Notes:

(a) If you decide to use the mclj.for program, you will have to edit the code and write a few lines as specified in the mclj.for file. The missing lines should specify the Metropolis Monte Carlo procedure.
(b) When running the \textit{mclj.for} program you will be asked for the initial and final temperature. A reasonable value for the initial temperature is 10 K (just type 10). Since we are trying to find the global minimum the final temperature must be zero.

(c) When asked ”Is the initial geometry random (yes/no)?”, type ”yes” to have the program select an initial guess of the geometry. You can eventually put your own initial guess in which case type ”no”. To create an initial geometry you must create a file called \textit{initial.xyz} in the standard xyz format, where the first line is the number of atoms, the second line is left blank or with any coment, and the following lines have the atom type and coordinates as shown below for a cluster of \( N \) argon atoms.

\begin{verbatim}
N
comment
Ar \( x_1 \ y_1 \ z_1 \\
Ar \( x_2 \ y_2 \ z_2 \\
... \\
Ar \( x_N \ y_N \ z_N \\
\end{verbatim}

(d) The \textit{mclj.for} program reports on the screen the numbers of steps, the average interatomic distance, the energy at that step and the ratio of accepted trials out of 100.

(e) The final geometry is recorded in the output file \textit{final.xyz}.

2. Visualize the final geometry using a molecular viewer program such as Rasmol or Molden. The file \textit{movie.xyz} contains snapshots of the accepted geometries along the simulation. The movie with the sequence of accepted geometries can be visualized by using Molden. Compare the minimum energy geometry (i.e., the minimum energy distance between the two Ar atoms) found by the simulated annealing algorithm with the exact value computed from the expression of the 12-6 Lennard-Jones potential.

3. To appreciate the power of the simulated annealing method, find the minimum energy geometry of clusters with 3 and 13 argon atoms and report the values of the minimum energy. For the cluster with 13 atoms run the program with three different initial temperatures, 10 K, 20 K and 30 K. Compare the final results. Do the final energy and geometry depend on the initial temperature? Why, or why not?

4. How would you compute a thermodynamic average at a constant temperature using the program for simulating annealing?

The link \underline{[http://ursula.chem.yale.edu/~batista/classes/vaa/LJ.m]} provides a Matlab solution to the computational assignment.
This section introduces Monte Carlo simulations of dynamical processes. We consider the stochastic simulation of a complex dynamical phenomenon that involves \( N \) independent processes. As an example, consider the problem of modeling the time-dependent evolution of a 2-dimensional Ising model with \( N \) spins, where spins are flipped in time due to the influence of thermal fluctuations. For simplicity, consider that the time-evolution of a spin \( j \) is described by the first order differential equation
\[
\frac{\partial s_j(t)}{\partial t} = -k_j^{(1)}(s_j(t) + s(0)),
\]
where \( s_j(t) = s_j(0)(2\exp(-k_j^{(1)}t) - 1) \). We assume that the rate constants \( k_j^{(1)} \) can take different values \( k_j^{(1)} = (k_j^{(0)}, k_j^{(1)}, k_j^{(2)}, k_j^{(3)}, k_j^{(4)}) \), depending on the number of nearest neighbors (1–4) of \( j \) that have the same spin.

Accurate MC simulations should sample event \( j \) with probability \( p_j = \frac{k_j^{(1)}}{k} \) where \( k = \sum_{j=1}^{N} k_j^{(1)} \) is the total rate. This can be accomplished according to the so-called kinetic Monte Carlo method as follows:

1. Set the simulation time to zero, \( t = 0 \).
2. Pick a random number \( r_1 \) between 0 and \( k \).
3. Select the process labeled by index that satisfies the condition,
\[
\sum_{j=1}^{\alpha-1} k_j^{(1)} \leq r_1 \leq \sum_{j=1}^{\alpha} k_j^{(1)}.
\] (392)
4. Carry out event \( \alpha \).
5. Assign the time \( t_\alpha = -\frac{1}{k}\ln(r_2) \) to the selected event, where \( r_2 \) is a random number between 0 and 1, and advance the simulation time \( t = t + t_\alpha \).
6. Update the values of \( k_j^{(1)} \) that have changed due to event \( \alpha \).
7. Recompute \( k \).
8. Goto (2).

Selecting the event \( \alpha \), according to Eq. (392), can be pictured as throwing a dart to a ruler of length \( k \), subdivided by segments of length \( k_1^{(1)}, k_2^{(1)}, k_3^{(1)}, \ldots, k_N^{(1)} \), as depicted in Fig. 1. The process \( \alpha \) corresponds to the segment targeted by the dart (\( \alpha = 7 \), in Fig. 38).

Unfortunately, finding out which segment was hit by the dart requires \( O(N) \) operations when the search is based on a naive linear search procedure, since it is necessary to evaluate Eq. (392) with \( \alpha = 1 \), then with \( \alpha = 2, \ldots, \) etc., until finding the value of \( \alpha \) that satisfies Eq. (392). Such a procedure is prohibitively expensive for most realistic applications. It is, therefore, necessary to implement an algorithm based on a binary tree where \( \alpha \) can be selected in \( O(\log_2 N) \) steps, as described later in this section [J.L. Blue; I. Beichl, Phys. Rev. E (1995) 51, R867-R868].
**Binary tree method:** To explain the binary tree method, consider a system with only 8 possible events, where rate constants $k^{(1)}_1, \ldots, k^{(1)}_8$ define the roots of the tree depicted in Fig. 1. The next layer of nodes in the tree, $k^{(2)}_1, \ldots, k^{(2)}_4$, is defined by computing the partial sums of pairs of rate constants, as follows:

- $k^{(2)}_1 = k^{(1)}_1 + k^{(1)}_2$
- $k^{(2)}_2 = k^{(1)}_3 + k^{(1)}_4$
- $k^{(2)}_3 = k^{(1)}_5 + k^{(1)}_6$
- $k^{(2)}_4 = k^{(1)}_7 + k^{(1)}_8$

The third layer of nodes, $k^{(3)}_1, \ldots, k^{(3)}_2$ is defined analogously, as follows:

- $k^{(3)}_1 = k^{(2)}_1 + k^{(2)}_2$
- $k^{(3)}_2 = k^{(2)}_3 + k^{(2)}_4$

Finally, the top of the tree is $k^{(4)}_1 = k^{(3)}_1 + k^{(3)}_2 = k$.

To select the dynamical process $\alpha$, we start from the top of the tree, where $k^{(4)}_1 = k^{(n)}_j$, with $j = 1$ and $n = 4$, and we proceed as follows:

1. Generate a random number $r_1$.
2. If $r_1 \leq k^{(n-1)}_{2j-1} = k^{(3)}_1$, make $j = 2j - 1$. Otherwise, substract from $r_1$ and make $j = 2j$.
3. If $n = 1$, then $\alpha = j$. Otherwise, make $n = n - 1$ and go to (1).

Updating the binary tree, after carrying out the selected event, can also be done recursively from $n = 1$ to the top of the tree, by propagating the effects of the new rate constants.
Exercise 1
(10 points) Item (1.1): Explain the underlying approximation of Mean Field theory and illustrate it with a specific Hamiltonian.
(20 points) Item (1.2): Show that Mean Field theory predicts spontaneous magnetization for the 2-dimensional Ising model when \( T < \frac{4J}{k} \), where \( J \) is the coupling constant between spins.
(20 points) Item (1.3): Derive the Gibbs-Bogoliubov-Feynman inequality.
(20 points) Item (1.4): Derive the renormalization group equations for the 1-dimensional Ising model.

Exercise 2
(30 points) Compute the grand canonical partition function of a 1-dimensional lattice gas by implementing the transfer matrix approach.

Hint: Assume that the total energy for a given set of occupation numbers \( \{ n_j \} \) is

\[
E = -\mu \sum_{j=1}^{N} n_j - \epsilon \sum_{j=1}^{N} \sum_{k} n_j n_k, \tag{393}
\]

where \( \mu \) is the chemical potential of the particles, the occupation numbers \( n_j = 0, 1 \). The indices \( k \), in Eq. (393) label the cells that are next to cell \( j \) and \( N \) is the total number of cells.

Solution
Item (1.1):
The underlying approximation of Mean Field theory is to assume that the most important contribution to the interaction between each particle and its neighboring particles is determined by the mean field due to the neighboring particles. Section Mean Field Theory on page 65 of your lecture notes illustrates this concept as applied to the description of the 1-dimensional Ising model.

**Item (1.2):**
In the 2-dimensional Ising model, the average force $F_k$ exerted on spin $S_k$ is

$$F_k \equiv -\frac{\partial H}{\partial S_k} = \bar{\mu}B + J \sum_j S_j,$$  \hspace{1cm} (394)

where the index $j$ includes all the nearest neighbors of spin $S_k$. Therefore, the average magnetic field $\bar{B}$ acting on spin $S_k$ is

$$\bar{B} \equiv \frac{F_k}{\bar{\mu}} = B + \Delta B,$$ \hspace{1cm} (395)

where

$$\Delta B = J4\bar{S}_k/\bar{\mu},$$ \hspace{1cm} (396)

is the contribution to the mean field due to the nearest neighbors. Note that $\bar{S}_k = \bar{S}_j$ when all spins are identical.

The partition function, under the mean field approximation, is

$$Z \approx \sum_{S_1} \sum_{S_2} \ldots \sum_{S_N} e^{\beta \sum_j S_j(B+\Delta B)\bar{\mu}} = 2^N \cosh^N(\beta \bar{\mu}B),$$ \hspace{1cm} (397)

and the average value of $S_k$ is

$$\bar{S}_k = \frac{1}{N} \frac{\partial \ln Z}{\partial (\beta \bar{\mu}B)} = \tanh(\beta \bar{\mu}(B + 4J\bar{S}_k/\bar{\mu})).$$ \hspace{1cm} (398)

Note that Eq. (398) involves a transcendental equation. Its solution corresponds to the value of $\bar{S}_k = m$ for which the function on the left hand side of Eq. (398) (i.e., $\bar{S}_k$) equals the function on the right hand side of Eq. (398) (i.e., $\tanh(\beta \bar{\mu}(B + 4J\bar{S}_k/\bar{\mu}))$).

In the absence of an external magnetic field (i.e., when $B = 0$), Eq. (398) always has the trivial solution $S_k = 0$ and a non-trivial solution $S_k = m$ only when $\beta 4J > 1$.

**Item (1.3):**
See derivation of Eq. (341) on page 69 of your lecture notes.

**Item (1.4):**
See derivation of Eqs. (355) and (356) on your lecture notes.

**Exercise 2:**
The Hamiltonian of the system is

$$H = -\mu \sum_j n_j - \epsilon \sum_{jk} n_j n_k,$$ \hspace{1cm} (399)

where the sum of products $n_j n_k$ defines the interaction between cells that are nearest neighbors.
The grand canonical partition function of the system is
\[ \Xi = \sum_{n_1=0,1} \sum_{n_2=0,1} \cdots \sum_{n_N=0,1} e^{\beta (\mu (n_1+n_2)/2 + \epsilon n_1 n_2)} e^{\beta (\mu (n_3+n_2)/2 + \epsilon n_2 n_3)} \cdots e^{\beta (\mu (n_N+n_1)/2 + \epsilon n_N n_1)} \]  
(400)

To perform a rigorous calculation of the grand canonical partition function introduced by Eq.(370), we define the transfer function as follows,
\[ T(n_i, n_{i+1}) \equiv \exp(\beta (\mu (n_i + n_{i+1})/2 + \epsilon n_i n_{i+1})). \]  
(401)

Substituting Eq.(371) into Eq.(370) we obtain
\[ \Xi = \sum_{n_1=0,1} \sum_{n_2=0,1} \cdots \sum_{n_N=0,1} T(n_1, n_2) T(n_2, n_3) \cdots T(n_N, n_1). \]  
(402)

This expression corresponds to the trace of a product of N identical $2 \times 2$ matrices. Thus the calculation of the grand canonical partition function is reduced to that of computing the trace of the $N$th power of the transfer matrix. Now, the trace of a matrix is the sum of its eigenvalues and the eigenvalues of $T^N$ are $\lambda_{\pm}^N$, where $\lambda_{\pm}$ are the eigenvalues of $T$ determined by the equation
\[ \begin{vmatrix} e^{\beta (\mu+\epsilon)} - \lambda & e^{\beta \mu/2} \\ e^{\beta \mu/2} & 1 - \lambda \end{vmatrix} = 0, \]  
(403)
with solutions
\[ \lambda_{\pm} = \frac{1}{2} [e^{\beta (\mu+\epsilon)} + 1] \pm \sqrt{[e^{\beta (\mu+\epsilon)} - 1]^2 / 4 + e^{\beta \mu}}. \]  
(404)

Hence, the partition function is simply,
\[ Z = \lambda_+^N + \lambda_-^N, \]  
(405)
where $\lambda_{\pm}$ are defined by Eq. [404].

**40 Classical Fluids**

To perform statistical mechanical calculations for classical fluids, we must be able to compute phase space averages,
\[ \langle A \rangle = \sum_\xi A(\xi) \frac{e^{-\beta E(\xi)}}{Z}, \]  
(406)
where $A(\xi)$ is the observable of interest evaluated in state $\xi$.

In a classical system of particles, the index $\xi$ labels the microscopic phase point
\[ \xi = (r_1, r_2, \ldots, r_n, p_1, p_2, \ldots, p_n) = (r^N, p^N), \]  
(407)
i.e., the list of coordinates and momenta \((r^N, p^N)\). Therefore, the ensemble average is

\[
\langle A \rangle = \int dr^N \int dp^N f(r^N, p^N) A(r^N, p^N),
\]

(408)

where

\[
f(r^N, p^N) = \frac{e^{-\beta E(r^N, p^N)}}{\int dr^N \int dp^N e^{-\beta E(r^N, p^N)}},
\]

(409)

is the probability density at phase-point \((r^N, p^N)\), where the system has total energy

\[
E(r^N, p^N) = V(r^N) + K(p^N),
\]

(410)

with total kinetic energy

\[
K(p^N) = \sum_{j=1}^{N} \frac{p_j^2}{2m_j},
\]

(411)

and total potential energy of interaction between particles \(V(r^N)\).

