



A Molecular Modeler's Guide to Statistical Mechanics

Course notes for BIOE575

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April 11, 2001

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Chapter 1

Basic Principles and the Microcanonical Ensemble

The first part of this course will consist of an introduction to the basic principles of statistical mechanics (or statistical physics) which is the set of theoretical techniques used to understand microscopic systems and how microscopic behavior is reflected on the macroscopic scale. In the later parts of the course we will see how the tool set of statistical mechanics is key in its application to molecular modeling. Along the way in our development of basic theory we will uncover the principles of thermodynamics. This may come as a surprise to those familiar with the classical engineering paradigm in which the laws of thermodynamics appear as if from the brain of Jove (or from the brain of some wise old professor of engineering). This is not the case. In fact, thermodynamics arises naturally from basic principles. So with this foreshadowing in mind we begin by examining the classical laws of motion¹.

1.1 Classical Laws of Motion

Recall Newton's famous second law of motion, often expressed as $\mathbf{f} = m\mathbf{a}$, where \mathbf{f} is the force acting to accelerate a particle of mass m with the acceleration \mathbf{a} . For a collection of N particles located at Cartesian positions $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ the law of motion becomes

$$m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i, \quad (1.1.1)$$

where $\mathbf{f}_1, \mathbf{f}_2, \dots, \mathbf{f}_N$ are the forces acting on the N particles².

We shall see that in the absence of external fields or dissipation the Newtonian equation of motion preserves total energy:

$$E = K + U = \frac{1}{2} \sum_{i=1}^N m_i \|\dot{\mathbf{r}}_i\|^2 + U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (1.1.2)$$

¹This course will be concerned primarily with classical physics. Much of the material presented will be applicable to quantum mechanical systems, and occasionally such references will be made.

²A note on notation: Throughout these notes vectors are denoted by bold lower case letters (e.g. $\mathbf{r}_i, \mathbf{f}_i$). The notation $\dot{\mathbf{r}}_i$ denotes the time derivative of \mathbf{r}_i , i.e., $\dot{\mathbf{r}}_i = d\mathbf{r}_i/dt$, and $\ddot{\mathbf{r}}_i = d^2\mathbf{r}_i/dt^2$.

where U is some potential energy function and $\mathbf{f}_i = -\partial U/\partial \mathbf{r}_i$ and K is the kinetic energy.

Another way to pose the classical law of motion is the Hamiltonian formulation, defined in terms of the particle positions $\{r_i\}$ and momenta $\{p_i = m_i \dot{r}_i\}$. It is convenient to adopt the notation (from quantum mechanics) $p \equiv$ momenta and $q \equiv$ positions, and to consider the scalar quantities p_i and q_i , which denote the entries of the vectors \mathbf{p} and \mathbf{q} . For a collection of N particles $\mathbf{p} \in \mathfrak{R}^{3N}$ and $\mathbf{q} \in \mathfrak{R}^{3N}$ are the collective positions and momenta vectors listing all $3N$ entries.

The so called Hamiltonian function is an expression of the total energy of a system:

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m_i} + U(q_1, q_2, \dots, q_{3N}) . \quad (1.1.3)$$

Hamilton's equations of motion are written as:

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad (1.1.4)$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} . \quad (1.1.5)$$

Hamilton's equations are equivalent to Newton's:

$$\dot{q}_i = p_i/m_i , \quad \dot{p}_i = -\partial U/\partial q_i = f_i . \quad (1.1.6)$$

So why bother with Hamilton when we are already familiar with Newton? The reason is that the Hamiltonian formulation is often convenient. For example, starting from the Hamiltonian formulation, it is straightforward to prove energy conservation:

$$\frac{dH}{dt} = \sum_{i=1}^{3N} \left(\frac{\partial H}{\partial q_i} \dot{q}_i + \frac{\partial H}{\partial p_i} \dot{p}_i \right) = \sum_{i=1}^{3N} \left[\left(\frac{\partial H}{\partial q_i} \right) \left(\frac{\partial H}{\partial p_i} \right) - \left(\frac{\partial H}{\partial p_i} \right) \left(\frac{\partial H}{\partial q_i} \right) \right] . \quad (1.1.7)$$

1.2 Ensembles and Thermodynamics

With our review of the equations of classical mechanics complete, we undertake our study of statistical physics with an introduction to the concepts of statistical thermodynamics. In this section thermodynamics will be briefly introduced as a consequence of the interaction of ensembles of large numbers of particles. The material loosely follows Chapter 1 of Pathria's *Statistical Mechanics* [3], and additional information can be found in that text.

1.2.1 An Ensembles of Particles

Consider a collection of N particles confined to a volume V , with total internal energy E . A system of this sort is often referred to as an NVE system, as N , V , and E are the three thermodynamic variables that are held fixed. [In general three variables are necessary to define the thermodynamic state of a system. Other thermodynamic properties, such as temperature for example, cannot be assigned in an NVE ensemble without changing at least one of the variables N , V , or E .] We will refer to the thermodynamic state as the *macrostate* of the system.

For a given macrostate, there is likely to be a large number of possible *microstates*, which correspond to different microscopic configurations of the particles in the system. According to the principles of quantum mechanics there is a finite fixed number of microscopic states that can be adopted by our NVE system. We denote this number of states as $\Omega(N, V, E)$ ³. For a classical system, the microstates are of course not discrete and the number of possible states for a fixed NVE ensemble is in general not finite. To see this imagine a system of a single particle ($N = 1$) travelling in an otherwise empty box of volume V . There are no external force fields acting on the particle so its total energy is $E = \frac{1}{2}mv^2$. The particle could be found in any location within the box, and its velocity could be directed in any direction without changing the thermodynamic macrostate defined by the fixed values of N , V , and E . Thus there are an infinite number of allowable states. Let us temporarily ignore this fact and move on with the discussion based on a finite (yet undeniably large) $\Omega(N, V, E)$. This should not bother those of us familiar with quantum mechanics. For classical applications we shall see that bookkeeping of the state space for classical systems is done as an integration of the continuous state space rather than a discrete sum as employed in quantum statistical mechanics.

At this point don't worry about how you might go about computing $\Omega(N, V, E)$, or how Ω might depend on N , V , and E for particular systems. We'll address these issues later. For now just appreciate that the quantity $\Omega(N, V, E)$ exists for an NVE system.

1.2.2 Microscopic Thermodynamics

Consider two such so called NVE systems, denoted system 1 and system 2, having macrostates defined by (N_1, V_1, E_1) and (N_2, V_2, E_2) , respectively.

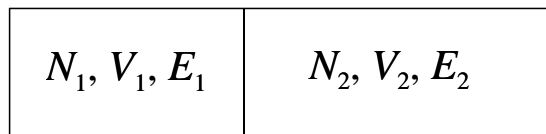


Figure 1.1: Two NVE systems in thermal contact.

Next, bring the two systems into thermal contact (see Fig. 1.1). By *thermal contact* we mean that the systems are allowed to exchange energy, but nothing else. That is E_1 and E_2 may change, but N_1 , N_2 , V_1 , and V_2 remain fixed. Of course the total energy remains fixed as well, that is,

$$E_0 = E_1 + E_2, \quad (1.2.8)$$

if the two systems interact only with one another.

Now we introduce a fundamental postulate of statistical mechanics: At any time, system 1 is equally likely to be in any one of its Ω_1 microstates and system 2 is equally likely to be in any one of its Ω_2 microstates (more on this assumption later). Given this assumption, the composite system is equally likely to be in an one of its $\Omega_0(E_1, E_2)$ possible microstates. The number $\Omega_0(E_1, E_2)$ can be expressed as the multiplication:

$$\Omega_0(E_1, E_2) = \Omega_1(E_1)\Omega_2(E_2). \quad (1.2.9)$$

³The number $\Omega(N, V, E)$ corresponds to the number of independent solutions to the Schrödinger equation that the system can adopt for a given eigenvalue E of the Hamiltonian.

Next we look for the value of E_1 (or equivalently, E_2) for which the number of microstates $\Omega_0(E_1, E_2)$ achieves its maximum value. We will call this achievement equilibrium, or more specifically thermal equilibrium. The assumption here being that physical systems naturally move from improbable macrostates to more probable macrostates⁴. Due to the large numbers with which we deal on the macro-level ($N \sim 10^{23}$), the most probable macrostate is orders of magnitude more probable than even closely related macrostates. That means that for equilibrium we must maximize $\Omega_0(E_1, E_2)$ under the constraint that the sum $E_0 = E_1 + E_2$ remains constant.