The factorization of the total energy into kinetic and potential energy terms, allows one to factorize the probability distribution function as follows,

\[
f(r^N, \rho^N) = \Phi(r^N) P(\rho^N),
\]

(412)

where

\[
P(\rho^N) = \exp(-\beta K(\rho^N)) / \int d\rho^N \exp(-\beta K(\rho^N)),
\]

(413)

and

\[
\Phi(r^N) = \exp(-\beta V(r^N)) / \int dr^N \exp(-\beta V(r^N)).
\]

(414)

Further factorization of the momentum distribution is possible, since the total kinetic energy of the system \(K(p^N)\) is the sum of the kinetic energy of individual particles

\[
\Phi(p^N) = \prod_{j=1}^{N} \phi(p_j), \quad \text{where} \quad \phi(p_j) = \frac{e^{-\beta p_j^2/2m_j}}{\int dp_j e^{-\beta p_j^2/2m_j}}.
\]

(415)

Eqs. (414) and (415) thus define the probability distribution functions that are necessary to sample an ensemble of configurations of the fluid at thermal equilibrium. Contrary to clusters of atoms or molecules, fluids with bulk properties usually involve an enormous number of particles \((i.e., \sim O(10^{23})\) particles where the fraction of particles near the walls of the container is negligibly small. However, computer memory and disk space requirements usually limit the capabilities of computer simulations to model systems with less than \(10^6\)–\(10^7\) particles. Contrary to macroscopic systems, these model systems have a significant fraction of particles near the walls of the container. Therefore, to simulate systems with bulk properties, it is necessary to implement a trick called periodic boundary conditions (p.b.c.) that minimizes surface effects.
Periodic Boundary Conditions: The implementation of p.b.c. for a one-dimensional "box" of length L converts the segment L into a circle of radius r, where $2\pi r = L$. The distance between any two particles is measured along the arc of such circle and hence the maximum separation between any two particles is $L/2$. One simple way of implementing p.b.c. for particles in a 1-dimensional box of length L is to add(subtract) L to the coordinate of any particle that crosses the left(right) boundary of the box after being slightly displaced to a new position. This can be implemented with an if-statement as follows:

\[
\text{if}(x > L) \\
\quad x = x - L \\
\text{else if}(x < 0) \\
\quad x = x + L \\
\text{end if}
\]  

(416)

To compute the minimum distance $dx$ between particles $p1$ and $p2$ at $x1$ and $x2$, respectively, we can write

\[
dx = x1 - x2 \\
\text{if}(dx > 0.5 * L) \\
\quad dx = dx - L \\
\text{else if}(dx < -0.5 * L) \\
\quad dx = dx + L \\
\text{end if}
\]

(417)

Note that when programming Eqs. (416) and (417) you will need to implement the logic characters and the punctuation marks required by the specific programing language of choice. The generalization of Eqs. (416) and (417) to the implementation of p.b.c. in two and three dimensions is straightforward.

40.1 Radial Distribution Function

The goal of this section is to introduce the radial distribution function $g(r)$ (also known as pair correlation function), a central quantity in studies of fluids since it determines the average density of particles at a coordinate $r$ relative to any particle in the fluid. The radial distribution function is defined as follows

\[
g(r) = \rho_{2/N}(0, r) / \rho^2,
\]

(418)

where $\rho = N/V$ is the density of a fluid of $N$ particles in a container of volume $V$ and $\rho_{2/N}(0, r)$ is the probability that a particle is at $r$ when there is another particle at the origen of coordinates.

The probability $P^{2/N}(R_1, R_2)$ that particle 1 is found at $R_1$ when particle 2 is at $R_2$, in an $N$ particle system, is

\[
P^{2/N}(R_1, R_2) = \frac{\int dr^N \delta(r_1 - R_1) \delta(r_2 - R_2) e^{-\beta V(r^N)}}{\int dr^N e^{V(r^N)}} = \frac{\int dr^{N-2} e^{-\beta V(R_1, R_2, r_3, ..., r_N)}}{\int dr^N e^{V(r^N)}},
\]

(419)
and the probability $\rho^{2/N}(R_1, R_2)$ that a particle (i.e., any particle) is found at $R_1$ when another one (i.e., any other one) is at $R_2$ is

$$\rho^{2/N}(R_1, R_2) = \frac{N!}{(N-2)!} P^{2/N}(R_1, R_2) = N(N-1) \rho^{2/N}(R_1, R_2). \tag{420}$$

In particular, in a fluid where the interaction between particles can be neglected,

$$P^{2/N}(R_1, R_2) = \frac{1}{V^2}, \tag{421}$$

or

$$\rho^{2/N}(R_1, R_2) = \frac{N(N-1)}{V^2} \approx \rho^2, \tag{422}$$

and $g(r) = 1$.

In an atomic fluid (e.g., liquid argon), $g(r_1, r_2) = g(r)$, where $r = |r_1 - r_2|$, since the fluid is uniform and isotropic. The presence of an atom at the origin of coordinates excludes other particles from all distances smaller than the radius of the first coordination shell where $g(r)$ has a maximum (see figure). The presence of the first coordination shell tends to exclude particles that are closer than the radius of the second coordination shell, where $g(r)$ has another maximum. This oscillatory form for $g(r)$ persists until $r$ is larger than the range of correlations between the particles. At distances larger than the correlation length $g(r) = 1$, since $\rho^{2/N}(0, r) \approx \rho^2$ for uncorrelated particles. Therefore, $h(r) = g(r) - 1$ describes the deviation from the asymptotic limit of uncorrelated particles (i.e., an ideal gas) and the product $\rho g(r)$ describes the average density of particles at a distance $r$ from any particle in the fluid.

Note that $\rho g(r) 4\pi r^2 dr$ is the average number of particles at a distance between $r$ and $r+dr$ from any particle in the fluid. Therefore, the calculation of $g(r)$ involves averaging the number of particles at a distance $r$ from any particle in the system and dividing that number by the element of volume $4\pi r^2 dr$.

**Exercise:**
Compute the radial distribution function $g(r)$ for a fluid of argon atoms at constant $T, N, V$ using the program developed in the assignment of simulating annealing.

### 41 Reversible Work Theorem

The theorem states that the radial distribution function $g(r)$ determines the reversible work $w(r)$ associated with the process by which two particles in a fluid are moved from an infinite separation to a separation $r$, as follows:

$$g(r) = \exp(-\beta w(r)) \tag{423}$$

Note that since the process is reversible at constant $T$, $N$ and $V$, $w(r) = \Delta A$, where $A$ is the Helmholtz free energy.
Proof:
Consider the mean force between particles 1 and 2, averaged over the equilibrium distribution of all other particles,

\[- \left< \frac{dV(r^N)}{dr_1} \right>_{r_1r_2} = - \int \frac{dV}{dr_1} e^{-\beta V(r^N)} dr_3 \cdots dr_N \frac{1}{e^{-\beta V(r^N)} dr_3 \cdots dr_N},\]

(424)

which gives

\[- \left< \frac{dV(r^N)}{dr_1} \right>_{r_1r_2} = \frac{1}{\beta} \frac{d}{dr_1} \ln \int e^{-\beta V(r^N)} dr_3 \cdots dr_N,\]

(425)

or

\[- \left< \frac{dV(r^N)}{dr_1} \right>_{r_1r_2} = \frac{1}{\beta} \frac{d}{dr_1} \ln \int e^{-\beta V(r^N)} dr_3 \cdots dr_N,\]

(426)

since both the number of particles N in the system and the partition function Z are constants, independent of \(r_1\).

Eq. (426) can be simplified according to Eqs. (418) and (419) as follows,

\[- \left< \frac{dV(r^N)}{dr_1} \right>_{r_1r_2} = \frac{1}{\beta} \frac{d}{dr_1} \ln g(r_1).\]

(427)

Integration of the expression for the average force, introduced by Eq. (427), gives the reversible work,

\[w(r_{12}) = \int_{r_{12}}^{\infty} dr_1 \left< \frac{dV(r^N)}{dr_1} \right> = kT \int_{r_{12}}^{\infty} dr_1 \frac{1}{\beta} \frac{d}{dr_1} \ln g(r_1),\]

(428)

Therefore, the reversible work \(w(r_{12})\) associated with the process by which particles 1 and 2 are moved from infinite separation to a relative separation \(r_{12}\) is

\[w(r_{12}) = kT \ln g(\infty) - kT \ln g(r_{12}) = -kT \ln g(r_{12}),\]

(429)

since \(g(\infty) = 1\).

Finally, note that

\[w(r) = kT \ln \frac{Z(r_{12} = \infty)}{Z(r_{12} = r)} = -(A(r_{12} = \infty) - A(r_{12} = r)),\]

(430)

where \(Z(r_{12} = r)\) and \(A(r_{12} = r)\) are the canonical partition function and the Helmholtz free energy of the system, subject to the constraint of fixed relative distance \(r_{12} = r\) between particles 1 and 2.

42 Thermodynamic Properties of Fluids

The goal of this section is to show that the thermodynamic properties of fluids (e.g., the internal energy, the virial coefficient, etc.) can be computed in terms of the corresponding properties of an
ideal gas plus a correction term that is determined by the radial distribution function of the fluid. This is illustrated by computing the internal energy of a classical fluid. The ensemble average of the internal energy $E$ is

$$
\langle E \rangle = \langle K(p^N) \rangle + \langle V(r^N) \rangle,
$$

where $K(p^N)$ is the total kinetic energy. The simplest model for the potential energy $V(r^N)$ is the pairwise additive potential

$$
V(r^N) = \sum_i \sum_{j<i} u(|r_i - r_j|),
$$

where $u(r)$ is, for example, a Lennard-Jones potential

$$
u(r) = 4\epsilon\left[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6\right],
$$

represented by the following diagram:

According to Eq. (432),

$$
\langle E \rangle = N\left(\frac{p^2}{2m}\right) + \sum_{j=1}^{N} \sum_{k\neq j} \frac{1}{2} \langle u(|r_j - r_k|) \rangle,
$$

therefore,

$$
\langle E \rangle = N^3 kT + \int dr_1 \int dr_2 u(|r_1 - r_2|) \frac{N(N-1)}{2} \int dr^N e^{-\beta V(r^N)}.
$$

Eq. (435) can be simplified, according to Eqs. (418) and (419), as follows:

$$
\langle E \rangle = \frac{3}{2} NkT + \frac{1}{2} \int dr_1 \int dr_2 u(|r_1 - r_2|) \rho^{2/N}(r_1, r_2),
$$
or

\[
\langle E \rangle = \frac{3}{2} NkT + \frac{V\rho^2}{2} \int dr u(r) g(r).
\] (437)

Therefore, the ensemble average internal energy per particle

\[
\frac{\langle E \rangle}{N} = \frac{3}{2} kT + \frac{\rho}{2} \int dr u(r) g(r),
\] (438)

is the sum of the internal energy per particle in an ideal gas (i.e., 3/2 k T) plus a correction term that can be obtained in terms of the radial distribution function \(g(r)\).

43 Solvation Free Energy: Thermodynamic Integration

The goal of this section is to show how to compute the free energy of solvation of structureless solute particles \(A\) dissolved in a solvent \(S\). The solvation free energy is computed according to the coupling parameter method in terms of the pair correlation function \(g(r_A, r_S)\), where \(r_A\) and \(r_S\) are the coordinates of the solute and solvent molecules, respectively.

Consider a solute-solvent mixture where solute particles with no internal structure interact with solvent molecules according to a pairwise additive potential \(V_{AS}\). Assume that the solute concentration is so low that the interactions between solute particles can be neglected. The canonical partition function of the system is

\[
Z_\lambda = \frac{Z_A^{(id)} Z_S^{(id)}}{V N_A + N_S} \int dr_A e^{-\beta V_S(r_N \rho^S)} \int dr_S e^{-\beta V_A(r_N \rho_A)} e^{-\beta V_{SA}(r_N \rho_A, r_N \rho_S)} \lambda,
\] (439)

where the coupling parameter \(\lambda = 1\) and where

\[
Z^{(id)} = \frac{1}{h^{3N} N!} \int dr_A e^{-\beta \frac{\rho_A^2}{2m}} = \frac{V^N}{N! h^{3N} \int dp e^{-\beta \frac{p^2}{2m}}}. \] (440)

In the absence of solute-solvent interactions (i.e., \(\lambda = 0\)), the energy of the system becomes factorizable into the solute and the solvent contributions to the total energy and the free energy of the system is \(A^{(id)}(N_S, N_A, V, T) = -\beta^{-1}\ln Z_\lambda=0\). The change in free energy due to a differential change in \(\lambda\) is

\[
-kT \frac{d\ln Z_\lambda}{d\lambda} = -kT \frac{\int dr_A e^{-\beta V_S(r_N \rho^S)} \int dr_S e^{-\beta V_A(r_N \rho_A)} \lambda}{\int dr_A e^{-\beta V_S(r_N \rho^S)} \int dr_S e^{-\beta V_A(r_N \rho_A)} \lambda}. \] (441)

and assuming that

\[
V_{SA}(r_N \rho_S, r_N \rho_A) = \sum_{j=1}^{N_A} \sum_{k=1}^{N_S} u_{AS}(|r_j - r_k|), \] (442)

we obtain

\[
-kT \frac{d\ln Z_\lambda}{d\lambda} = N_A N_S \int dr_A (A_1) \int dr_S (S_1) u_{AS}(|r_A - r_S|) \int dr_{N_A} \int dr_{N_S} e^{-\beta V_{SA}}. \] (443)
Introducing the pair correlation function $g_{AS} = \rho_{AS}/(\rho_A \rho_B)$, where $\rho_{AS}$ is the joint probability of finding a solute particle at $r_{A1}$ and a solvent molecule at $r_{S1}$,

$$\rho_{AS} = N_A N_S \int dr_{A1} \int dr_{S1} e^{-\beta V_S - \beta V_{SA}} \frac{1}{\int dr_{A} \int dr_{S} e^{-\beta V_S - \beta V_{SA}}} ,$$  (444)

we obtain

$$-kT \frac{d \ln Z_{\lambda}}{d \lambda} = \int dr_{A1} \int dr_{S1} u(|r_{A1} - r_{S1}|) \rho_A \rho_S g_{AS},$$  (445)

or

$$-kT \frac{d \ln Z_{\lambda}}{d \lambda} = \rho_A \rho_S V \int dr_{AS} \rho_{AS} g_{AS}. $$  (446)

Therefore, the change in free energy due to a differential change in the coupling parameter $\lambda$ is

$$-kT \frac{d \ln Z_{\lambda}}{d \lambda} = N_A \int dr_{AS} \rho_{AS} g_{AS},$$  (447)

and the total free energy of the system is

$$A(N_S, N_A, V, T) = A(id)(N_S, N_A, V, T) + (\Delta A)_{solv},$$  (448)

where the free energy of solvation $(\Delta A)_{solv}$ is,

$$(\Delta A)_{solv} = N_A \int_0^1 d \lambda \int dr_{AS} \rho_{AS} g_{AS}^{(\lambda)}(r).$$  (449)

The approach implemented in this section, where a coupling parameter is introduced to investigate the contributions of specific interactions to an ensemble average, is called coupling parameter method.