At the maximum $\partial\Omega_0/\partial E_1 = 0$, or

$$\frac{\partial [\Omega_1(E_1)\Omega_2(E_2)]}{\partial E_1} = \left[\frac{\partial\Omega_1}{E_1}\Omega_2 + \Omega_1 \frac{\partial E_2}{\partial E_1} \cdot \frac{\partial\Omega_2}{\partial E_2} \right]_{E_1=E_1^*, E_2=E_2^*} = 0, \quad (1.2.10)$$

where (E_1^*, E_2^*) denote the maximum point. Since $\partial E_2/\partial E_1 = -1$ from Eq. (1.2.8), Equation (1.2.10) reduces to:

$$\frac{1}{\Omega_1} \cdot \frac{\partial\Omega_1}{\partial E_1}(E_1^*) = \frac{1}{\Omega_2} \cdot \frac{\partial\Omega_2}{\partial E_2}(E_2^*), \quad (1.2.11)$$

which is equivalent to

$$\frac{\partial}{\partial E_1} \log \Omega_1(E_1^*) = \frac{\partial}{\partial E_2} \log \Omega_2(E_2^*). \quad (1.2.12)$$

To generalize, for any number of systems in equilibrium thermal contact,

$$\frac{\partial}{\partial E} \log \Omega = \beta = \text{constant} \quad (1.2.13)$$

for each system.

Let us pause and think for a moment: From our experience, what do we know about systems in equilibrium thermal contact? One thing that we know is that they should have the same temperature. Most people have an intuitive understanding of what temperature is. At least we can often gauge whether or not two objects are of equal or different temperatures. You might even know of a few ways to measure temperature. But do you have a precise physical definition of temperature?

It turns out that the constant β is related to the temperature T via

$$\beta = 1/kT, \quad (1.2.14)$$

where k is Boltzmann's constant. Therefore temperature of the NVE ensemble is expressed as

$$T = \frac{1}{k} \frac{\partial E}{\partial \log \Omega(N, V, E)}. \quad (1.2.15)$$

Until now some readers may have had a murky and vague mental picture of what the thermodynamic variable temperature represents. And now we all have a murky and vague mental picture of what temperature represents. Hopefully the picture will become more clear as we proceed.

Next consider that systems 1 and 2 are not only in thermal contact, but also their volumes are allowed to change in such a way that the total volume $V_0 = V_1 + V_2$ remains constant. For this

⁴Again, the term *macrostate* refers to the thermodynamic state of the composite system, defined by the variables N_1, V_1, E_1 , and N_2, V_2, E_2 . A more probable macrostate will be one that corresponds to more possible microstates than a less probable macrostate.

example imagine a flexible wall separates the two chambers – the wall flexes to allow pressure to equilibrate between the chambers, but the particles are not allowed to pass. Thus N_1 and N_2 remain fixed. For such a system we find that maximizing $\Omega_0(V_1, V_2)$ yields

$$\frac{\partial [\Omega_1(V_1)\Omega_2(V_2)]}{\partial V_1} = \left[\frac{\partial \Omega_1}{\partial V_1} \Omega_2 + \Omega_1 \frac{\partial \Omega_2}{\partial V_1} \cdot \frac{\partial \Omega_2}{\partial V_2} \right]_{V_1=V_1^*, V_2=V_2^*} = 0, \quad (1.2.16)$$

or

$$\frac{1}{\Omega_1} \cdot \frac{\partial \Omega_1}{\partial V_1}(V_1^*) = \frac{1}{\Omega_2} \cdot \frac{\partial \Omega_2}{\partial V_2}(V_2^*), \quad (1.2.17)$$

or

$$\frac{\partial}{\partial V_1} \log \Omega_1(V_1^*) = \frac{\partial}{\partial V_2} \log \Omega_2(V_2^*), \quad (1.2.18)$$

or

$$\frac{\partial}{\partial V} \log \Omega = \eta = \text{constant}. \quad (1.2.19)$$

We shall see that the parameter η is related to pressure, as you might expect. But first we have one more case to consider, that is mass equilibration. For this case, imagine that the partition between the chambers is perforated and particles are permitted to freely travel from one system to the next. The equilibrium statement for this system is

$$\frac{\partial}{\partial N} \log \Omega = \zeta = \text{constant}. \quad (1.2.20)$$

To summarize, we have the following:

1. **Thermal (Temperature) Equilibrium:** $\frac{\partial}{\partial E} \log \Omega = \beta.$
2. **Volume (Pressure) Equilibrium:** $\frac{\partial}{\partial V} \log \Omega = \eta.$
3. **Number (Concentration) Equilibrium:** $\frac{\partial}{\partial N} \log \Omega = \zeta.$

How do these relationships apply to the macroscopic world with which we are familiar? Recall the fundamental expression from thermodynamics:

$$dE = TdS - PdV + \mu dN \quad (1.2.21)$$

which tells us how to relate changes in energy E to changes in the variables entropy S , volume V , and number of particles N , occurring at temperature T , pressure P , and chemical potential μ . Equation (1.2.21) arose as an empiricism which relates the three intrinsic thermodynamic properties T , P , and μ to the three extrinsic properties N , V , and E . In developing this relationship, it was necessary to introduce a novel idea, entropy, which we will try to make some sense of below.

For constant V and N Equation (1.2.21) gives us

$$\left(\frac{\partial S}{\partial E} \right)_{N,V} = \frac{1}{T}. \quad (1.2.22)$$

Going back to Equation (1.2.13) we see that

$$S = k \log \Omega , \quad (1.2.23)$$

which makes sense if we think of entropy as a measure of the total disorder in a system. The greater the number of possible states, the greater the entropy. For pressure and chemical potential we find the following relationships:

For constant E and N we arrive at

$$\left(\frac{\partial S}{\partial V} \right)_{E,N} = \frac{P}{T} \quad \text{or} \quad \frac{\partial}{\partial V} \log \Omega = \eta, \quad \text{and} \quad \eta = \frac{P}{kT} . \quad (1.2.24)$$

For constant E and V we obtain

$$\left(\frac{\partial S}{\partial N} \right)_{E,V} = -\frac{\mu}{T} \quad \text{or} \quad \frac{\partial}{\partial N} \log \Omega = \zeta, \quad \text{and} \quad \zeta = -\frac{\mu}{kT} . \quad (1.2.25)$$

For completeness we repeat:

$$\left(\frac{\partial S}{\partial E} \right)_{N,V} = \frac{1}{T} \quad \text{or} \quad \frac{\partial}{\partial E} \log \Omega = \beta, \quad \text{and} \quad \beta = \frac{1}{kT} . \quad (1.2.26)$$

Through Eqs. (1.2.24)-(1.2.26) the internal thermodynamic parameters familiar to our everyday experience – temperature, pressure, and chemical potential – are related to the microscopic world of N , V , and E . The key to this translation is the formula $S = k \log \Omega$. As Pathria puts it, this formula “provides a bridge between the microscopic and the macroscopic” [3].

After introducing such powerful theory it is compulsory that we work out some example problems in the following sections. But I recommend that readers tackling this subject matter for the first time should pause to appreciate what they have learned so far. By asserting that entropy (the most mysterious property to arise in thermodynamics) is simply proportional to the log of the number of accessible microstates, we have derived direct relationships between the microscopic to the macroscopic worlds.

Before moving on to the application problems I should point out one more thing about the number Ω – that is its name. The quantity Ω is commonly referred to as the *microcanonical partition function*, a partition function being a statistically weighted sum over the possible states of a system. Since Ω is a non-biased enumeration of the microstates, we refer to it as microcanonical. Similarly, another name for the NVE ensemble is the microcanonical ensemble. Later we will meet the canonical (NVT) and grand canonical (μ VT) ensembles.

1.2.3 Formalism for Classical Systems

The microcanonical partition function for a classical system is proportional to the volume of *phase space* accessible by the system. For a system of N particles the phase space is a $6N$ -dimensional space encompassing the $3N$ variables q_i and the $3N$ variables p_i , and the partition function is

proportional to the integral:

$$\Omega(N, V, E) \sim \int \delta(H(p_1, p_2, \dots, p_{3N}; q_1, q_2, \dots, q_{3N}) - E) dp_1 dp_2 \dots dp_{3N} dq_1 dq_2 \dots dq_{3N} \quad (1.2.27)$$

or using vector shorthand

$$\Omega(N, V, E) \sim \int \delta(H(\mathbf{p}, \mathbf{q}) - E) d^{3N} \mathbf{p} d^{3N} \mathbf{q} \quad (1.2.28)$$

where the notation d^{3N} reminds us that the integration is over $3N$ -dimensional space.

In Eqs. (1.2.27)-(1.2.28) the delta function restricts the integration to the the constant energy hypersurface defined by $H(\mathbf{p}, \mathbf{q}) = E = \text{constant}$. [In general we won't be integrating this difficult-looking delta function directly. Just think of it as a mathematical shorthand for restricting the phase space to a constant-energy subspace.]

We notice that Equation (1.2.28) lacks a constant of proportionality that allows us to replace the proportionality symbol with the equality symbol and compute $\Omega(N, V, E)$. This constant comes from relating a given volume of the classical phase space to a discrete number of quantum microstates. It turns out that this constant of proportionality is $1/N!h^{3N}$, where h is Planck's constant. Thus

$$\Omega(N, V, E) = \frac{1}{N!h^{3N}} \int_H d^{3N} \mathbf{p} d^{3N} \mathbf{q}, \quad (1.2.29)$$

where the integration \int_H is over the subspace defined by $H(\mathbf{p}, \mathbf{q}) = E$.

From where does the constant $N!h^{3N}$ come? We know from quantum mechanics that to specify the position of a particle, we have to allow its momentum to lose coherence. Similarly, when we specify the momentum with increasing certainty, the position loses coherence. If we consider Δq and Δp to be the fundamental uncertainties in position and momenta, then Planck's constant tells us how these uncertainties depend upon one another:

$$h \approx \Delta p \Delta q. \quad (1.2.30)$$

Thus the minimal discrete volume element of phase space is approximately h for a single particle in one dimension, or h^{3N} when there are $3N$ degrees of freedom. This explains (heuristically at least) the factor of h^{3N} . From where does the $N!$ come? We shall see when we enumerate the quantum states of the ideal gas, the indistinguishability of the particles further reduces the partition function by a factor of $N!$, which fixes Ω as the number of distinguishable microstates.

1.3 Example Problem: Classical Ideal Gas

A system of noninteracting monatomic particles is referred to as the ideal gas. For such a system the kinetic energy is the only contribution to the Hamiltonian $H = \sum p_i^2/2m$, and

$$\Omega(N, V, E) = \frac{1}{N!h^{3N}} \int_V d^{3N} \mathbf{q} \int_H d^{3N} \mathbf{p} \quad (1.3.31)$$

where \int_V represents integration over the volume of the container. [The integral can be split into \int_V and \int_H components because $H(\mathbf{p})$ does not depend on particle positions in any way.] Therefore

$$\Omega(N, V, E) = \frac{1}{N!h^{3N}} V^N \int_H d^{3N} \mathbf{p}. \quad (1.3.32)$$

It turns out that knowing $\Omega \sim V^N$ is enough to derive the ideal gas law:

$$\frac{P}{kT} = \frac{\partial \log \Omega}{\partial V} = \frac{N}{V} \quad (1.3.33)$$

or

$$PV = kNT = nRT, \quad (1.3.34)$$

where $R = kN_A$ is the gas constant, n is the number of particles in moles, and N_A is Avogadro's number. For other properties (like energy and entropy) we need to do something with the \int_H integral in Equation (1.3.32).

We approach this integral by first noticing that the constant energy surface $\sum_{i=1}^{3N} p_i^2 = 2mE$ defines a sphere of radius $R = (2mE)^{1/2}$ in $3N$ -dimensional space. We can find the volume and surface area of such a sphere from a handbook of mathematical functions. In \mathfrak{R}^{3N} the volume and surface area of a sphere are given by:

$$V_{3N}(R) = \frac{\pi^{3N/2}}{(3N/2)!} R^{3N} \quad \text{and} \quad S_{3N}(R) = \frac{2\pi^{3N/2}}{(3N/2 - 1)!} R^{3N-1}, \quad (1.3.35)$$

[One may wonder what to do in the case where $3N/2$ is non-integral. Specifically, how would one define the $(3N/2)!$ and $(3N/2 - 1)!$ factorials? We could use gamma functions $\Gamma(3N/2 + 1)$ and $\Gamma(3N/2)$, where $\Gamma(\mu)$ is a generalization of the factorial function: $\Gamma(\mu) = \int_0^\infty e^{-x} x^{\mu-1} dx$. It turns out that $\Gamma(\mu) = (\mu - 1)!$ for $\mu > 0$. So in the above equations for surface area and volume we are using the generalized factorial function $\mu! = \int_0^\infty e^{-x} x^\mu dx$, which is the same as the regular factorial function for non-negative integer arguments.]

Returning to the task at hand: we wish to evaluate the integral $\int_H d^{3N} \mathbf{p}$ over the constant energy surface in \mathfrak{R}^{3N} defined by $\sum_{i=1}^{3N} p_i^2 = 2mE$. One way to do this is to take

$$\int_H d^{3N} \mathbf{p} = S_{3N}((2mE)^{1/2}) \quad (1.3.36)$$

which gives us

$$\Omega(N, V, E) = \frac{3N}{N!(3N/2)!} \left[\frac{V}{h^3} (2\pi mE)^{3/2} \right]^N (2mE)^{1/2}. \quad (1.3.37)$$

Taking the log of this function, we will employ Stirling's approximation, that $\log N! \approx N \log N - N$, for large N . Thus

$$\log \Omega(N, V, E) = N \log \left[\frac{V}{h^3} (2\pi mE)^{3/2} \right] + \frac{5N}{2} - N \log \left[N \left(\frac{3N}{2} \right)^{3/2} \right] + \log(3N) - \frac{1}{2} \log(2mE). \quad (1.3.38)$$

In the limit of large N , we know that the first three terms grow faster than the last two. So combining the $N \log(\cdot)$ terms and keeping only terms of order N and $N \log(N)$ results in

$$\log \Omega(N, V, E) \approx N \log \left[\frac{V}{h^3 N} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{5N}{2}, \quad (1.3.39)$$

or the entropy

$$S(N, V, E) \approx kN \log \left[\frac{V}{h^3 N} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{5kN}{2}. \quad (1.3.40)$$

Using our thermodynamic definition of temperature,

$$\left(\frac{\partial S}{\partial E} \right)_{N,V} = \frac{3}{2} kN \frac{1}{E} = \frac{1}{T}, \quad \text{or} \quad (1.3.41)$$

$$E = \frac{3}{2} NkT \quad \text{and} \quad T = \frac{2}{3k} \left(\frac{E}{N} \right). \quad (1.3.42)$$

As you can see, the internal energy is proportional to the temperature and, as expected, the number of particles. Inserting $E = 3NkT/2$ into Equation (1.3.40), we get:

$$S(N, V, T) = Nk \log \left(\frac{V}{N} \right) + \frac{3}{2} Nk \left[\frac{5}{3} + \log \left(\frac{2\pi mkT}{h^2} \right) \right] \quad (1.3.43)$$

which is the Sackur-Tetrode equation for entropy.

We should note that if, instead of taking the integral $\int_H d^{3N} \mathbf{p}$ to be the surface area of the constant-energy sphere, we had allowed the energy to vary within some small range, we would have arrived at the same results. In fact we shall see that, for the quantum mechanical ideal gas, that is precisely what we will have to do.

1.4 Example Problem: Quantum Ideal Gas

As we saw for the classical ideal gas, analysis of the quantum mechanical ideal gas will hinge on the enumeration of the partition function, and not on the analysis of the underlying equations of motion. Nevertheless, it is necessary to introduce some quantum mechanical ideas to understand the ideal gas from the perspective of quantum mechanics. It will be worthwhile to go through this exercise to appreciate how statistical mechanics naturally applies to the discrete states observed in quantum systems.

First we must find the quantum mechanical state, or wave function $\psi(x, y, z)$, of a single particle living in an otherwise empty box. The equation describing the shape of the constant-energy wave function for a single particle in the presence of no potential field is

$$-\frac{\hbar^2}{8\pi^2 m} \nabla^2 \psi(x, y, z) = -\frac{\hbar^2}{8\pi^2 m} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \psi(x, y, z) = E_1 \psi(x, y, z). \quad (1.4.44)$$

We solve Equation (1.4.44), a form of Schrödinger's equation, with the condition that $\psi(x, y, z) \rightarrow 0$ on the walls of the container. The constant energy E_1 (the subscript "1" reminds us that this is

the energy of a single particle) is an eigenvalue of the Hamiltonian operator on the left hand side of Equation (1.4.44). Under these conditions the single-particle wave function has the form:

$$\psi(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \quad (1.4.45)$$

where the n_x , n_y , and n_z can be any of the positive integers (1, 2, 3, ...). Here the box is assumed to be a cube with sides of length L . The energy E_1 is related to these numbers via

$$E_1 = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) . \quad (1.4.46)$$

If energy E_1 is fixed then the number of possible quantum states is equal to the number of sets $\{n_x, n_y, n_z\}$ for which

$$(n_x^2 + n_y^2 + n_z^2) = \frac{8mV^{2/3}}{h^2} E_1 \quad (1.4.47)$$

where $V^{2/3} = L^2$. For a system of N noninteracting particles, we have N such sets of three integers, and the energy is the sum of the energies from each particle:

$$\sum_{i=1}^{3N} n_i^2 = \frac{8mV^{2/3}}{h^2} E = E^* \quad (1.4.48)$$

where E now represents the total energy of the system, and E^* is a nondimensionalization of energy.