### 43.1 Zwanzig Equation

The goal of this subsection is to show that the free energy change due to a change in the coupling parameter $\lambda$ can be computed according the equation that Zwanzig derived here at Yale, *J. Chem. Phys.* 22 1420-1426 (1954), as follows:

$$A(\lambda_2) - A(\lambda_1) = -\beta^{-1} \ln \langle e^{-\beta [E(\lambda_2) - E(\lambda_1)]} \rangle_\beta, $$  (450)

where $\langle \cdots \rangle_\beta$ indicates the ensemble average at temperature $T = \beta^{-1}/k$.

Considering that

$$A(\lambda, \beta) = -\beta^{-1} \ln Z(\lambda, \beta),$$  (451)

where $Z(\lambda, \beta) = \sum_j \exp(-\beta E_j(\lambda))$, we obtain:

$$\frac{Z(\lambda_2, \beta_2)}{Z(\lambda_1, \beta_1)} = \frac{1}{Z(\lambda_1, \beta_1)} \sum_j e^{-[\beta_2 E_j(\lambda_2) - \beta_1 E_j(\lambda_1)]} e^{-\beta_1 E_j(\lambda_1)}, $$  (452)

$$= \langle e^{-[\beta_2 E(\lambda_2) - \beta_1 E(\lambda_1)]} \rangle_{\beta_1}.$$
From (452), we obtain:

\[- \beta_2 A(\lambda_2, \beta_2) - \beta_1 A(\lambda_1, \beta_1) = \ln \langle e^{-[\beta_2 E(\lambda_2) - \beta_1 E(\lambda_1)]} \rangle_{\beta_1} \] (453)

When \( \beta_1 = \beta_2 = \beta \), Eq. (453) is identical to Eq. (450).

In addition, when \( \lambda_1 = \lambda_2 \), we obtain that the change in free energy per unit temperature due to a change in temperature from \( T_1 = \beta^{-1}_1 / k \) to \( T_2 = \beta^{-1}_2 / k \) is

\[ \beta_2 A(\lambda, \beta_2) - \beta_1 A(\lambda, \beta_1) = -\ln \langle e^{-[\beta_2 E(\lambda) - \beta_1 E(\lambda)]} \rangle_{\beta_1} \] (454)

which is computed as the ensemble average of \( e^{-[\beta_2 - \beta_1]E} \) at the temperature defined by \( \beta_1 \), as indicated in Problem 6.6 of the textbook.

Other properties could also be computed by thermodynamic integration, analogously, as implemented above for free energy calculations. As an example, consider the ensemble average of property \( \hat{N} \):

\[ \langle N(\lambda_1, \beta_1) \rangle = \frac{\sum_j N_j e^{-\beta_1 E(\lambda_1)}}{\sum_j e^{-\beta_1 E(\lambda_1)}} = \frac{\sum_j e^{-\beta_2 E(\lambda_2)} \sum_j N_j e^{-\beta_1 E(\lambda_1) + \beta_2 E(\lambda_2)} e^{-\beta_2 E(\lambda_2)}}{\sum_j e^{-\beta_2 E(\lambda_2)}} \] (455)

where

\[ \frac{\sum_j e^{-\beta_1 E(\lambda_1)}}{\sum_j e^{-\beta_2 E(\lambda_2)}} = \frac{\sum_j e^{-\beta_1 E(\lambda_1) + \beta_2 E(\lambda_2)} e^{-\beta_2 E(\lambda_2)}}{\sum_j e^{-\beta_2 E(\lambda_2)}} \] (456)

Therefore,

\[ \langle N(\lambda_1, \beta_1) \rangle = \frac{\sum_j p_j(\lambda_2, \beta_2) N_j e^{-\beta_1 E(\lambda_1) + \beta_2 E(\lambda_2)}}{\sum_j p_j(\lambda_2, \beta_2) e^{-\beta_1 E(\lambda_1) + \beta_2 E(\lambda_2)}} \] (457)
44 Quiz 3

Quiz 3 CHEM 430b/530b
Statistical Methods and Thermodynamics

Metropolis Monte Carlo
(25 points) Item 1a: Describe the implementation of a Metropolis Monte Carlo algorithm to generate an ensemble of configurations with probability distribution $P(\xi)$.

(25 points) Item 1b: Prove that the Metropolis Monte Carlo algorithm described in item (1a) evolves any arbitrary distribution of configurations toward the equilibrium distribution $P(\xi)$.

Classical Fluids
(25 points) Item 2a: Explain how to compute the radial distribution function $g(r)$ of liquid Ar, after having generated an ensemble of configurations of the system at thermal equilibrium.

(25 points) Item 2b: Derive an expression for the internal energy of liquid argon in terms of the radial distribution function $g(r)$.

Solution:
Item 1a:
Read the description of the Metropolis Monte Carlo algorithm on page 74 of the lecture notes.

Item 1b:
Read the proof of the Metropolis Monte Carlo algorithm described on pages 75 and 76 of the lecture notes.

Item 2a:
The number of particles at a distance between $r$ and $r+dr$ from any particle in the fluid is

$$N(r) = \rho g(r)4\pi r^2 dr. \quad (458)$$

Therefore, the calculation of $g(r)$ involves averaging the number of particles at a distance between $r$ and $r + dr$ from any particle in the system and dividing that number by the element of volume $4\pi r^2 dr$.

Item 2b:
See derivation of Eq. (438) of the lecture notes.

45 Lars Onsager’s Regression Hypothesis

The goal of this section is to introduce Lars Onsager’s regression hypothesis, a consequence of the fluctuation-dissipation theorem proved by Callen and Welton in 1951. Here, we derive the regression hypothesis from the principles of statistical mechanics.
The regression hypothesis states that \textit{the regression of microscopic thermal fluctuations at equilibrium follows the macroscopic law of relaxation of small non-equilibrium disturbances} (L. Onsager, \textit{Phys. Rev.} \textbf{37}, 405 (1931); \textbf{38}, 2265 (1931)).

To understand this hypothesis, consider an observable $A$ for a system at thermal equilibrium. Such property fluctuates in time with \textit{spontaneous microscopic fluctuations}

$$\delta A(t) = A(t) - \langle A \rangle. \tag{459}$$

Here, $A(t)$ is the instantaneous value of the observable and $\langle A \rangle$ is the equilibrium ensemble average

$$\langle A \rangle = \frac{\text{Tr}\{A(t)e^{-\beta H_0}\}}{\text{Tr}\{e^{-\beta H_0}\}}. \tag{460}$$

The average correlation between $\delta A(t)$ and an instantaneous fluctuation at time zero $\delta A(0)$ is described by the correlation function

$$C(t) = \langle \delta A(t) \delta A(0) \rangle = \langle A(t)A(0) \rangle - \langle A \rangle^2, \tag{461}$$

where $\langle \rangle$ represents the \textit{equilibrium ensemble average}. Note that at small times, instantaneous fluctuations are correlated and therefore,

$$\lim_{t \to 0} C(t) = \langle (\delta A(0))^2 \rangle, \tag{462}$$

has a finite value. However, at large times $C(t)$ vanishes, i.e.,

$$\lim_{t \to \infty} C(t) = 0, \tag{463}$$

since $\delta A(t)$ becomes uncorrelated to $\delta A(0)$. This decay of correlations is the \textit{regression of microscopic thermal fluctuations} referred to in Onsager’s hypothesis. Therefore, Onsager’s regression hypothesis can be formulated as follows

$$\bar{A}(t) - \langle A \rangle \over A(0) - \langle A \rangle = \langle \delta A(t) \delta A(0) \rangle \over \langle (\delta A(0))^2 \rangle, \tag{464}$$

where $\bar{A}(t)$ describes the \textit{macroscopic relaxation} of the observable towards its equilibrium value $\langle A \rangle$, while the system evolves from an initial state that is not far from equilibrium to its final state in equilibrium with a thermal reservoir.

To derive Eq.\,(464) from the ensemble postulates of statistical mechanics, consider preparing the system in a state that is not far from equilibrium by applying to the system a weak perturbational field $f$ (e.g., an electric field) that couples to the dynamical variable $A(t)$ (e.g., the instantaneous total dipole moment). The external field is assumed to be so weak that the perturbation Hamiltonian $\Delta H$, written as an expansion in powers of $f$, can be approximated to be first order in the field as follows,

$$\Delta H = -fA(0). \tag{465}$$
Assume that such perturbational field was applied until the system equilibrated according to total Hamiltonian

$$H = H_0 + \Delta H,$$

(466)

The macroscopic relaxation of the system is analyzed by switching off the external perturbational field and computing the evolution of the non-equilibrium ensemble average

$$A(t) = \text{Tr}\left\{ A(t) e^{-\beta(H_0 + \Delta H)} \right\} / \text{Tr}\left\{ e^{-\beta(H_0 + \Delta H)} \right\},$$

(467)

as the system evolves towards equilibrium. Since the perturbation $\Delta H$ is small, we can introduce the approximation

$$e^{-\beta(H_0 + \Delta H)} \approx e^{-\beta H_0} (1 - \beta \Delta H).$$

(468)

Substituting Eq. (468) into Eq. (467), we obtain

$$A(t) \approx \text{Tr}\left\{ e^{-\beta H_0} (1 - \beta \Delta H + ...) A(t) e^{-\beta H_0} \right\} / \text{Tr}\left\{ e^{-\beta H_0} \right\} = \frac{\text{Tr}\left\{ e^{-\beta H_0} A(t) \right\} - \beta \text{Tr}\left\{ e^{-\beta H_0} \Delta H A(t) \right\}}{\text{Tr}\left\{ e^{-\beta H_0} \right\} - \beta \text{Tr}\left\{ e^{-\beta H_0} \Delta H \right\}},$$

(469)

or

$$A(t) \approx \frac{\text{Tr}\left\{ e^{-\beta H_0} A(t) \right\}}{\text{Tr}\left\{ e^{-\beta H_0} \right\} (1 - \beta \Delta H + ...)} = \frac{\text{Tr}\left\{ e^{-\beta H_0} \Delta H A(t) \right\}}{\text{Tr}\left\{ e^{-\beta H_0} \right\} (1 - \beta \Delta H)},$$

(470)

which gives

$$A(t) \approx \frac{\langle A(t) \rangle}{1 - \beta \langle \Delta H \rangle} - \beta \frac{\langle \Delta H A(t) \rangle}{1 - \beta \langle \Delta H \rangle}.$$  

(471)

Introducing the approximation

$$1/(1 - x) \approx 1 + x,$$

(472)

for small $x$, in Eq. (471), we obtain

$$A(t) \approx \langle A \rangle - \beta \langle \Delta H A(t) \rangle + \beta \langle \Delta H \rangle \langle A \rangle - \beta \langle \Delta H A(t) \rangle.$$  

(473)

Therefore, according to Eq. (473),

$$A(t) \approx \langle A \rangle - \beta \langle \Delta H A(t) \rangle + \beta \langle \Delta H \rangle \langle A \rangle + O((\Delta H)^2).$$  

(474)

Substituting Eq. (465) into Eq. (474) and keeping only the terms that are first order in $\Delta H$ we obtain,

$$A(0) - \langle A \rangle \approx f \beta (\langle A(0) \rangle^2 - \langle A(0) \rangle^2),$$

(475)

and

$$A(t) - \langle A \rangle \approx f \beta (\langle A(0) A(t) \rangle - \langle A(0) \rangle \langle A(t) \rangle).$$

(476)

Finally, Eqs. (475) and (476) complete the derivation of Eq. (463) in terms of the ensemble average postulates of statistical mechanics, since according to Eq. (459),

$$\langle \delta A(t) \delta A(0) \rangle = \langle A(t) A(0) \rangle - \langle A \rangle^2.$$  

(477)
45.1 Response Function: Generalized Susceptibility

The goal of this section is to introduce the concept of response function $\chi(t,t')$, or generalized susceptibility, for the description of non-equilibrium disturbances. According to Eqs. (476) and (477), the response to a perturbation $\Delta H$ in the linear regime (i.e., a perturbation that is linear in the field $f$) is

$$\Delta A(t, f) \approx f \beta \langle \delta A(t) \delta A(0) \rangle,$$

(478)

where $\Delta A(t, f) = \bar{A}(t) - \langle A \rangle$. Therefore,

$$\Delta A(t, \lambda f) = \lambda \Delta A(t, f).$$

(479)

The most general expression for a macroscopic response that is consistent with Eq. (479) is

$$\Delta A(t, f) = \int_{-\infty}^{\infty} dt' \chi(t, t') f(t') = \sum_j \chi(t, t_j) f(t_j) dt_j,$$

(480)

where $dt_j = (t_{j+1} - t_j)$ is the time increment, $f(t)$ is the external perturbational field and $\chi(t, t')$ is the response function. Note that the name response function is due to the fact that $\chi(t, t_0)$ is equal to the response at time $t$ when the perturbational field is an impulse at time $t_0$ (i.e., $\chi(t, t_0) = \Delta A(t, \delta(t - t_0))$). In addition, any other perturbational field can always be written as a linear superposition of impulses since any function can be expanded as a linear combination of delta functions.