The similarities between the classical ideal gas and Equation (1.4.48) are striking. As in the classical system, the constant energy condition limits the quantum phase space to the surface of a sphere in $3N$ dimensional space. The important difference is that for the quantum mechanical system the phase space is discrete because the $\{n_i\}$ are integers. This discrete nature of the phase space means that $\Omega(N, V, E)$ can be more difficult to pin down than it was for the classical case. To see this imagine the regularly spaced lattice in $3N$ dimensional space which is defined by the set of positive integers $\{n_i\}$. The number $\Omega(N, V, E)$ is equal to the number of lattice points which fall on the surface of the sphere defined by Equation (1.4.48)—this number is an irregular function of (N, V, E) . As an illustration, return to the single particle case. There is one possible quantum state for $E_1 = \frac{3h^2}{8mV^{2/3}}$ and three possible states for $E_1 = \frac{3h^2}{4mV^{2/3}}$. Yet there are no possible states for energies falling between these two energies. Thus the distinct microstates can be difficult to enumerate. We shall see that as E and N become large, the discrete spectrum becomes more regular and smooth and easier to handle.

Consider the number $\Sigma(N, V, E)$ which we define to be the number of microstates with energy less than or equal to E . In the limit of large E and large N , $\Sigma(N, V, E)$ is equal to the volume of the “positive compartment” of a $3N$ dimensional sphere. Recalling Equation (1.3.35) gives

$$\Sigma(E^*) = \left(\frac{1}{2}\right)^{3N} \left[\frac{\pi^{3N/2}}{(3N/2)!} E^{*3N/2} \right] . \quad (1.4.49)$$

[The factor $(1/2)^{3N}$ comes from limiting $\Sigma(E^*)$ to the volume spanned by the positive values of $\{n_i\}$.] Plugging in $E^* = 8mV^{2/3} E/h^2$ results in

$$\Sigma(N, V, E) = \left(\frac{V}{h^3}\right)^N \frac{(2\pi m E)^{3N/2}}{(3N/2)!} . \quad (1.4.50)$$

Next we calculate $\Omega(N, V, E)$ from $\Sigma(N, V, E)$ by assuming that the energy varies over some small range $E \pm \Delta$, where $\Delta \ll E$. The enumeration of microstates within this energy range can be calculated as

$$\Omega(N, V, E; \Delta) \approx \Delta \frac{\partial \Sigma(N, V, E)}{\partial E}, \quad (1.4.51)$$

which is valid for small Δ (relative to E). From Equation (1.4.50), we have

$$\frac{\partial \Sigma}{\partial E} = \left(\frac{3N}{2} \right) \frac{\Sigma}{E}, \quad (1.4.52)$$

and thus

$$\Omega(N, V, E; \Delta) = \left(\frac{3N}{2} \right) \frac{\Sigma}{E} \Delta \quad (1.4.53)$$

and

$$\log \Omega(N, V, E; \Delta) = N \log \left[\frac{V}{h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{3N}{2} + \log \left(\frac{3N}{2} \right) + \log \left(\frac{\Delta}{E} \right). \quad (1.4.54)$$

As for the classical ideal gas, we take terms of order $N \log N$ and order N which grow much faster than $\log N$ and the constant terms. Thus

$$\log \Omega(N, V, E) = N \log \left[\frac{V}{h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{3N}{2}. \quad (1.4.55)$$

From Equation (1.4.55) we could derive the thermodynamics of the system, just as we did for the classical ideal gas. However we notice that the entropy, which is given by

$$S(N, V, E) = kN \log \left[\frac{V}{h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{3kN}{2}, \quad (1.4.56)$$

is not equivalent to the Sackur-Tetrode expression, Equation (1.3.43). [The difference is a factor of $1/N!$ in the partition function, which is precisely the factor that we added to the classical partition function, Equation (1.2.29), with no solid justification.]

In fact, one might notice that the entropy, according to Equation (1.4.56) is not an extensive measure! If we increase the volume, energy, and number of particles by some fixed proportion, then the entropy will not increase by the same proportion. What have we done wrong? How can we recover the missing factor of $1/N!$?

To justify this extra factor, we need to consider that the particles making up the ideal gas system are not only identical, they are also indistinguishable. We label the possible states that a given particle can be in as state 1, state 2, etc., and denote the number that exist in each state at a given instant as w_1, w_2 , etc. Thus there are w_1 particles in state 1, and w_2 particles in state 2, and so on. Since the particles are indistinguishable, we can rearrange the particles of the system (by switching the states of the individual particles) in any way as long as the numbers $\{w_i\}$ remain unchanged, and the microstate of the system is unchanged. The number of ways the particles can be rearranged is given by

$$\frac{N!}{w_1! w_2! \dots}$$

Introducing another assumption, that if the temperature is high enough that the number of possible microstates of a single particle is so fantastically large that each possible single particle state is represented by, at most, one particle, then $w_i! = 1$ (because each w_i is either 1 or 0). Thus we need to correct the partition function by a factor $1/N!$, and as a result Equation (1.4.55) reduces to Equation (1.3.39).

Problems

- (Warm-up Problem) Invert Equation (1.3.40) to produce an equation for $E(S, V, N)$. Using this equation and our basic thermodynamic definitions, derive the pressure-volume law (equation of state). How does this compare with Equation (1.3.34)?
- (Particle in a box) Verify that Equation (1.4.45) is a solution to Equation (1.4.44). Evaluate the integral $\int_V \psi^2 dx dy dz$, for the one-particle system. What are the 6 lowest possible energies of this system? For each of the 6 lowest energies count the number of corresponding quantum states. Are the energy levels equally spaced? Does the number of quantum states increase monotonically with E ?
- (Gas of finite size particles) Consider a gas of particles that do not interact in any way except that, each particle occupies a finite volume v_o which cannot be overlapped by other particles. What consequences does this imply for the ideal gas law? [Hint: return to the relationship $\Omega(V) \sim \int d^{3N} \mathbf{q}$. You might try assuming that each particle is a solid sphere.] Plot P vs. V for both the ideal gas law and the P - V relationship for the finite-volume particles. (Use $T = 300\text{K}$ and $n = 1$ mole.) Discuss the following questions: Where do the curves differ? Where are they the same? Why?
- (Phase space of simple harmonic oscillator) Consider a system made up of a single particle of mass m attached to a linear spring, with spring constant a . One end of the spring is attached to the particle, the other is fixed in space, and the particle is free to move in one dimension, q . What is the Hamiltonian $H(p, q)$ for this system? Plot the phase space for $H(p, q) = E$. Find an expression for the entropy $S(E)$ of this system. You can assume that energy varies over some small range: $E \pm \Delta$, $\Delta \ll E$. Using $1/T = \partial S / \partial E$, derive an expression for the “temperature” of this system. We saw that the ideal gas has an internal temperature of $3kT/2$ per particle. How does the energy as a function of temperature for the simple harmonic oscillator compare to that for the ideal gas? Does it make sense to calculate the “temperature” of a one-particle system? Why or why not?

Chapter 2

Canonical Ensemble and Equipartition

In Chapter 1 we studied the statistical properties of a large number of particles interacting within the microcanonical ensemble – a closed system with fixed number of particles, volume, and internal energy. While the microcanonical ensemble theory is sound and useful, the canonical ensemble (which fixes the number of particles, volume, and temperature while allowing the energy to vary) proves more convenient than the microcanonical for numerous applications. For example, consider a solution of macromolecules stored in a test tube. We may wish to understand the conformations adopted by the individual molecules. However each molecule exchanges energy with its environment, as undoubtedly does the entire system of the solution and its container. If we focus our attention on a smaller subsystem (say one molecule) we adopt a canonical treatment in which variations in energy and other properties are governed by the statistics of an ensemble at a fixed thermodynamic temperature.