Another important observation is that according to Eq. (480),

$$\chi(t, t_j) = \frac{\partial \Delta \bar{A}(t)}{\partial f(t_j)},$$

(481)

Therefore, $\chi(t, t_j)$ defines the first nonvanishing term in an expansion of $\Delta A(t, f)$ in powers of $f(t)$. The response function $\chi(t, t')$ is thus also called generalized susceptibility, since the electric susceptibility $\chi_e$ defines the first nonvanishing term in an expansion of the polarization $\vec{P}$ (i.e., the total electric dipole moment per unit volume) in powers of the electric field $\vec{E}$ as follows,

$$\vec{P} = \chi_e \vec{E}.$$

(482)

In analogy to the electric susceptibility $\chi_e$, that is a property of the unperturbed system, the response function $\chi(t, t_j)$ is a function of the unperturbed system at equilibrium. To show this important aspect of the response function, consider that the perturbational field represented by the following diagram:
which is defined as follows:

\[
    f(t) = \begin{cases} 
        f, & \text{when } t \leq 0, \\
        0, & \text{otherwise}.
    \end{cases}
\]  
(483)

The response at time \( t > 0 \) is

\[
    \Delta A(t) = f \int_{-\infty}^{0} dt' \chi(t - t') = -f \int_{\infty}^{t} dt'' \chi(t''),
\]  
(484)

where \( t'' = t - t', dt'' = -dt' \) and we have assumed that \( \chi(t, t') = \chi(t - t') \). Therefore,

\[
    \frac{d\Delta A(t)}{dt} = -f \chi(t),
\]  
(485)

since, according to the second fundamental theorem of calculus,

\[
    \chi(t) = \frac{d}{dt} \int_{a}^{t} dt' \chi(t'),
\]  
(486)

where \( a \) is an arbitrary constant value. Substituting Eq. (478) into Eq. (485), we obtain

\[
    \chi(t) = -\beta \frac{d}{dt} \langle \delta A(0) \delta A(t) \rangle,
\]  
(487)

where \( t > 0 \).

### 45.2 Linear Spectroscopy

The goal of this section is to show that the linear absorption spectrum \( \sigma(\omega) \) of a system is determined by the regression of spontaneous polarization fluctuations at equilibrium as follows:

\[
    \sigma(\omega) = 2\omega f_0^2 \varepsilon^2 \int_{0}^{\infty} \chi(t') \sin(\omega t') dt',
\]  
(488)

\[
    = \beta 2\omega^2 f_0^2 \varepsilon^2 \int_{0}^{\infty} \langle \delta A(0) \delta A(t') \rangle \cos(\omega t') dt',
\]  

where \( A(t) \) is the time-dependent polarization

\[
    A(t) = \sum_j p_j \langle \phi_j(t) \mid \hat{A} \mid \phi_j(t) \rangle,
\]  
(489)

where the functions \( \phi_j(t) \) evolve according to the unperturbed system Hamiltonian \( H_0 \), as follows:

\[
    i\hbar \frac{\partial}{\partial t} \phi_j(t) = \hat{H}_0 \phi_j(t).
\]  
(490)
To derive Eq. (488), consider that the system is perturbed by a monochromatic electric field,

$$ f(t) = f_0 \bar{\varepsilon} (e^{-i\omega t} + e^{i\omega t}), $$

where $f_0$ is the amplitude of the field and $\bar{\varepsilon}$ is the unit vector along the spatially uniform electric field. In the linear regime, the interaction between the system and the field is

$$ \Delta \hat{H}(t) = -f(t) \hat{A}. $$

The total energy of the system is

$$ E(t) = \sum_j p_j \langle \phi_j(t) | \hat{H}_0 + \Delta \hat{H}(t) | \phi_j(t) \rangle, $$

and the differential change of energy per unit time is

$$ \dot{E}(t) = \sum_j p_j \langle \phi_j(t) | \frac{\partial \Delta \hat{H}(t)}{\partial t} | \phi_j(t) \rangle = -\dot{f}(t) \dot{A}(t), $$

since,

$$ \langle \frac{\partial \phi_j(t)}{\partial t} | \hat{H}_0 + \Delta \hat{H}(t) | \phi_j(t) \rangle = -\langle \phi_j(t) | \hat{H}_0 + \Delta \hat{H}(t) | \frac{\partial \phi_j(t)}{\partial t} \rangle. $$

Equation (495) can be proved by considering that $i\hbar \langle \dot{\phi}_j \rangle = \hat{H}_0 | \phi_j \rangle$ and, therefore, $i\hbar \langle \phi_j | \hat{H} | \phi_j \rangle = \langle \phi_j | \hat{H} \hat{H}_0 | \phi_j \rangle$, and conjugating both sides of this equality gives $-i\hbar \langle \phi_j | \hat{H} | \dot{\phi}_j \rangle = \langle \phi_j | \hat{H} \hat{H}_0 | \phi_j \rangle$ and therefore $\langle \dot{\phi}_j | \hat{H} | \phi_j \rangle = -\langle \phi_j | \hat{H} | \phi_j \rangle$.

Therefore, the total energy change $\sigma$ due to the interaction with the external field for time $T$ is

$$ \sigma = \frac{1}{T} \int_0^T dt (-\dot{f}(t)) \dot{A}(t), $$

where, according to Eq. (491),

$$ \dot{f}(t) = -if_0 \bar{\varepsilon} \omega [e^{-i\omega t} - e^{+i\omega t}]. $$

Substituting Eq. (497) into Eq. (496) we obtain,

$$ \sigma = -i\omega \int_0^T f_0 \bar{\varepsilon} [e^{+i\omega t} - e^{-i\omega t}] \left( \langle \hat{A} \rangle + \int_{-\infty}^{\infty} \chi(t-t') f(t') dt' \right). $$

Note that

$$ \int_{-\infty}^{\infty} \chi(t-t') f(t') dt' = \int_{-\infty}^{\infty} \chi(-t') f(-t'-t) dt' = \int_{-\infty}^{\infty} \chi(t') f(-t'-t) dt', $$

thus Eq. (498) becomes

$$ \sigma = -i\omega \int_0^T dt f_0 \bar{\varepsilon} [e^{+i\omega t} - e^{-i\omega t}] \left( \langle \hat{A} \rangle + \int_{-\infty}^{\infty} \chi(t') f(-t'-t) dt' \right). $$

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To simplify Eq. (500), we note that
\[
\lim_{T \to \infty} \frac{1}{T} \int_0^T e^{i\omega t'} dt' = \begin{cases} 1, & \text{when } n=0 \\ 0, & \text{otherwise.} \end{cases}
\] (501)

Therefore, Eq. (500) becomes
\[
\sigma = -\frac{i\omega}{T} \int_0^T dt' f_0 \bar{\varepsilon} [e^{i\omega t'} - e^{-i\omega t'}] \int_{-\infty}^{\infty} \chi(t') f_0 \bar{\varepsilon} [e^{i\omega(t+t')} + e^{-i\omega(t+t')}] dt',
\] (502)
or
\[
\sigma = -i\omega f_0^2 \bar{\varepsilon}^2 \int_{-\infty}^{\infty} \chi(t') [e^{i\omega t'} - e^{-i\omega t'}] dt',
\] (503)

Therefore,
\[
\sigma = 2\omega f_0^2 \bar{\varepsilon}^2 \int_{-\infty}^{\infty} \chi(t') \sin(\omega t') dt'.
\] (504)

Substituting Eq. (487) into Eq. (504) we obtain
\[
\sigma = -\beta 2\omega f_0^2 \bar{\varepsilon}^2 \int_0^\infty \frac{d}{dt} <\delta A(0)\delta A(t')> \sin(\omega t') dt'.
\] (505)

Finally, integrating Eq. (505) by parts we obtain Eq. (488), since Eq. (505) can be written as
\[
\int dt' u(t') dv/dt' = u(t')v(t') - \int dt' v(t') du/dt',
\]
with \(u(t') = \sin(\omega t')\) and \(v(t') = <\delta A(0)\delta A(t')>\).

### 46 Langevin Equation

In previous sections we have shown how to implement the regression hypothesis to describe the dissipation of macroscopic disturbances in terms of the regression of spontaneous fluctuations. As an example, we have analyzed the relaxation of a polarization disturbance \(A(t) - \langle A \rangle\), in the linear regime, in terms of the regression of spontaneous polarization fluctuations \(\langle \delta(t)\delta A(0) \rangle\). The goal of this section is to describe another application of this general theoretical approach to relate the fluctuations of a physical quantity with the dissipation of a macroscopic disturbance.

Consider the motion of a particle through a medium after being initially prepared in a certain state of motion (e.g., after being pushed by an external force). As a result of friction with the medium, the particle will be slowed down (i.e., its initial kinetic energy will be dissipated by heating up the medium). The motion of such particle is described by the generalized Langevin equation, which is derived in this section as follows.

Consider the Hamiltonian that describes a particle with coordinates \(x(t)\), linearly coupled to the bath coordinates \(y_j(t)\),
\[
H = \frac{m x^2}{2} + V(x) + H_b - \sum_j c_j y_j(t)x(t),
\] (506)
where $c_j$ are the coupling constants that linearly couple $x(t)$ and $y_j(t)$. The terms $V(x)$ and $H_b$, introduced by Eq. (506), describe the interactions among system coordinates and among bath coordinates, respectively.

The total force acting on the particle is

$$F(t) = -\frac{\partial V}{\partial x} + f(t), \quad (507)$$

where the fluctuating force $f(t)$ can be readily identified from Eq. (506),

$$f(t) = \sum_j c_j y_j(t). \quad (508)$$

Note that the motion of $y_j(t)$ depends on $x(t)$ since, according to Eq. (506), the force acting on $y_j(t)$ is $f_j = -\partial H/\partial y_j = -\partial H_b/\partial y_j + c_j x(t)$. Therefore, $f(t)$ is also a function of $x(t)$. Assuming that $f(t)$ is linear in $x(t)$,

$$f(t) = f_b(t) + \int_{-\infty}^{\infty} dt' \chi_b(t-t') x(t'), \quad (509)$$

where, according to Eq. (487),

$$\chi_b(t-t') = \begin{cases} -\beta \frac{dC_b(t-t')}{d(t-t')} , & \text{when } t > t' , \\ 0 , & \text{otherwise} , \end{cases} \quad (510)$$

with

$$C_b(t) = \langle \delta f(0) \delta f(t) \rangle . \quad (511)$$

Therefore, the equation of motion for the particle is

$$m \ddot{x} = -\frac{dV}{dx} + f_b(t) + \int_{-\infty}^{t} dt' (\beta \frac{dC_b(t-t')}{d(t-t')} - x(t')). \quad (512)$$

Changing the integration variable $t'$ to $t'' = t - t'$, in Eq. (512), we obtain

$$m \ddot{x} = -\frac{dV}{dx} + f_b(t) - \int_{t}^{0} dt'' (\beta \frac{dC_b(t''-t)}{dt''} - x(t-t'')), \quad (513)$$

where the lower integration limit includes only values of $x(t-t'')$ with $(t-t'') > 0$. Integrating Eq. (513) by parts, we obtain

$$m \ddot{x} = -\frac{dV}{dx} + f_b(t) - [x(t-t'') \beta C_b(t'')]_{t''=0}^{t''=t} + \int_{t}^{0} dt'' (\beta C_b(t'') \frac{\partial x(t-t'')}{\partial t''}). \quad (514)$$

Changing the integration variable $t''$ to $t' = t - t''$, in Eq. (514), we obtain

$$m \ddot{x} = -\frac{dV}{dx} + f_b(t) + [x(0) \beta C_b(t) - x(t) \beta C_b(0)] - \int_{0}^{t} \beta C_b(t-t') \dot{x}(t') dt'. \quad (515)$$

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Eq. (515) is the Generalized Langevin Equation, which can be written in terms of the potential of mean force

\[ \nabla(x) \equiv V(x) + \frac{1}{2} x^2 \beta \bar{C}_b(0), \]  

(516)

and the fluctuating force

\[ \bar{F}(t) \equiv f_b(t) + \chi(0) \beta \bar{C}_b(t), \]  

(517)

as follows,

\[
\begin{align*}
    m \ddot{x} &= -\frac{\partial V}{\partial x} + \bar{F}(t) - \int_0^t \beta \bar{C}_b(t-t') \dot{x}(t') dt', \\
    &\text{where the third term on the r.h.s. of Eq. (518) is the generalized frictional force, a force that is linear in the velocity. The connection between the frictional force and the regression of thermal fluctuations of } f(t), \text{ introduced by Eq. (518), is known as the second fluctuation-dissipation theorem.}
\end{align*}
\]

Note (Laplace transform method): Equation (518) can be used to obtain the equation of motion for the correlation function \( c(t) = \langle x(t)x(0) \rangle \) when \( V(x) = \frac{1}{2} m \omega^2 x^2 \). Multiplying Eq. (518) by \( x(0) \) and computing the ensemble average to obtain:

\[
m \ddot{c}(t) = -m \bar{\omega}^2 c(t) - \int_0^t dt' \beta \bar{C}_b(t-t') \dot{c}(t'), 
\]

(519)

where \( \bar{\omega}^2 = \omega^2 + \beta \bar{C}_b(0)/m \), since \( \langle \bar{F}(t)x(0) \rangle = 0 \).