2.1 The Canonical Distribution

2.1.1 A Derivation

Our study of the canonical ensemble begins by treating a large heat reservoir thermally coupled to a smaller system using the microcanonical approach. The energy of the heat reservoir denoted E_r and the energy of the smaller subsystem, E . The system is assumed closed and the total energy is fixed: $E + E_r = E_o = \text{constant}$.

This system is illustrated in Fig. (2.1). For a given energy E of the subsystem, the reservoir can obtain $\Omega_r(E_o - E)$ microstates, where Ω_r is the microcanonical partition function. According to our standard assumption that the probability of a state is proportional to the number of microstates available:

$$P \sim \Omega_r(E_r) = \Omega(E_o - E) . \quad (2.1.1)$$

We take the log of the microcanonical partition function and expand about $\log \Omega_r(E_o)$:

$$\log P \sim \log \Omega_r(E_o) - \left. \frac{\partial \log \Omega_r}{\partial E_r} \right|_{E_r=E_o} (E) + O(E^2) . \quad (2.1.2)$$



Figure 2.1: A system with energy E thermally coupled to a large heat reservoir with energy E_r .

For large reservoirs ($E \ll E_o$) the higher order terms in Equation (2.1.2) vanish and we have

$$\log P \sim \log \Omega_r = \text{constant} - \frac{E}{kT}, \quad (2.1.3)$$

where we have used the microcanonical definition of thermodynamic temperature T . Thus

$$P \sim e^{-\beta E} \quad (2.1.4)$$

where $\beta = 1/kT$ has been defined previously. Equation 2.1.4) is the central result in canonical ensemble theory. It tells us how the probability of a given energy of a system depends on its energy.

2.1.2 Another Derivation

A second approach to the canonical distribution found in Feynman's lecture notes on statistical mechanics [1] is also based on the central idea from microcanonical ensemble theory that the probability of a microstate is proportional to Ω . Thus

$$\frac{P(E_1)}{P(E_2)} = \frac{\Omega(E_o - E_1)}{\Omega(E_o - E_2)} \quad (2.1.5)$$

where again E_o is the total energy of system and a heat reservoir to which the system is coupled. The energies E_1 and E_2 are possible energies of the system and Ω is the microcanonical partition function for the reservoir. (The subscript r has been dropped.)

Next Feynman makes us of the fact that energy is defined only up to an additive constant. In other words, there is no absolute energy value, and we can always add a constant, say ϵ , so long as we add the same ϵ to all relevant values of energy. Without changing its physical meaning Equation (2.1.5) can be modified:

$$\frac{P(E_1)}{P(E_2)} = \frac{\Omega(E_o - E_1 + \epsilon)}{\Omega(E_o - E_2 + \epsilon)}. \quad (2.1.6)$$

Next we define the function $g(x) = \Omega(E_o - E_2 + x)$. Equating the right hand sides of Eqs. (2.1.5) and (2.1.6) results in

$$\Omega(E_o - E_1)\Omega(E_o - E_2 + \epsilon) = \Omega(E_o - E_2)\Omega(E_o - E_1 + \epsilon) \quad (2.1.7)$$

or

$$g(E_2 - E_1)g(\epsilon) = g(0)g(\epsilon + E_2 - E_1). \quad (2.1.8)$$

Equation (2.1.8) is uniquely solved by:

$$g(\epsilon) = g(0)e^{-\beta\epsilon}, \quad (2.1.9)$$

where β is some constant. Therefore the probability of a given energy E is proportional to $e^{-E/kT}$, which is the result from Section 2.1.1. To take the analysis one step further we can normalize the probability:

$$P(E) = \frac{e^{-\beta E}}{Q}, \quad (2.1.10)$$

where

$$Q = \sum_i e^{-\beta E_i} \quad (2.1.11)$$

is the canonical partition function and Equation (2.1.10) defines the canonical distribution function. [Feynman doesn't go on to say why $\beta = 1/kT$; we will see why later.] Summation in Equation (2.1.11) is over all possible microstates. Equation (2.1.11) is equation #1 on the first page of Feynman's notes on statistical mechanics [1]. Feynman calls Equation (2.1.10) the "summit of statistical mechanics, and the entire subject is either the slide-down from this summit...or the climb-up." The climb took us a little bit longer than it takes Feynman, but we got here just the same.

2.1.3 One More Derivation

Since the canonical distribution function is the summit, it may be instructive to scale the peak once more from a different route. In particular we seek a derivation that stands on its own and does not rely on the microcanonical theory introduced earlier.

Consider a collection of M identical systems which are thermally coupled and thus share energy at a constant temperature. If we label the possible states of the system $i = 1, 2, \dots$ and denote the energy these obtainable microstates as E_i , then the total number of systems is equal to the summation,

$$\sum_i n_i = M, \quad (2.1.12)$$

where the n_i are the number of systems which correspond to microstate i . The total energy of the ensemble can be computed as

$$\sum_i n_i E_i = MU \quad (2.1.13)$$

where U is the average internal energy of the systems in the ensemble.

Eqs. (2.1.12) and (2.1.13) $\{n_i\}$ represent constraints on the ways microstates can be distributed amongst the members of the ensemble. Analogous to our study of microcanonical statistics, here we assume that the probability of obtaining a given set $\{n_i\}$ of numbers of systems in each microstate is proportional to the number of ways this set can be obtained. Imagine the numbers n_i to represent bins count the number of systems at a given state. Since the systems are identical, they can be shuffled about the bins as long as the numbers n_i remain fixed. The number of possible ways to shuffle the states about the bins is given by:

$$W(\{n_i\}) = \frac{M!}{n_1!n_2!\dots}. \quad (2.1.14)$$

One way to arrive at the canonical distribution is via maximizing the number W under the constraints imposed by Eqs. (2.1.12) and (2.1.13). At the maximum value,

$$\nabla W \cdot \vec{\delta} = 0, \quad (2.1.15)$$

where the gradient operator is $\nabla = \frac{\partial}{\partial n_1} + \frac{\partial}{\partial n_2} + \dots$, and $\vec{\delta}$ is a vector which represents a direction allowed by the constraints.

[The occasional mathematician will point out the hazards of taking the derivative of a discontinuous function with respect to a discontinuous variable. Easy-going types will be satisfied with the explanation that for astronomically large numbers of possible states, the function W and the variables $\{n_i\}$ are effectively continuous. Sticklers for mathematical rigor will have to find satisfaction elsewhere.]

We can maximize the number W by using the method of Lagrange multipliers. Again, it is convenient to work with the log of the number W , which allows us to apply Stirling's approximation.

$$\log W = M \log(M!) - \sum_i n_i \log(n_i!). \quad (2.1.16)$$

This equation is maximized by setting

$$\nabla \log W - \alpha \nabla \sum_i n_i - \beta \nabla \sum_i n_i E_i = 0, \quad (2.1.17)$$

where α and β are the unknown Lagrange multipliers. The second two terms in this equations are the gradients of the constraint functions. Evaluating Equation (2.1.17) results in:

$$-\log n_i - 1 - \alpha - \beta E_i = 0 \quad (2.1.18)$$

in which the entries of the gradients in Equation (2.1.17) are entirely uncoupled. Thus Equation (2.1.18) gives us a straightforward expression for the optimal n_i :

$$n_i = e^{-(\alpha + \beta E_i)} \quad (2.1.19)$$

where the unknown constants α and β can be obtained by returning to the constraints.

The probability of a given state follows from the first constraint (2.1.12)

$$P_j = \frac{e^{-\beta E_j}}{\sum_i e^{-\beta E_i}} \quad (2.1.20)$$

which is by now familiar as the canonical distribution function. As you might guess, the parameter β will once again turn out to be $1/kT$ when we examine the thermodynamics of the canonical ensemble.

[Note that the above derivation assumed that the numbers of states $\{n_i\}$ assumes the most probable distribution, e.g., maximizes W . For a more rigorous approach which directly evaluates the expected values of n_i see Section 3.2 of Pathria [3].]