To solve Eq. (519) and find \( c(t) \), we implement the Laplace transform method, as follows. We compute the Laplace transform of both sides of Eq. (519) to obtain,

\[
m \int_0^\infty dt e^{-st} \frac{d^2}{dt^2} c(t) = -m \bar{\omega}^2 \int_0^\infty dt e^{-st} c(t) - \int_0^\infty dt e^{-st} \int_0^t dt' \beta \bar{C}_b(t-t') \frac{d}{dt'} \dot{c}(t'). 
\]

(520)

Integrating by parts, we obtain:

\[
\int_0^\infty dt e^{-st} \dot{c}(t) = c(t)e^{-st}|_0^\infty + s \int_0^\infty dt e^{-st} c(t), 
\]

(521)

\[
= -\langle x(0)^2 \rangle + s \bar{c}(s),
\]

with \( \bar{c}(s) = \int_0^\infty dt e^{-st} c(t) \) since \( c(0) = \langle x(0)^2 \rangle \). In addition,

\[
\int_0^\infty dt e^{-st} \frac{d^2}{dt^2} \langle x(0)x(t) \rangle = \langle x(0) \dot{x}(t) \rangle e^{-st}|_0^\infty + s \int_0^\infty dt e^{-st} \dot{c}(t), 
\]

(522)

\[
= s(-\langle x(0)^2 \rangle + s \bar{c}(s)),
\]

since \( \langle x(0) \dot{x}(0) \rangle = 0 \).
Substituting into Eq. (520), we obtain:

\[ ms(-\langle x(0)^2 \rangle + s\tilde{c}(s)) = -m\bar{\omega}^2\tilde{c}(s) - \beta \int_0^\infty dt e^{-st} \int_0^t dt' C_b(t-t')\dot{c}(t'), \]

\[ = -m\bar{\omega}^2\tilde{c}(s) - \beta \int_0^\infty dt' \dot{c}(t') \int_{t'}^\infty dt e^{-st} C_b(t-t'), \]

\[ = -m\bar{\omega}^2\tilde{c}(s) - \beta \int_0^\infty dt' e^{-st} \dot{c}(t') \int_0^\infty dt'' e^{-st''} C_b(t''), \]

\[ = -m\bar{\omega}^2\tilde{c}(s) - \beta(-\langle x(0)^2 \rangle + s\tilde{c}(s))\tilde{C}_b(s). \]

(523)

Distributing and solving for \( \tilde{c}(s) \), we obtain:

\[ -ms\langle x(0)^2 \rangle + ms^2\tilde{c}(s) = -m\bar{\omega}^2\tilde{c}(s) - \beta s\tilde{C}_b(s)\tilde{c}(s) + \beta \langle x(0)^2 \rangle\tilde{C}_b(s), \]

(524)

and

\[ \tilde{c}(s) = \langle x^2 \rangle \frac{s + \beta\tilde{C}_b(s)/m}{s^2 + \bar{\omega}^2 + \beta s\tilde{C}_b(s)/m}, \]

(525)

giving \( c(t) \) according to the inverse Laplace transform \( c(t) = \int_0^\infty dse^{st}\tilde{c}(s). \)

**Markovian Approximation**

Changing the iteration variable \( t' \), in Eq. (518), to \( t'' = t - t' \) and considering a time \( t \) much larger than the relaxation time scale for the correlation function \( C_b \) (so that \( C_b(t) = 0 \) and \( \partial x(t-t'')/\partial(t-t'') \approx \partial x(t)/\partial t \)), we obtain

\[ m\ddot{x} = -\frac{\partial V}{\partial x} + f_b(t) - \beta \int_0^\infty C_b(t'')\dot{x}(t')dt''. \]

(526)

Note that Eq. (526) becomes the traditional Langevin Equation,

\[ m\ddot{x} = f_b(t) - \gamma \dot{x}(t), \]

(527)

when \(-\partial V/\partial x = 0\). The friction coefficient \( \gamma \) is, therefore, determined by the regression of spontaneous thermal fluctuations as follows

\[ \gamma = \beta \int_0^\infty C_b(t'')dt''. \]

(528)

The approximation implemented to obtain Eq. (526) involves considering that the relaxation time for fluctuating forces in the bath is much shorter than the time over which one observes the particle. Such approximation removes the “memory effects” from the equation of motion (note that Eq. (526) does not involve the nonlocality in time introduced by the time integral in Eq. (518)). This approximation is thus called Markovian approximation since it makes the instantaneous force independent of the state of the particle at any previous time.

Note that, according to Eq. (527),

\[ m\langle \dot{v} \rangle = -\gamma \langle v(t) \rangle, \]

(529)
where \( \mathbf{v} = \dot{x} \), since \( \langle f(t) \rangle = 0 \). The solution to Eq. (529) is,
\[
\langle \mathbf{v}(t) \rangle = \langle \mathbf{v}(0) \rangle \exp(-\gamma t/m).
\] (530)

Eq. (530) indicates that the average initial momentum of the particle is dissipated into the bath at an exponential rate (i.e., the average velocity vanishes at an exponential rate). However, it is important to note that the condition \( \langle \mathbf{v}(t) \rangle = 0 \) at \( t >> m/\gamma \) (e.g., at equilibrium) does not imply that the particle is at rest! At equilibrium, the fluctuating force \( f_b(t) \) keeps buffeting the particle and the distribution of velocities is given by the Boltzmann distribution (see Eq. (413)). The average squared velocity for the particle is
\[
\langle \mathbf{v}^2 \rangle = \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z (v_x^2 + v_y^2 + v_z^2) \exp(-\beta m(v_x^2 + v_y^2 + v_z^2)/2) = \frac{3kT}{m},
\] (531)
and the velocity autocorrelation function is
\[
\langle \mathbf{v}(t)\mathbf{v}(0) \rangle = \langle \mathbf{v}(0)\mathbf{v}(0) \rangle \exp(-\gamma t/m) = \frac{3kT}{m} \exp(-\gamma t/m),
\] (532)
since Eq. (529) is valid not only for the dynamical variable \( \mathbf{v}(t) \) but also for \( \mathbf{v}(t)\mathbf{v}(0) \).

The motion of the particle is called Brownian Motion, in honor to the botanist Robert Brown who observed it for the first time in his studies of pollen. In 1828 he wrote “the pollen become dispersed in water in a great number of small particles which were perceived to have an irregular swarming motion”. The theory of such motion, however, was derived by A. Einstein in 1905 when he wrote: “In this paper it will be shown that ... bodies of microscopically visible size suspended in a liquid perform movements of such magnitude that they can be easily observed in a microscope on account of the molecular motions of heat ...”

To compute the average mean squared displacement \( \langle \bar{x}^2 \rangle \) of the particle we substitute the variable \( \bar{x} = x(t) - x(0) \), we multiply both sides of Eq. (527) by such variable and we average over the ensemble distribution as follows,
\[
m \langle \bar{x} \frac{\partial \dot{\bar{x}}}{\partial t} \rangle = -\gamma \langle \bar{x}\dot{\bar{x}} \rangle,
\] (533)
since \( \langle \bar{x} f(t) \rangle = \langle \bar{x} \rangle \langle f(t) \rangle = 0 \). Eq. (533) is equivalent to
\[
m \langle \frac{\partial \bar{x}\dot{\bar{x}}}{\partial t} \rangle = -\gamma \langle \bar{x}\dot{\bar{x}} \rangle + m \langle \bar{x}^2 \rangle,
\] (534)
which, according to Eq. (531), gives
\[
m \frac{\partial \langle \bar{x}\dot{\bar{x}} \rangle}{\partial t} = -\gamma \langle \bar{x}\dot{\bar{x}} \rangle + 3kT.
\] (535)
The solution to Eq. (535) is
\[
\langle \bar{x}\dot{\bar{x}} \rangle = \frac{1}{2} \frac{\partial}{\partial t} \langle \bar{x}^2 \rangle = -\frac{3kT}{\gamma} (\exp(-\gamma t/m) - 1).
\] (536)
Therefore, the mean squared displacement is

\[
\langle \bar{x}^2 \rangle = -\frac{6kT}{\gamma} \left( -\frac{m}{\gamma} (\exp(-\gamma t/m) - 1) - t \right).
\] (537)

At short times (i.e., when \( \exp(-\gamma t/m) - 1 \approx -\gamma t/m + t^2/2 * \gamma^2/m^2 \)),

\[
\langle \bar{x}^2 \rangle = \frac{3kT}{m} t^2,
\] (538)

i.e., the mean squared displacement at short times is quadratic in time. This is the so-called ballistic regime, since it corresponds to ballistic motion (motion without collisions) for a particle with velocity equal to \( \sqrt{3kT/m} \).

At long times (i.e., when \( m/\gamma (\exp(-\gamma t/m) - 1) < < t \)),

\[
\langle \bar{x}^2 \rangle = \frac{6kT}{\gamma} t = 6Dt,
\] (539)

where the constant

\[
D = \frac{kT}{\gamma},
\] (540)

is the diffusion coefficient. Therefore, at long times the mean squared displacement is linear in time. This long time limit is the so-called diffusional regime.

The remaining of this section shows that the diffusion coefficient can be computed in terms of the velocity autocorrelation function \( \langle v(0)v(t) \rangle \) as follows:

\[
D = \frac{1}{3} \int_0^t dt' \langle v(0)v(t') \rangle.
\] (541)

Note that Eq. (540) can be readily obtained by substituting Eq. (532) into Eq. (541).

To prove Eq. (541), consider the particle displacement at time \( t \),

\[
\bar{x}(t) = \int_0^t dt' v(t'),
\] (542)

and compute the time derivative of the squared displacement as follows

\[
\frac{\partial}{\partial t} \bar{x}^2 = \frac{\partial}{\partial t} \left( \int_0^t dt' v(t') \right)^2,
\] (543)

which according to Eq. (486) gives,

\[
\frac{\partial}{\partial t} \langle \bar{x}^2 \rangle = 2 \int_0^t dt' \langle v(t)v(t') \rangle.
\] (544)
Changing integration variables from \( t' \) to \( t'' = t - t' \) we obtain
\[
\frac{\partial}{\partial t} \langle \bar{x}^2 \rangle = 2 \int_0^t dt'' \langle v(t)v(t - t'') \rangle = 2 \int_0^t dt'' \langle v(0)v(-t'') \rangle,
\]
(545)
since \( C(t' + t - t) = \langle v(t)v(t' + t) \rangle \) is equal to \( C(t' - 0) = \langle v(0)v(t') \rangle \). Finally, since \( C(t'') = C(-t'') \) we obtain
\[
\frac{\partial}{\partial t} \langle \bar{x}^2 \rangle = 2 \int_0^t dt'' \langle v(0)v(t'') \rangle,
\]
(546)
Eq. (541) is obtained by substituting Eq. (539) into the l.h.s. of Eq. (546).

47 Velocity Verlet Algorithm

The goal of this section is to introduce the velocity Verlet algorithm for molecular dynamics (MD) simulations and to show how to implement it to compute time-correlation functions (e.g., \( \langle v(t)v(0) \rangle \)) and transport coefficients (e.g., the diffusion coefficient \( D \)).

Consider the task of computing the diffusion coefficient according to Eq. (541). The quantity of interest is, therefore, the equilibrium ensemble average of the velocity autocorrelation function
\[
\langle v(0)v(t) \rangle = \text{Tr} \{ \rho (v(0)v(t)) \},
\]
(547)
The computation of \( \langle v(0)v(t) \rangle \) thus requires sampling initial conditions according to the ensemble distribution described by \( \rho \) and for each initial condition compute the value of the particle velocity \( v(t) \) at time \( t \).

The velocity Verlet algorithm (W. C. Swope, H. C. Andersen, P. H. Berens, and K. R. Wilson, J. Chem. Phys. 76, 637 (1982)) computes the particle velocity \( v(t + \tau) \) and position \( x(t + \tau) \) at time \( t+\tau \) as follows:
\[
\begin{align*}
x(t + \tau) &= x(t) + v(t)\tau + \frac{1}{2}\tau^2 \frac{f(t)}{m}, \\
v(t + \tau) &= v(t) + \frac{f(t) + f(t + \tau)}{2m} \tau,
\end{align*}
\]
(548)
where \( \tau \) is a small time increment, \( m \) is the particle mass and \( f(t) \) is the total force acting on the particle at time \( t \). Given the initial conditions \( x(0) \) and \( v(0) \) one can compute \( v(t) \) and \( x(t) \) simply by applying Eqs. (548) successively \( n \) times, with \( n = t/\tau \). Note that by implementing the algorithm one generates a phase space trajectory (i.e., a sequence of “snapshots” for the particle coordinates and velocities at all intermediate times \( t_j = j * \tau \) (with \( j=1,2,...,n) \)).

Molecular dynamics simulations thus provide the sequence of microscopic configurations through which the model system passes in time. Such detailed microscopic information allows one to compute the result of a measurement of an observable (i.e., an ensemble average) according to the time average introduced by Eq. (117) (i.e., simply by averaging the value of the observable through the whole manifold of microscopic configurations generated during the time of the measurement).

Therefore, another way of computing the ensemble average introduced by Eq. (547) is
\[
\langle v(0)v(t) \rangle = \frac{1}{T} \int_0^T dt' v(t')v(t' + t),
\]
(549)
where $T$ is the time of the measurement of the diffusion constant $D$, a time that is much larger than the relaxation time of the velocity autocorrelation function.