2.2 More Thermodynamics

With the canonical distribution function defined according to Equation (2.1.20), we can calculate the expected value of a property of a canonical system

$$\langle f \rangle = \frac{\sum_i f_i e^{-\beta E_i}}{Q} \quad (2.2.21)$$

where $\langle f \rangle$ is the expected value of some observable property f , and f_i is the value of f corresponding to the i^{th} state. For example, the internal energy of a system in the canonical ensemble is defined as the expected, or average, value of E :

$$U = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = -\frac{\partial}{\partial \beta} \log \left[\sum_i e^{-\beta E_i} \right] = -\frac{\partial}{\partial \beta} \log Q. \quad (2.2.22)$$

The Helmholtz free energy A is defined as $A = U - TS$, and incremental changes in A can be related to changes in internal energy, temperature, and entropy by $dA = dU - Tds - SdT$. Substituting our basic thermodynamics accounting for the internal energy $dU = TdS - PdV + \mu dN$, results in:

$$dA = -SdT - PdV + \mu dN. \quad (2.2.23)$$

Thus, the internal energy $U = A + TS$ can be expressed as:

$$U = A - T \left(\frac{\partial A}{\partial T} \right)_{N,V} = -T^2 \left[\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right]_{N,V} = \left[\frac{\partial(A/T)}{\partial(1/T)} \right]_{N,V}. \quad (2.2.24)$$

We can equate Eqs. (2.2.22) and (2.2.24) by setting $\beta = 1/kT$. [So far we have still not shown that k is the same constant (Boltzmann's constant) that we introduced in Chapter 1; here k is assumed to be some undetermined constant.] The Helmholtz free energy can be calculated directly from the canonical partition function:

$$A = -kT \log Q. \quad (2.2.25)$$

How do we equate the constant k of this chapter to Boltzmann's constant of the previous chapter? We know that the probability of a given state i in the canonical ensemble is given by:

$$P_i = e^{-\beta E_i} / Q. \quad (2.2.26)$$

Next we take the expected value of the log of this quantity:

$$\langle \log P_i \rangle = -\log Q - \beta \langle E_i \rangle = -\log Q - \beta U = \beta(A - U). \quad (2.2.27)$$

[You might think that in the study of statistical mechanics, we are terribly eager to take logarithms of every last quantity that we derive, perhaps with no *a priori* justification. Of course, the justification is sound in hindsight. So when in doubt in statistical mechanics, try taking a logarithm. Maybe something useful will appear!]

A useful relationship follows from Equation (2.2.27). Since $A - U = -TS$, $S = -k\langle \log P_i \rangle$. The expected value of $(\log P_i)$ is straightforward to evaluate:

$$S = -k \sum_i P_i \log P_i . \quad (2.2.28)$$

From this equation, we can make a connection to the microcanonical ensemble, and the k from Chapter 1. In a microcanonical ensemble, each state is equally likely. Therefore $P_i = \Omega^{-1}$, and Equation (2.2.28) becomes

$$S = k \sum_i \Omega^{-1} \log \Omega = k \sum_i \frac{d}{d\Omega} \log \Omega = k \log \Omega , \quad (2.2.29)$$

which should look familiar. Thus the k of Chapter 2 is identical to the k of Chapter 1, Boltzmann's constant.

2.3 Formalism for Classical Systems

As in the construction of the classical microcanonical partition function, in defining the canonical partition function for classical systems we make use of the correction factor described in Chapter 1 which relates the volume of classical phase space to a distinct number of microstates. An elementary volume of classical phase space $d^{3N} \mathbf{q} d^{3N} \mathbf{p}$ is assumed to correspond to $d^{3N} \mathbf{q} d^{3N} \mathbf{p} / N! h^{3N}$ distinguishable microstates. The partition function becomes:

$$Q = \frac{1}{N! h^{3N}} \int e^{-\beta H} d^{3N} \mathbf{q} d^{3N} \mathbf{p} , \quad (2.3.30)$$

and mean values of a physical property f are expressed as:

$$\langle f \rangle = \frac{\int f(\mathbf{q}, \mathbf{p}) e^{-\beta H(\mathbf{q}, \mathbf{p})} d^{3N} \mathbf{q} d^{3N} \mathbf{p}}{\int e^{-\beta H(\mathbf{q}, \mathbf{p})} d^{3N} \mathbf{q} d^{3N} \mathbf{p}} . \quad (2.3.31)$$

2.4 Equipartition

The study of molecular systems often makes use of the equipartition theorem, which describes the correlation structure of the variables of a Hamiltonian system in the canonical ensemble. Recalling that the classical Hamiltonian of a system H is a function of $6N$ independent momentum and position coordinates. We denote these coordinates by x_i and seek to evaluate the ensemble average:

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{\int \left(\frac{\partial H}{\partial x_j} \right) e^{-\beta H} d^{6N} \mathbf{x}}{\int e^{-\beta H} d^{6N} \mathbf{x}} , \quad (2.4.32)$$

where the integration is over all possible values of the $6N$ x coordinates. The Hamiltonian H depends on the internal coordinates although the dependence is not explicitly stated in Equation (2.4.32).

Using integration by parts in the numerator to carry out the integration over the x_j coordinate produces:

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{\int \left[\left(-\frac{x_i}{\beta} e^{-\beta H} \right) \Big|_{x_j^-}^{x_j^+} + \int \frac{1}{\beta} \left(\frac{\partial x_i}{\partial x_j} \right) e^{-\beta H} dx_j \right] d^{6N-1} \mathbf{x}}{\int e^{-\beta H} d^{6N} \mathbf{x}} \quad (2.4.33)$$

where the integration over $d^{6N-1} \mathbf{x}$ indicates integration over all x coordinates excluding x_j . The notation x_j^- and x_j^+ indicates the extreme values accessible to the coordinate x_j . Thus for a momentum coordinate these extreme values would be $\pm\infty$, while for a position coordinate the extreme values would come from the boundaries of the container. In either case, the first term of the numerator in Equation (2.4.33) vanishes because the Hamiltonian is expected to become infinite at the extreme values of the coordinates.

Equation (2.4.33) can be further simplified by noting that since the coordinates are independent, $\partial x_i / \partial x_j = \delta_{ij}$, where δ_{ij} is the usual Kronecker delta function. [$\delta_{ij} = 1$ for $i = j$; $\delta_{ij} = 0$ for $i \neq j$.] After simplification we are left with

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = kT \delta_{ij}, \quad (2.4.34)$$

which is the general form of the equipartition theorem for classical systems. It should be noted that this theorem is only valid when all coordinates of the system can be freely and independently excited, which may not always be the case for certain systems at low temperatures. So we should keep in mind that the equipartition theorem is rigorously true only in the limit of high temperature.

Equipartition tells us that for any coordinate $\langle x \frac{\partial H}{\partial x} \rangle = kT$. Applying this theorem to a momentum coordinate, p_i , we find,

$$\langle p_i \frac{\partial H}{\partial p_i} \rangle = \langle p_i \dot{q}_i \rangle = kT. \quad (2.4.35)$$

[Remember the basic formulation of Hamiltonian mechanics.] Similarly,

$$\langle q_i \dot{p}_i \rangle = -kT. \quad (2.4.36)$$

From Equation (2.4.35), we see that the average kinetic energy associated with the i^{th} coordinate is $\langle mv_i^2/2 \rangle = kT/2$. For a three dimensional system, the average kinetic energy of each particle is specified by $3kT/2$. If the potential energy of the Hamiltonian is a quadratic function of the coordinates, then each degree of freedom will contribute $kT/2$ energy, on average, to the internal energy of the system.

2.5 Example Problem: Harmonic Oscillators and Blackbody Radiation

A classical problem in statistical mechanics is that of a blackbody radiation. What is the equilibrium energy spectrum associated with a cavity of a given volume and temperature?

2.5.1 Classical Oscillator

The vibrational modes of a simple material can be approximated by modeling the material as a collection of simple harmonic oscillators, with Hamiltonian (for the case of classical mechanics):

$$H = \sum_{i=1}^N \left[\frac{m\omega_o^2}{2} q_i^2 + \frac{1}{2m} p_i^2 \right], \quad (2.5.37)$$

where each of the identical N oscillators vibrates with one degree of freedom. The natural frequency of the oscillators is denoted by ω_o . The partition function for such a system is expressed as:

$$Q = \frac{1}{N! h^N} \int \exp \left\{ -\beta \sum_{i=1}^N \left[\frac{m\omega_o^2}{2} q_i^2 + \frac{1}{2m} p_i^2 \right] \right\} d^N \mathbf{q} d^N \mathbf{p}, \quad (2.5.38)$$

which is product of N single-particle integrals:

$$Q = \frac{1}{N!} \left[\frac{1}{h} \int \exp \left\{ -\beta \left(\frac{m\omega_o^2}{2} q^2 + \frac{1}{2m} p^2 \right) \right\} dq dp \right]^N. \quad (2.5.39)$$

Using the identity for Gaussian distributions $\int e^{-x^2} dx = \sqrt{\pi}$, Equation (2.5.39) is reduced to

$$Q = \frac{1}{N!} \left[\frac{1}{h} \left(\frac{2\pi}{\beta m \omega_o^2} \right)^{1/2} \left(\frac{2\pi m}{\beta} \right)^{1/2} \right]^N \quad (2.5.40)$$

or

$$Q = \frac{1}{N!} \left[\frac{2\pi}{\beta h \omega_o} \right]^N. \quad (2.5.41)$$

Remember that the factor $1/N!$ corrects for the fact that the particles in the system are indistinguishable. If the particles in the system are distinguishable, then the partition function is given by:

$$Q = \left[\frac{2\pi}{\beta h \omega_o} \right]^N, \quad (2.5.42)$$

which is the single-particle partition function raised to the N power.

2.5.2 Quantum Oscillator

The one-dimensional Schrödinger wave equation for a particle in a harmonic potential is:

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + \frac{1}{2} m \omega_o^2 x^2 \psi = E \psi, \quad (2.5.43)$$

where the constant \hbar is equal to $h/2\pi$, ω_o is the angular frequency associated with the classical oscillator, and E is the energy eigenvalue of the Schrödinger operator. This equations has, for quantum numbers $n = 0, 1, 2, \dots$, energy values of $E_n = \hbar\omega_o/2, 3\hbar\omega_o/2, 5\hbar\omega_o/2, \dots$. The so-called Planck oscillator excludes the $n = 0$ eigenvalue. [For a complete analysis and associated wave functions, see any introductory quantum physics text, such as French and Taylor [2].]

Thus the single-particle partition function is given by (for the Schrödinger oscillator):

$$Q_1 = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega_o} \quad (2.5.44)$$

which can be simplified

$$Q_1 = \frac{e^{-\beta\hbar\omega_o/2}}{1 - e^{-\beta\hbar\omega_o}} . \quad (2.5.45)$$

For N distinguishable oscillators the partition function becomes

$$Q_N = Q_1^N = \frac{e^{-N\beta\hbar\omega/2}}{(1 - e^{-\beta\hbar\omega_o})^N} . \quad (2.5.46)$$

From our thermodynamic analysis, we calculate internal energy of the N -particle system as

$$U = -\frac{\partial}{\partial\beta} \log Q_n = N \left[\frac{\hbar\omega_o}{2} + \frac{\hbar\omega_o}{e^{\beta\hbar\omega_o} - 1} \right] . \quad (2.5.47)$$

The Planck analysis of this system (excluding the zero-point energy $n = 0$ eigenvalue), results in a mean-energy per oscillator of:

$$\langle \epsilon \rangle = \frac{U}{N} = \frac{\hbar\omega_o}{e^{\beta\hbar\omega_o} - 1} \quad (2.5.48)$$

2.5.3 Blackbody Radiation

Consider a large box or cavity with length dimensions L_x , L_y , and L_z , in which radiation is reflected off the six internal walls. [It is assumed that radiation is absorbed and emitted by the container, resulting in thermal equilibrium of the photons.] In this cavity, a given frequency ω corresponds to wavenumber $k = \omega/c$, where c is the speed of light and k is wavenumber measured in units of inverse length. Wavenumbers obtainable in the rectangular cavity are specified by the Cartesian components $k_x = 2\pi n_x/L_x$, $k_y = 2\pi n_y/L_y$, and $k_z = 2\pi n_z/L_z$, where n_x , n_y , and n_z are integers and $k = (k_x^2 + k_y^2 + k_z^2)^{1/2}$. Angular frequency, expressed in terms of the integers n_x , n_y , and n_z , is:

$$\omega_o = 2\pi c \left[(n_x/L_x)^2 + (n_y/L_y)^2 + (n_z/L_z)^2 \right]^{1/2} . \quad (2.5.49)$$

The total number of modes corresponding to a given frequency range, as $\omega_o \leq \omega$, can be calculated from the integral (in the continuous limit):

$$\int_{\omega_o \leq \omega} dn_x dn_y dn_z . \quad (2.5.50)$$

Changing integration variables to $\lambda_x = n_x/L_x$, $\lambda_y = n_y/L_y$, $\lambda_z = n_z/L_z$, yields

$$L_x L_y L_z \int_{(\lambda_x^2 + \lambda_y^2 + \lambda_z^2)^{1/2} \leq \omega/2\pi c} d\lambda_x d\lambda_y d\lambda_z . \quad (2.5.51)$$

Evaluating this integral gives the number of modes with frequency of less than ω :

$$L_x L_y L_z \left(\frac{4}{3}\right) \pi \left(\frac{\omega}{2\pi c}\right)^3 \quad (2.5.52)$$

and the number with frequencies between ω and $\omega + d\omega$ is

$$\frac{L_x L_y L_z \omega^2}{2\pi^2 c^3} d\omega \quad \text{or} \quad \frac{V \omega^2}{2\pi^2 c^3} d\omega, \quad (2.5.53)$$

where V is the volume of the cavity. Multiplying by a factor of 2, for the two possible opposite polarizations of a given mode, we obtain:

$$\frac{V \omega^2}{\pi^2 c^3} d\omega \quad (2.5.54)$$

for the number of obtainable states for a photon of frequency between ω and $\omega + d\omega$. Multiplying by the Planck expression for $\langle \epsilon \rangle$ the mean energy per oscillator, we get

$$dE_\omega = \frac{V \hbar \omega^3 d\omega}{\pi^2 c^3 (e^{\beta \hbar \omega} - 1)}, \quad (2.5.55)$$

the radiation energy (sum total of energy of the photons) in the frequency range.

2.6 Example Application: Poisson-Boltzmann Theory

As an example application of canonical ensemble theory to biomolecular systems, we next consider the distribution of ions around a solvated charged macromolecule. If the electric field \mathbf{E} can be expressed as the gradient of a potential $\mathbf{E} = -\nabla\Phi$, the Gauss' Law can be expressed

$$\nabla \cdot \epsilon(\mathbf{r}) \nabla \Phi(\mathbf{r}) = -\rho(\mathbf{r}), \quad (2.6.56)$$

where $\epsilon(\mathbf{r})$ is the position-dependent permittivity, and $\rho(\mathbf{r})$ is the charge density. This *electrostatic* approximation is valid if the length scale of the system is much smaller than the wavelengths of the electromagnetic radiation.

We can split the charge density $\rho(\mathbf{r})$ into two contributions:

$$\rho(\mathbf{r}) = \rho_m(\mathbf{r}) + \rho_s(\mathbf{r}), \quad (2.6.57)$$

where $\rho_m(\mathbf{r})$ is the charge density associated with the ionized residues on the macromolecule, and $\rho_s(\mathbf{r})$ is the charge density of the salt ions surrounding the molecule. For a mono-monovalent salt the mobile ions, distributed according to Boltzmann statistics (thermal equilibrium canonical distribution), have a mean-field concentration of

$$\rho_s(\mathbf{r}) = -q_e N_A C_s (e^{q_e \phi / kT} - e^{-q_e \phi / kT}), \quad (2.6.58)$$

where C_s is the bulk concentration of the salt, and N_A is Avogadro's number, and q_e is the elementary charge. This distribution assumes that ions interact with one another only through the electrostatic field, and thus is strictly valid only in the limit of dilute solutions.

The two terms on the right-hand side of Equation (2.6.58) correspond to concentrations of positive and negative valence ions. Substitution of Equation (2.6.58) into Gauss' Law leads to the Poisson-Boltzmann equation:

$$\nabla \cdot \epsilon(\mathbf{r}) \nabla \Phi(\mathbf{r}) - 2q_e N_A C_s \sinh(q_e \phi / kT) = -\rho_m(\mathbf{r}) , \quad (2.6.59)$$

a nonlinear partial differential equation for electrostatic potential surrounding a macromolecule. Once the electrostatic potential is calculated, the ion concentration field is straightforward provided by Equation (2.6.58).

2.7 Brief Introduction to the Grand Canonical Ensemble

Grand canonical ensemble theory is the statistical treatment of a system which exchanges not only energy, but also particles, with its environment in thermal equilibrium. Derivation of the basic probability distribution for the grand canonical distribution is similar to that of the canonical ensemble, except that both E and N are treated as statistically-varying quantities. The resulting probability distribution is of the form:

$$P_{i,j} = \frac{e^{\mu\beta N_i - \beta E_j}}{\Theta(\mu, V, T)} , \quad (2.7.60)$$

where each state is specified by number of particles N_i , and energy E_j .