**Exercise:**
Compute the velocity autocorrelation function for a fluid of argon atoms using the program developed for computing the radial distribution function. (Hint: substitute the Metropolis Monte Carlo algorithm by the velocity Verlet algorithm).

### 48 Golden Rule

The goal of this section is to introduce the so-called *Fermi Golden Rule* expression, given by first-order time dependent perturbation theory.

We consider a system initially prepared in state $|i\rangle$. At time $t = 0$, we turn on the perturbation $\hat{W}(t)$ and we analyze the decay to the final state $|f\rangle$, as described by first order time-dependent perturbation theory:

$$c_f(t) = -i \frac{\hbar}{\mathcal{E}_f - \mathcal{E}_i} \int_0^t dt' \langle f | \hat{W}(t') | i \rangle e^{i(\mathcal{E}_f - \mathcal{E}_i)t'} .$$

(550)

Therefore, the probability of observing the system in the final state is

$$P_{fi}(t) = \frac{1}{\hbar^2} \int_0^t dt'' \int_0^t dt' \langle i | \hat{W}^*(t'') \rangle \langle f | \hat{W}(t') | i \rangle e^{i(\mathcal{E}_f - \mathcal{E}_i)(t' - t'')} .$$

(551)

#### 48.1 Monochromatic Plane Wave

Assuming that the perturbation involves a single frequency component, $\hat{W}(t') = \hat{A} e^{-i\omega t'}$, we obtain:

$$c_f(t) = \langle f | \hat{A} | i \rangle \frac{1 - e^{i(w_f - w)t}}{\hbar(w_f - \omega)} .$$

(552)

$$= -i \frac{\hbar}{t} \langle f | \hat{A} | i \rangle e^{i(w_f - w)t/2} \frac{\sin[(w_f - w)t/2]}{(w_f - \omega)t/2} .$$

Therefore, the probability of observing the system in the final state is

$$P_{fi}(t) = \frac{t^2}{\hbar^2} |\langle f | \hat{A} | i \rangle|^2 \frac{\sin^2[(w_f - w)t/2]}{[(w_f - \omega)t/2]^2} .$$

(553)

To compute the survival probability that the system remains in the initial state, we must add up the probability over all possible final states,

$$P(t) = 1 - \frac{t^2}{\hbar^2} \sum_f |\langle f | \hat{A} | i \rangle|^2 \frac{\sin^2[(w_f - w)t/2]}{[(w_f - \omega)t/2]^2} .$$

(554)
If the very short time limit, \( P(t) = \exp(-\alpha t^2) \approx 1 - \alpha t^2 + \cdots \), where
\[
\alpha = \lim_{t \to 0} \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dE_f |\langle f | \hat{A} | i \rangle|^2 \rho(E_f) \frac{\sin^2[(E_f - E_i - \hbar \omega)t/(2\hbar)]}{[(E_f - E_i - \hbar \omega)t/(2\hbar)]^2},
\]
(555)

\[
= \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dE_f |\langle f | \hat{A} | i \rangle|^2 \rho(E_f),
\]

In the longer time limit, the kernel of Eq. (554) is approximated as the delta function to obtain:
\[
P(t) = 1 - \frac{t}{\hbar^2} \int_{-\infty}^{\infty} d(tE_f) \rho(E_f) |\langle f | \hat{A} | i \rangle|^2 2\pi \delta((E_f t - (E_i + \hbar \omega) t)/(2\hbar))
\]
\[
= 1 - \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} d\xi \rho(\xi 2\hbar/t) |\langle f | \hat{A} | i \rangle|^2 \delta(\xi - (E_i + \hbar \omega) t/(2\hbar))
\]
(556)
\[
= 1 - \frac{2\pi}{\hbar} \rho(E_i + \hbar \omega) |\langle f | \hat{A} | i \rangle|^2
\]

so \( P(t) = \exp(-\Gamma t) \approx 1 - \Gamma t + \cdots \), where
\[
\Gamma = \frac{2\pi}{\hbar} \rho(E_i + \hbar \omega) |\langle f | \hat{A} | i \rangle|^2,
\]
(557)

or as a discrete sum over states,
\[
\Gamma = \frac{2\pi}{\hbar} \sum_f |\langle f | \hat{A} | i \rangle|^2 \delta(E_f - E_i - \hbar \omega),
\]
(558)

which is known as Fermi’s Golden rule.

Without introducing the approximation of the kernel of Eq. (554), we obtain:
\[
P(t) = 1 - \frac{t^2}{\hbar^2} \int_{-\infty}^{\infty} dE_f \rho(E_f) |\langle f | \hat{A} | i \rangle|^2 \frac{\sin^2[(w_f - w)t/2]}{[(w_f - \omega)t/2]^2}
\]
\[
= 1 - \frac{2}{\hbar} \int_{-\infty}^{\infty} dE_f \rho(E_f) \frac{t}{2\hbar} |\langle f | \hat{A} | i \rangle|^2 \frac{\sin^2((E_f - E_i - \hbar \omega) t/(2\hbar))}{((E_f - E_i - \hbar \omega) t/(2\hbar))^2}
\]
(559)
\[
= 1 - \frac{2}{\hbar} \int_{-\infty}^{\infty} d\xi \rho(\xi 2\hbar/t) |\langle f | \hat{A} | i \rangle|^2 \frac{\sin^2(\xi - (E_i + \hbar \omega) t/(2\hbar))}{(\xi - (E_i + \hbar \omega) t/(2\hbar))^2}
\]
\[
= 1 - \frac{2}{\hbar} \int_{-\infty}^{\infty} d\xi \rho(\xi 2\hbar/t) |\langle f | \hat{A} | i \rangle|^2 \frac{\sin^2(\xi)}{\xi^2}
\]

which gives, in the time-range when the decay is exponential (i.e., \( P(t) = \exp(-\Gamma t) \approx 1 - \Gamma t \)),
\[
\Gamma = \frac{2}{\hbar} \int_{-\infty}^{\infty} d\xi \rho(\xi 2\hbar/t) |\langle f | \hat{A} | i \rangle|^2 \frac{\sin^2(\xi)}{\xi^2},
\]
(560)
Substituting the delta function in Eq. (558) by its integral form, we obtain:

\[
\Gamma_{fi} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt \langle f | \hat{A} | i \rangle \langle i | \hat{A} | f \rangle e^{\frac{i}{\hbar}(E_f - E_i - \hbar w)t},
\]

\[
= \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt e^{\frac{i}{\hbar} \hat{H}t} \hat{A} e^{-\frac{i}{\hbar} \hat{H}t} \langle i | \hat{A} | f \rangle e^{-iwt},
\]

\[
= \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt e^{-iwt} A_{fi}(t) A_{if}(0),
\]

\[
= \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt e^{-iwt} A_{fi}(t) A_{if}(0).
\]

The equilibrium ensemble average is

\[
\langle \Gamma_{fi} \rangle = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt e^{-iwt} \sum_{\alpha} p_{\alpha} \langle \alpha | A_{fi}(t) A_{if}(0) | \alpha \rangle,
\]

\[
= \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt e^{-iwt} \langle A_{fi}(t) A_{if}(0) \rangle,
\]

\[
= \frac{[1 + e^{-\beta \hbar \omega}]^{-1}}{\hbar^2} \int_{-\infty}^{\infty} dt e^{-iwt} \langle [A_{fi}(t) A_{if}(0) + A_{fi}(0), A_{if}(t)] \rangle,
\]

(562)

where \( p_{\alpha} = Z^{-1} e^{-\beta E_{\alpha}} \) with \( Z = \sum_{\alpha} e^{-\beta E_{\alpha}} \).

The rest of this subsection shows that, according to Eq. (562), \( \langle \Gamma_{fi} \rangle \) can be written as follows:

\[
\langle \Gamma_{fi} \rangle = \frac{[1 + e^{-\beta \hbar \omega}]^{-1}}{\hbar^2} \int_{-\infty}^{\infty} dt e^{-iwt} \langle [A_{fi}(t) A_{if}(0) + A_{fi}(0), A_{if}(t)] \rangle,
\]

(563)

where the symmetrized correlation function \( C(t) = A_{fi}(t) A_{if}(0) + A_{fi}(0), A_{if}(t) \) is real, and is an even function of time just like its classical analogue correlation function. Therefore, Eq. (563) has often been used for estimations of \( \langle \Gamma_{fi} \rangle \) based on classical simulations. However, it has been pointed out by Berne and co-workers that the classical version of \( C(t) \) underestimates \( \langle \Gamma_{fi} \rangle \) by a factor of \((\beta \hbar \omega/2) \coth(\beta \hbar \omega/2)\) [J. Chem. Phys. (1994) 100: 8359-8366].
The derivation of the last line of Eq. (563) is as follows:

\[
\langle \Gamma_{fi} \rangle = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{\alpha,\gamma} p_\alpha \langle \alpha | A_{fi}(t) | \gamma \rangle \langle \gamma | A_{if}(0) | \alpha \rangle,
\]

\[
= \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{\alpha,\gamma} p_\alpha \langle \alpha | A_{fi}(t) | \gamma \rangle \langle \gamma | A_{if}(0) | \alpha \rangle \frac{1 + e^{-\beta\omega}}{1 + e^{-\beta\omega h}} \delta(E_\gamma - E_\alpha - h\omega)[1 + e^{-\beta\omega}],
\]

\[
= \frac{2\pi}{h} \frac{1}{1 + e^{-\beta\omega h}} \sum_{\alpha,\gamma} p_\alpha \langle \alpha | A_{fi}(0) | \gamma \rangle \langle \gamma | A_{if}(0) | \alpha \rangle \delta(E_\gamma - E_\alpha - h\omega)[1 + e^{-\beta(E_\gamma - E_\alpha)}],
\]

\[
= \frac{1 + e^{-\beta\omega h} - 1}{h^2} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{\alpha,\gamma} p_\alpha \langle \alpha | A_{fi}(t) | \gamma \rangle \langle \gamma | A_{if}(0) | \alpha \rangle [1 + e^{-\beta(E_\gamma - E_\alpha)}],
\]

\[
= \frac{1 + e^{-\beta\omega h} - 1}{h^2} \int_{-\infty}^{\infty} dt e^{-i\omega t} \left[ \sum_{\alpha,\gamma} p_\alpha \langle \alpha | A_{fi}(t) | \gamma \rangle \langle \gamma | A_{if}(0) | \alpha \rangle \right]
\]

\[
+ \sum_{\alpha,\gamma} p_\alpha \langle \alpha | A_{fi}(t) | \gamma \rangle \langle \gamma | A_{if}(0) | \alpha \rangle e^{-\beta(E_\gamma - E_\alpha)} \right],
\]

\[
= \frac{1 + e^{-\beta\omega h} - 1}{h^2} \int_{-\infty}^{\infty} dt e^{-i\omega t} \left[ \sum_{\alpha,\gamma} p_\alpha \langle \alpha | A_{fi}(t) | \gamma \rangle \langle \gamma | A_{if}(0) | \alpha \rangle \right]
\]

\[
+ \sum_{\alpha,\gamma} p_\gamma \sum_{\alpha,\gamma} p_\alpha \langle \alpha | A_{fi}(0) | \alpha \rangle \langle \alpha | A_{fi}(t) | \gamma \rangle e^{-\beta(E_\gamma - E_\alpha)} \right],
\]

\[\tag{564}\]

\[
\langle \Gamma_{fi} \rangle = \frac{1 + e^{-\beta\omega h} - 1}{h^2} \int_{-\infty}^{\infty} dt e^{-i\omega t} \left[ \sum_{\alpha,\gamma} p_\alpha \langle \alpha | A_{fi}(t) | \gamma \rangle \langle \gamma | A_{if}(0) | \alpha \rangle + \sum_{\alpha,\gamma} p_\gamma \langle \gamma | A_{if}(0) | \alpha \rangle \langle \alpha | A_{fi}(t) | \gamma \rangle \right]
\]

\[
= \frac{1 + e^{-\beta\omega h} - 1}{h^2} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{\alpha,\gamma} p_\alpha \langle \alpha | A_{fi}(t) | \gamma \rangle \langle \gamma | A_{if}(0) | \alpha \rangle + \langle \alpha | A_{if}(0) | \gamma \rangle \langle \gamma | A_{fi}(t) | \alpha \rangle,
\]

\[
= \frac{1 + e^{-\beta\omega h} - 1}{h^2} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{\alpha} p_\alpha \langle \alpha | A_{fi}(t) A_{if}(0) + A_{if}(0) A_{fi}(t) | \alpha \rangle,
\]

\[
= \frac{1 + e^{-\beta\omega h} - 1}{h^2} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle A_{fi}(t) A_{if}(0) + A_{if}(0) A_{fi}(t) | \rangle,
\]

\[
= \frac{1 + e^{-\beta\omega h} - 1}{h^2} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle [A_{fi}(t) A_{if}(0) + A_{if}(0) A_{fi}(t)] | \rangle,
\]

\[\tag{565}\]
### 48.2 Field with Exponential Decay

Assuming that the perturbation decays exponentially with a single frequency component, \( \hat{W}(t') = \hat{A} e^{-t'/\tau} e^{-i\omega t'} \), we obtain the probability of observing the system in the final state:

\[
P_{fi}(t) = \frac{1}{\hbar^2} \int_0^t dt'' \int_0^t dt' \langle i|\hat{W}^*(t'')|f\rangle \langle f|\hat{W}(t')|i\rangle e^{i(E_f - E_i)(t'-t'')} ,
\]

\[
= \frac{1}{\hbar^2} \int_0^t dt'' e^{-t''/\tau + i(\omega - \omega_{fi})t''} \int_0^t dt' \langle i|\hat{W}^*(0)|f\rangle \langle f|\hat{W}(t')|i\rangle e^{i(E_f - E_i)t'},
\]

where \( \omega_{fi} = (E_f - E_i)/\hbar \). Taking the limit \( t \to \infty \), we obtain:

\[
\lim_{t \to \infty} P_{fi}(t) = \frac{1}{\hbar^2} \int_0^\infty dt'' e^{-t''/\tau + i(\omega - \omega_{fi})t''} \int_0^\infty dt' \langle i|\hat{W}^*(0)|f\rangle \langle f|\hat{W}(t')|i\rangle e^{i(E_f - E_i)t'},
\]

\[
= \frac{1}{\hbar^2} \frac{1}{(-1/\tau + i(\omega - \omega_{fi}))} \int_0^\infty dt' \langle i|\hat{A}^*|f\rangle \langle f|\hat{A}|i\rangle e^{-t'/\tau - i(\omega - \omega_{fi})t'},
\]

\[
= \frac{|\langle i|\hat{A}|f\rangle|^2}{\hbar^2(1/\tau^2 - (\omega - \omega_{fi})^2)}
\]

Therefore, the transfer probability from \( |i\rangle \) to all possible final states \( |f\rangle \) is:

\[
\lim_{t \to \infty} P(t) = \sum_f \frac{|\langle i|\hat{A}|f\rangle|^2}{\hbar^2(1/\tau^2 - (\omega - \omega_{fi})^2)}
\]

### 48.3 Vibrational Cooling

In the subsection, we illustrate the Golden Rule as applied to the description of vibrational cooling of a harmonic diatomic molecule coupled to a metal surface as implemented by Head-Gordon and Tully [J. Chem. Phys. (1992) 96:3939-3949].

For a molecule interacting with a surface, the general form of the coupling matrix element \( A_{fi} \) follows from the Born-Oppenheimer approximation in which the nuclear kinetic energy term is neglected when obtaining the electronic wave functions. The states are Born-Oppenheimer products of nuclear (vibrational) and electronic wave functions which we write, as follows:

\[
|i\rangle = |\nu_i\rangle |e_i\rangle ,
\]

\[
|f\rangle = |\nu_f\rangle |e_f\rangle ,
\]

Therefore, the coupling between the two states is the matrix element of the nuclear kinetic-energy operator (for simplicity, we consider only a single normal mode \( x \), which will be the high-frequency
adsorbate vibration):

\[ \langle f | \hat{A} | i \rangle = -\frac{\hbar^2}{2m} \langle \nu_f \nu_i | \frac{\partial^2}{\partial x^2} | \nu_i \nu_i \rangle \]

\[ = -\frac{\hbar^2}{2m} \left[ \langle \nu_f \nu_i | \langle \nu_f \nu_i | \frac{\partial^2}{\partial x^2} | e_i \rangle + 2 \langle \nu_f \nu_i | \frac{\partial}{\partial x} | e_i \rangle \frac{\partial}{\partial x} | \nu_i \rangle \right] \] (570)

where \( m \) is the reduced mass of the vibrational mode \( x \).

To obtain a tractable expression, the nuclear and electronic coordinates in the matrix element must be separated. Following Brivio and Grimley (G. P. Brivio and T. B. Grimley, J. Phys. C 10, 2351 (1977); G. P. Brivio and T. B. Grimley, Surf. Sci. 89, 226 (1979)), this can be done by observing that since the amplitude of vibration is small (about 1/100 of the bondlength for diatomics in low vibrational states), it is reasonable to expand the electronic matrix elements in powers of the displacement \( x \), keeping only the leading term. If we also assume that the electronic states \( |e_f\rangle \) and \( |e_i\rangle \) represent parallel potential-energy surfaces then \( |\nu\rangle \) and \( |\nu'\rangle \) will be orthogonal members of the same complete set, and the first term of Eq. (570) vanishes, leaving

\[ \langle f | \hat{A} | i \rangle = -\frac{\hbar^2}{m} \left[ \langle \nu_f \nu_i | \langle \nu_f | \frac{\partial}{\partial x} | e_i \rangle \langle e_f | \frac{\partial}{\partial x} | e_i \rangle \right] \] (571)

To compute \( \langle \nu_f | \frac{\partial}{\partial x} | \nu_i \rangle \), we assume that the vibrational states can be approximated as harmonic oscillator wave functions with frequency \( w \), for which:

\[ \hat{a}|\nu\rangle = \sqrt{\nu}|\nu - 1\rangle, \]

\[ \hat{N}|\nu\rangle = \nu|\nu\rangle = \hat{a}^{\dagger} \hat{a}|\nu\rangle = \sqrt{\nu} \hat{a}^{\dagger}|\nu - 1\rangle, \] (572)

so \( \hat{a}^{\dagger}|\nu\rangle = \sqrt{\nu + 1}|\nu + 1\rangle \), with \( \hat{a} = \frac{1}{\sqrt{2}}(\hat{x} + \hat{p}) \), \( \hat{a}^{\dagger} = \frac{1}{\sqrt{2}}(\hat{x} - \hat{p}) \). Here, \( \hat{x} = \hat{x} \sqrt{\frac{m \hbar}{w}} \) and \( \hat{p} = \hat{p} \sqrt{\frac{1}{m \hbar w}} \), with \( \hat{p} = -i \frac{\hbar}{\partial \hat{x}} \). Therefore, \( \hat{a} = \hat{a}^{\dagger} = i \sqrt{\frac{2}{m \hbar w}} \hat{p} = \sqrt{\frac{2 \hbar}{m \hbar w}} \frac{\partial}{\partial x} \) which gives,

\[ \langle \nu_f | \frac{\partial}{\partial x} | \nu_i \rangle = \sqrt{\frac{m \hbar w}{2 \hbar}} \left[ \langle \nu_f | \hat{a} | \nu_i \rangle - \langle \nu_f | \hat{a}^{\dagger} | \nu_i \rangle \right], \] (573)

Substituting Eq. (573) into Eq. (571), with \( \nu_f = \nu_i - 1 \), we obtain:

\[ \langle f | \hat{A} | i \rangle = -\hbar \sqrt{\frac{\hbar w \nu_i}{2m}} \langle \nu_f | \frac{\partial}{\partial x} | e_i \rangle \] (574)

and

\[ |\langle f | \hat{A} | i \rangle|^2 = h^2 \frac{\hbar w \nu_i}{2m} |\langle \nu_f | \frac{\partial}{\partial x} | e_i \rangle|^2 \] (575)
Substituting Eq. (575) into Eq. (558), we obtain:

\[
\Gamma = \frac{\hbar}{m} \sum_{f} \hbar \nu_{i} |\langle e_{f} | \frac{\partial}{\partial x} | e_{i} \rangle|^{2} \delta(e_{f} - e_{i} - \hbar w),
\]  

(576)

Integrating over the number of electrons that could be promoted to an unoccupied state by absorbing a quantum of energy \(\hbar w\), we obtain the total vibrational linewidth:

\[
\Gamma = 2 \frac{\hbar}{m} \int de_{i} \frac{\rho(e_{i})}{e^{\beta(e_{i} - \mu_{F})} + 1} \sum_{f} \hbar \nu_{i} |\langle e_{f} | \frac{\partial}{\partial x} | e_{i} \rangle|^{2} \delta(e_{f} - e_{i} - \hbar w),
\]

(577)

where \(\mu_{F}\) is the Fermi energy. In the low-temperature limit \((\beta \to \infty)\), for \(\nu_{i} = 1\), we obtain:

\[
\Gamma = 2 \frac{\hbar}{m} \sum_{i < F} \sum_{f > F} \hbar w |\langle e_{f} | \frac{\partial}{\partial x} | e_{i} \rangle|^{2} \delta(e_{f} - e_{i} - \hbar w)
\]

(578)

Reinserting the kernel of Eq. (555) and introducing the change of variables \(\Delta = e_{f} - e_{i}\), we can rewrite Eq. (577), as follows:

\[
\Gamma = 2 \frac{\hbar}{m} \int de_{i} \frac{\rho(e_{i})}{e^{\beta(e_{i} - \mu_{F})} + 1} \sum_{f} \hbar \nu_{i} |\langle e_{f} | \frac{\partial}{\partial x} | e_{i} \rangle|^{2} \delta(e_{f} - e_{i} - \hbar w),
\]

\[
= 2 \frac{\hbar}{m} \int de_{i} \int de_{f} \frac{\rho(e_{i})}{e^{\beta(e_{i} - \mu_{F})} + 1} \frac{\rho(e_{f})}{e^{-\beta(e_{f} - \mu_{F})} + 1} \hbar \nu_{i} |\langle e_{f} | \frac{\partial}{\partial x} | e_{i} \rangle|^{2} \delta(e_{f} - e_{i} - \hbar w),
\]

(579)

where

\[
f(\Delta) = \sum_{i} \frac{\rho(e_{i})}{e^{\beta(e_{i} - \mu_{F})} + 1} \frac{\rho(e_{i} + \Delta)}{e^{-\beta(e_{i} + \Delta - \mu_{F})} + 1} \hbar \nu_{i} |\langle e_{i} + \Delta | \frac{\partial}{\partial x} | e_{i} \rangle|^{2},
\]

(580)

and \(t\) is a time sufficiently long so that the decay is no longer Gaussian but rather exponential so that \(\Gamma\) is time independent.

### 48.4 Electron Transfer

The rate of electron transfer from the initial state \(|i\rangle = |\nu_{i}\rangle |e_{i}\rangle\) to the final state \(|f\rangle = |\nu_{f}\rangle |e_{f}\rangle\) of weakly coupled redox species can also be described according to the Golden rule expression...
derived from first order perturbation theory:

\[ \Gamma_i \approx \frac{2\pi}{\hbar} \sum_f |\langle f | \hat{A} | i \rangle|^2 \delta(E_f - \hbar(w_i + w)), \]

\[ \approx \frac{2\pi}{\hbar} |H_{if}|^2 \sum_f |\langle \nu_f | \nu_i \rangle|^2 \delta(E_f - E_i - \Delta E), \]  

(581)

where \( H_{if} = \langle e_f | \hat{A} | e_i \rangle \) is the coupling between electronic states, assumed to be independent of vibrational coordinates, and \( \Delta E = \hbar \omega \) is the change in vibrational energy.

For the harmonic potentials shown in Fig. (48.4), it can be shown that

\[ \sum_f |\langle \nu_f | \nu_i \rangle|^2 \delta(E_f - E_i - \Delta E) \approx \frac{1}{\hbar \Omega \pi x_{if} k^*}, \]

(582)

when \( E_i, E_f > E^* \), with \( k^* = \sqrt{2m(E_i - E^*)/\hbar} \) and \( x_{if} = \sqrt{2E\lambda/(m\Omega^2)} \), giving

\[ \Gamma_i \approx \frac{2|H_{if}|^2}{\hbar \Omega \pi x_{if} k^*} \]

\[ \approx \frac{|H_{if}|^2}{\hbar \sqrt{E\lambda} \sqrt{(E_i - E^*)}} \]  

(583)

Computing the thermal average over all initial states, we obtain the overall rate:

\[ \Gamma \approx |H_{if}|^2 \frac{1}{\hbar \sqrt{E\lambda}} \frac{\int dE_i \exp(-\beta E_i) \frac{1}{\sqrt{(E_i - E^*)}}}{\int dE_i \exp(-\beta E_i)} \]

\[ \approx |H_{if}|^2 \frac{1}{\hbar \sqrt{E\lambda}} \exp(-\beta E^*) \frac{\int dE \exp(-\beta E) \frac{1}{\sqrt{E}}}{\int dE \exp(-\beta E)} \]

\[ \approx |H_{if}|^2 \frac{1}{\hbar \sqrt{E\lambda}} \exp(-\beta E^*) \frac{\int_0^\infty dp \exp(-\beta p^2) \frac{1}{p}}{\int dE \exp(-\beta E)} \]

\[ \approx |H_{if}|^2 \frac{1}{\hbar \sqrt{E\lambda}} \exp(-\beta E^*) \frac{\sqrt{\pi/\beta}}{\beta^{-1}} \]

\[ \approx |H_{if}|^2 \frac{1}{\hbar \sqrt{E\lambda}} \exp(-\beta E^*) \sqrt{\pi \beta} \]

\[ \approx |H_{if}|^2 \frac{\sqrt{2\pi \beta/m}}{\hbar \Omega x_{if}} \exp(-\beta E^*) \]

(584)

Figure 48.4 shows a schematic description of the energy diagram, assuming that the potential energy surfaces along the vibronic coordinates are parabolas displaced in \( x_{fi} = x_f - x_i \) with
frequency $\Omega$, we have $V_i = 1/2m\Omega^2(x - x_i)^2$ and $V_f = 1/2m\Omega^2(x - x_f)^2 - \Delta E$, which cross at $x^*$ with energy

$$E^* = (E_\lambda - \Delta E)^2/(4E_\lambda).$$

(585)

To derive Eq. (585), we observe that $E_\lambda = 1/2m\Omega^2(x^* - x_i)^2 = 1/2m\Omega^2(x^* - x_i - x_{fi})^2 - \Delta E$. Therefore, $E^* = E^* + E_\lambda - m\Omega^2(x^* - x_i)x_{fi} - \Delta E$ which gives $E^* = E^* + E_\lambda - m\Omega^2(x^* - x_i)x_{fi} - \Delta E$. Simplifying, we obtain:

$$E_\lambda = m\Omega^2(x^* - x_i)x_{fi} + \Delta E = m\Omega^2\sqrt{2E^*/(m\Omega^2)} + \Delta E.$$

48.4.1 Jortner Marcus Expression

The goal of this section is to introduce a simple expression for Monte Carlo calculations of electron transfer rates $k = A_NB_e$, as described by the Marcus-Jortner equation derived in J. Chem. Phys. (1978) 63:4358-4369, with the nuclear contribution

$$A_N = \sqrt{\frac{\pi}{\hbar^2E_\lambda k_BT}}e^{-\frac{1}{2}\sum_{i=1}^{N}\Delta_{ci}^2} \sum_{\nu_1=0}^{\infty} \cdots \sum_{\nu_N=0}^{\infty} \prod_{i=1}^{N} \left(\frac{\Delta_{ci}^2}{\nu_i!}\right)^{\nu_i} e^{-\beta \left(\Delta E - E_\lambda - \sum_{i=1}^{N} \nu_i h\omega_{ci}\right)^2/(4E_\lambda)}$$

(586)

where $\Delta_{ci} = \Delta Q_i^0 \sqrt{\mu_i/\omega_{ci}/\hbar}$ are defined in terms of the displacements $\Delta Q_i^0$ of the $i$-th normal mode minimum energy position. The electronic contribution is defined, as follows:

$$B_e = \int d\mathbf{R}|H_{ij}(\mathbf{R})|^2 \exp(-\beta E(\mathbf{R}))$$

(587)

Introducing the sampling function,

$$f_\gamma(\nu_1, \cdots, \nu_N) = Z_{\gamma}^{-1} \exp\left(-\gamma \sum_{i=1}^{N} \nu_i h\omega_{ci}\right),$$

(588)
with \( Z_\gamma = \prod_{i=1}^{N} \sum_{\nu_i=0}^{\infty} \exp(-\gamma \nu_i \hbar \omega_{ci}) = \prod_{i=1}^{N} (1 - \exp(-\gamma \hbar \omega_{ci}))^{-1} \), we obtain

\[
A_N = \chi_{\gamma} \sum_{\nu_1=0}^{\infty} \cdots \sum_{\nu_N=0}^{\infty} \prod_{i=1}^{N} f_{\gamma} \left( \frac{\Delta Q_i^2}{\nu_i} \right)^{\nu_i} e^{-\beta (\Delta E - E_\lambda - \sum_{i=1}^{N} \nu_i \hbar \omega_{ci})^2 / (4E_\lambda)} e^{\gamma \sum_{i=1}^{N} \nu_i \hbar \omega_{ci}} \tag{589}
\]

with \( \chi_{\gamma} = Z_\gamma \sqrt{\frac{\pi}{\hbar^2 E_\lambda k_B T}} e^{-\frac{1}{2} \sum_{i=1}^{N} \Delta Q_i^2} \), which can be estimated by Monte Carlo, as follows:

\[
A_N = \frac{\chi_{\gamma} N_c}{N_c} \sum_{k=1}^{N_c} \prod_{i=1}^{N} \left( \frac{\Delta Q_i^2}{\nu_i^{(k)}} \right)^{\nu_i^{(k)}} e^{-\beta (\Delta E - E_\lambda - \sum_{i=1}^{N} \nu_i^{(k)} \hbar \omega_{ci})^2 / (4E_\lambda)} e^{\gamma \sum_{i=1}^{N} \nu_i \hbar \omega_{ci}} \tag{590}
\]

where the quantum numbers \( \nu_i^{(k)} \) are sampled according to the distribution function \( f_{\gamma} \).

48.4.2 Computational Problem: Jortner-Marcus

1. Write a program to implement the Monte Carlo estimator of \( A_N \), introduced by Eq. (590) for a system with 4 normal modes with \( \beta = 3.0 \), frequencies \( \omega_{ci} = 0.75 \), reduced masses \( \mu_i = 1.0 \), displacements \( \Delta Q_i^0 = 1.0 \) and \( E_\lambda = 0.25 \) in atomic units (i.e., \( \hbar = 1.0 \)). Compare your results for \( N_c = 10^6 \) with the corresponding calculations obtained by summing the contributions of each normal mode up to \( \nu = 3 \).

Solution: Sec. 48.5

48.5 Problem Jortner-Marcus

1. Write a program to implement the Monte Carlo estimator of \( A_N \), introduced by Eq. (590) for a system with 4 normal modes with \( \beta = 3.0 \), frequencies \( \omega_{ci} = 0.75 \), reduced masses \( \mu_i = 1.0 \), displacements \( \Delta Q_i^0 = 1.0 \) and \( E_\lambda = 0.25 \) in atomic units (i.e., \( \hbar = 1.0 \)). Compare your results for \( N_c = 10^6 \) with the corresponding calculations obtained by summing the contributions of each normal mode up to \( \nu = 3 \).

   Download the source code from here.
   Untar the tarball files by typing
   \[
   \text{tar -xvf mck.tar}
   \]
   change directory by typing
   \[
   \text{cd mck}
   \]
   Visualize results by typing
   \[
   \text{gnuplot < scr}
   \]
   The visualization script generates the plot showing the comparison of MC and straight sum calculation of log(k).
   Compile by typing
gfortran mck.f -o mck

and run the program by typing

./mck

**Parameter file:**
Save the following parameter file as `param.dat`:

```plaintext
IMPLICIT NONE
INTEGER nm, nd, NMC, np, NFR
REAL*8 gamm, hbar, Es, beta
PARAMETER(nm=3, nd=4)
PARAMETER (NMC=10000001, np=10, NFR=0, hbar=1.0)
PARAMETER (beta=3.0, gamm=beta-0.1, Es=0.25)
```

! nm: max quantum number nu
! nd: # of modes
! Es: reorganization energy
! beta = 1/(kB T) ! in atomic units
! gamm: sampling function exponent
! NFR: reading flag
! NFR=1 when reading from input file freq_mass_displ.dat

**Code:**
Save the following code file as `mck.f`:

```plaintext
PROGRAM mck

c

MC calculation of Jortner-Marcus ET rate constant:
nd-dimensional normal modes
Eq (III 4’’) JCP 63: 4358-4369 (1978)

INCLUDE ‘param.dat’
INTEGER i, j, l, iseed, nflag, nu2, nu1, nu
INTEGER IND, ncount, kk
REAL*8 dGmin, dGmax, dG, pi, A, Ar, re, mu, Dq, D, D2, Prod
REAL*8 f, f1, fn, rsum, rsum2, his, y, gn, om, w, Z, pf
DIMENSION his(nm+1), y(nd), nu1(nd), nu2(nd), w(nd)
DIMENSION D2(nd), mu(nd), Dq(nd)
COMMON/counts/ncount

pi=acos(-1.0)
dGmin=-Es-1.5
```
dGmax=-Es+4.5
ncount=0
om=.750

OPEN(1,FILE="freq_mass_displ.dat")
DO i=1,nd
  IF(NFR.EQ.1) THEN
    READ(1,*) w(i),mu(i),Dq(i)
  ELSE
    w(i)=om
    mu(i)=1.0
    Dq(i)=1.0
  END IF!
END DO
CLOSE(1)

OPEN(1,FILE="conv")
DO k=1,np
  iseed=87212
  CALL srand(iseed) ! Initialize random sequence
  nflag=-1 ! Sets that it’s the first MC iteration
  CALL BIN(nu2,his,nflag)
  CALL MMC(nu1,nu2,nflag,w)
  nflag=1 ! No longer the first iteration
  dG=dGmin+(k-1)*(dGmax-dGmin)/(np-1)
  A=0.0 ! Initialize the partition function
  DO i=1,NMC ! # of MC configs
    CALL MMC(nu1,nu2,nflag,w)
    CALL BIN(nu2,his,nflag) ! Build histogram of nu2
    A = A + sqrt(pi/hbar**2*beta/Es)*Prod(nu2,D2) ! Eq (III. 4’’)
    1 *gn(nu2,w,dG)/fn(nu2,w)
  END DO
  CALL A_analytic(Ar,w,dG,D2)
  1 ,log(sqrt(pi/hbar**2*beta/Es)*Ar) ! comment for nd > 4
  PRINT *, "DG,MC(A), Analy(A)", dG+Es,log(A*Z(w)/NMC)
END DO
CLOSE(1)
OPEN (1, FILE= "histo")

rsum=0.0
rsum2=0.0

DO i=1,nm+1
    nu=i-1
    rsum=rsum+his(i) ! check normalization
    rsum2=rsum2+f1(nu,w(1))
    WRITE(1,22) nu*1.0, his(i),f1(nu,w(1)) ! check histogram
END DO

CLOSE(1)

PRINT *, "norm_his=", rsum
PRINT *, "norm_f=", rsum2

22 FORMAT(6(e13.6,2x))

END

SUBROUTINE BIN(nu2,his,nflag)

Histogram of configs for quantum number nu2(1)

nflag < 0 initializes the histogram to zero

nflag >= 0 increments the histogram beans with nu2(1)

INCLUDE 'param.dat'

INTEGER IND,nflag,i,nu2
REAL*8 his
DIMENSION nu2(nd),his(nm+1)

IF(nflag.LT.0) THEN ! Initialize histogram
    DO i=1,nm+1
        his(i)=0.0
    END DO
ELSE
    IND=1+nu2(1) ! IND = 1,..., nm+1
    his(IND)=his(IND)+1.0/NMC
END IF

RETURN

END

SUBROUTINE MMC(nu1,nu2,nflag,w)
Metropolis MC:
Given an initial config \( \nu_1 \), generate the next one \( \nu_2 \)

```fortran
INCLUDE 'param.dat'

INTEGER kk, k, nflag, \( \nu_1 \), \( \nu_2 \), ncount, dnu
REAL*8 ratio, \( r \), \( y \), \( f \), \( w \)
DIMENSION \( \nu_1 \) (nd), \( \nu_2 \) (nd), \( w \) (nd)

IF(nflag.LT.0) THEN ! Initial config of quantum numbers \( \nu \)
  DO k=1,nd
    \( \nu_1 \) (k) = rand() * (nm+1)
  END DO
ELSE
  DO k=1,nd
    \( \nu_2 \) (k) = \( \nu_1 \) (k)
  END DO
  kk = rand() * nd + 1
  \( \nu_2 \) (kk) = rand() * (nm+1)

ratio = f(\( \nu_2 \), \( \nu_1 \), \( w \)) ! Metropolis MC criteria
r = rand()
IF(r.GT.ratio) THEN
  DO k=1,nd
    \( \nu_2 \) (k) = \( \nu_1 \) (k)
  END DO
ELSE
  ncount = ncount + 1
  DO k=1,nd
    \( \nu_1 \) (k) = \( \nu_2 \) (k)
  END DO
END IF
END IF
RETURN
END
```

```
FUNCTION gn(\( \nu_2 \), \( w \), dG)
INCLUDE 'param.dat'
INTEGER round, k, \( \nu_2 \)
REAL*8 gn, \( w \), nut, dG
DIMENSION \( \nu_2 \) (nd), \( w \) (nd)

nut = 0.0
```

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DO k=1,nd ! Summing all nd-dimensional nus in the exponent
    nut=nut+hbar*w(k)*nu2(k)
END DO

gn=exp(-beta*(dG-Es-nut)**2/(4.0*Es))
RETURN
END

FUNCTION f(nu2,nu1,w)
INCLUDE 'param.dat'
INTEGER k,nu1,nu2
REAL *8 f,nut,w
DIMENSION nu2(nd),nu1(nd),w(nd)
nut=0.0
DO k=1,nd
    nut=nut+gamm*hbar*w(k)*(nu2(k)-nu1(k))
END DO
f=exp(-nut)
RETURN
END

FUNCTION fn(nu2,w)
INCLUDE 'param.dat'
INTEGER k,nu2
REAL *8 fn,nut,w
DIMENSION nu2(nd),w(nd)
fn=1.0
DO k=1,nd
    fn=fn*exp(-gamm*hbar*w(k)*nu2(k))
END DO
RETURN
END

FUNCTION f1(nu,w1)
INCLUDE 'param.dat'
INTEGER nu
REAL*8 f1,w1
f1=exp(-gamm*hbar*w1*nu)
1/(1.0/(1.0-exp(-gamm*hbar*w1)))
RETURN
END

FUNCTION Z(w)
INCLUDE 'param.dat'
INTEGER i,j
REAL*8 Z,rn,w
DIMENSION w(nd)
Z=1.0
DO j=1,nd
  rn=0.0
  DO i=1,nm+1
    rn=rn+exp(-gamm*hbar*w(j)*(i-1))
  END DO
  rn=1.0/(1.0-exp(-gamm*hbar*w(j)))
  Z=Z*rn
END DO
RETURN
END

FUNCTION Prod(nu2,D2)
  Prod = Prod_{i=1}^{nd} (D^2)^{nu(i)/nu(i)!}
  INCLUDE ’param.dat’
  INTEGER nu2,i,j,fac
  REAL*8 Prod,D2
  DIMENSION nu2(nd),D2(nd)

  Prod=1.0
  DO i=1,nd
    fac=1 ! Compute fac = n2(i) !
    IF(nu2(i).GT.1) THEN
      DO j=1,nu2(i)
        END DO
    END IF
    Prod=Prod*exp(-D2(i)/2.0)*D2(i)**(nu2(i))/fac
  END DO
  RETURN
END

SUBROUTINE A_analytic(Ar,w,dG,D2)
  INCLUDE ’param.dat’
  REAL*8 Ar,re,dG,w,pi,Prod,D2
  INTEGER nu2,i1,i2,i3,i4
  DIMENSION nu2(nd),w(nd),D2(nd)

pi=acos(-1.0)

Assumes nd=4
(modified for smaller nd by commenting out do loops)

Ar=0.0

DO i1=0,3
   nu2(1)=i1
   DO i2=0,3
      nu2(2)=i2
      i2=0.0 ! uncommented when DO loop i2 is commented out
   END DO
   DO i3=0,3
      nu2(3)=i3
      i3=0.0 ! uncommented when DO loop i3 is commented out
   END DO
   DO i4=0,3
      nu2(4)=i4
      i4=0.0 ! uncommented when DO loop i4 is commented out
      re=dG-Es
      re=re-hbar*w(1)*i1
      re=re-hbar*w(2)*i2
      re=re-hbar*w(3)*i3
      re=re-hbar*w(4)*i4
      Ar=Ar+Prod(nu2,D2)*exp(-beta*re**2/(4.0*Es)) ! Eq (III. 4’’)
   END DO
END DO
END DO
RETURN
END