The grand partition function is defined by summation over all i and j states:

$$\Theta(\mu, V, T) = \sum_i \sum_j e^{\mu\beta N_i - \beta E_j} , \quad (2.7.61)$$

which is often written in a form like:

$$\Theta(z, V, T) = \sum_i z^{N_i} \sum_j e^{-\beta E_j} , \quad (2.7.62)$$

where $z = e^{\mu/kT}$ is called the fugacity (the tendency to be unstable or fly away, from the Latin *fugere* meaning *to flee* according to the Oxford English Dictionary [5]).

Problems

- (Derivation of canonical ensemble) Show that Equation (2.1.8) is uniquely solved by Equation (2.1.9).
- (Simple harmonic oscillators and blackbody radiation) Compare the classical oscillator with the Schrödinger and Planck oscillators. (a) What is the energy per oscillator in the canonical ensemble for the classical case? Which oscillators (if any) obey equipartition? For those that do not, is there a limiting case in which equipartition is valid? [Hints: plot U/N as a function of temperature. Perhaps Taylor expansions of these expressions will be helpful.] (b) From Equation (2.5.55) obtain a nondimensional expression for energy per unit frequency spectrum, and plot the nondimensional energy distribution of blackbody radiation versus nondimensional frequency $\beta\hbar\omega$. At what frequency does the spectral energy distribution obtain a maximum?

- (Electrical double layer) Consider a one-dimensional model of a metal electrode/solution electrolyte interface. The potential in the solution is governed by the Poisson-Boltzmann equation:

$$\frac{d^2\phi}{dx^2} = \frac{2q_e^2 N_A C_s}{\epsilon kT} \sinh \phi .$$

- Show that the above equation is the Poisson-Boltzmann equation in terms of the dimensionless potential $\phi = q_e \Phi / kT$. Show that this equation can be linearized as

$$\frac{d^2\phi}{dx^2} = \kappa^2 \phi .$$

- Evaluate the Debye length ($1/\kappa$) for the case of 0.1 M and 0.0001 M solution of NaCl.
- Using the boundary condition

$$\left[\frac{d\phi}{dx} \right]_{x=0} = -\frac{q_e \sigma}{\epsilon kT}$$

(where σ is the charge density on the surface of the electrode), find $\phi(x)$. Plot the concentrations of Na and Cl as functions of x (assume a positively-charged electrode).

- (Donnan equilibrium) Consider a gel which carries a certain concentration $C_i(\mathbf{r})$ of immobile charges and is immersed in an aqueous solution. The bulk solution carries mono-monovalent mobile ions of concentration $C_+(\mathbf{r})$ and $C_-(\mathbf{r})$. Away from the gel, the concentration of the salt ions achieves the bulk concentration, denoted C_o . What is the difference in electrical potential between the bulk solution and the interior of the gel? [Hint: assume that inside the gel, the overall concentration of negative salt ion balances immobile gel charge concentration.]

Chapter 3

Brownian Motion, Fokker-Planck Equations, and the Fluctuation-Dissipation Theorem

Armed with our understanding of the basic principles of microscopic thermodynamics, we are finally ready to examine the motions of microscopic particles. In particular, we will study these motions from the perspective of stochastic equations, in which random processes are used to approximate thermal interactions between the particles and their environment.

3.1 One-Dimensional Langevin Equation and Fluctuation-Dissipation Theorem

Consider the following *Langevin* equation for the one-dimensional motion of a particle:

$$m\dot{v}(t) + \xi v(t) = f_s(t) + f_r(t) \quad (3.1.1)$$

where m is the mass of the particle, ξ is the coefficient of friction, f_s is the systematic (deterministic) force acting on the particle, and f_r is a random process used to induce thermal fluctuations in the energy of the particle. Equation (3.1.1) can be thought of as Newton's second law with three forces acting on the particle: viscous damping, random thermal noise, and a systematic force.

Equation (3.1.1) can be factored

$$m e^{-\xi t/m} \frac{d}{dt} [e^{+\xi t/m} v] = f_s + f_r, \quad (3.1.2)$$

and has the general solution:

$$v(t) = e^{-\xi t/m} \left[v(0) + \frac{1}{m} \int_0^t e^{+\xi s/m} (f_s(s) + f_r(s)) ds \right]. \quad (3.1.3)$$

Using angled brackets $\langle \cdot \rangle$ to denote averaging over trajectories, we can calculate the covariance

in particle velocity:

$$\begin{aligned} \langle v(t_1)v(t_2) \rangle = & e^{-\xi(t_1+t_2)/m} \left[v^2(0) + \right. \\ & \frac{v(0)}{m} \int_0^{t_1} e^{+\xi s_1/m} \langle f_s(s_1) + f_r(s_1) \rangle ds + \\ & \frac{v(0)}{m} \int_0^{t_2} e^{+\xi s_2/m} \langle f_s(s_2) + f_r(s_2) \rangle ds + \\ & \left. \frac{1}{m^2} \int_0^{t_2} \int_0^{t_1} e^{+\xi(s_1+s_2)/m} \langle f_r(s_1)f_r(s_2) \rangle ds_1 ds_2 \right], \end{aligned} \quad (3.1.4)$$

assuming that the deterministic forces have zero averages. Equation (3.1.4) can be further simplified:

$$\langle v(t_1)v(t_2) \rangle = v^2(0)e^{-\xi(t_1+t_2)/m} + \frac{e^{-\xi(t_1+t_2)/m}}{m^2} \int_0^{t_2} \int_0^{t_1} e^{+\xi(s_1+s_2)/m} \langle f_r(s_1)f_r(s_2) \rangle ds_1 ds_2. \quad (3.1.5)$$

And if we assume that the random force is a white noise process, then its correlation can be described by:

$$\langle f_r(s_1)f_r(s_2) \rangle = A\delta(s_1 - s_2). \quad (3.1.6)$$

Integrating Equation (3.1.5) over s_1 we obtain:

$$\langle v(t_1)v(t_2) \rangle = v^2(0)e^{-\xi(t_1+t_2)/m} + \frac{e^{-\xi(t_1+t_2)/m}}{m^2} \int_0^{t_2} A e^{+2\xi s_2/m} u(t_1 - s_2) ds_2, \quad (3.1.7)$$

where $u(t)$ is the step function defined by

$$u(t) = \begin{cases} 1 & t > 0 \\ 1/2 & t = 0 \\ 0 & t < 0. \end{cases} \quad (3.1.8)$$

Finally, integration of Equation (3.1.7) yields:

$$\langle v(t_1)v(t_2) \rangle = v^2(0)e^{-\xi(t_1+t_2)/m} + \frac{A}{2\xi m} \left[e^{-\xi|t_1-t_2|/m} - e^{-\xi(t_1+t_2)/m} \right]. \quad (3.1.9)$$

To obtain the mean kinetic energy, we take $t_1 = t_2 = t$:

$$\langle v^2(t) \rangle = v^2(0)e^{-2\xi t/m} + \frac{A}{2m\xi} \left[1 - e^{-2\xi t/m} \right], \quad (3.1.10)$$

which approaches

$$\langle v^2(t) \rangle = \frac{A}{2m\xi} \quad (3.1.11)$$

at equilibrium. From equipartition we have $\langle v^2 \rangle = kT/m$. So

$$\langle f_r(s_1)f_r(s_2) \rangle = 2\xi kT\delta(s_1 - s_2), \quad (3.1.12)$$

which is a statement of the fluctuation-dissipation theorem. To obtain thermal equilibrium, the strength of the random (thermal) noise must be proportional to the frictional damping constant, as prescribed by Equation (3.1.12).

3.2 Fokker-Planck Equation

Imagine integrating a stochastic differential equation such as Equation (3.1.1) a number of times so that the noisy trajectories converge into a probability density of states. Considering an N -dimensional problem with the vector $\vec{x}(t)$ representing the state space, we denote the probability distribution as $W(\vec{x}(t), t)$ and introduce $P(\vec{x}(t + \tau), t + \tau | \vec{x}'(t), t)$ as the probability of transition from state $\vec{x}'(t)$ at time t to $\vec{x}(t + \tau)$ at time $t + \tau$.

From the transition probability it follows:

$$W(\vec{x}(t + \tau), t + \tau) = \int P(\vec{x}(t + \tau), t + \tau | \vec{x}'(t), t) W(\vec{x}'(t), t) d\vec{x}' . \quad (3.2.13)$$

Expanding the transition probability as a power series, we obtain

$$\begin{aligned} W(\vec{x}(t + \tau), t + \tau) = \int \left[P(\vec{x}(t), t | \vec{x}'(t), t) + \sum_{n=1}^{\infty} \frac{1}{n!} (x_{i_1}(t + \tau) - x_{i_1}(t)) \dots \right. \\ \left. (x_{i_n}(t + \tau) - x_{i_n}(t)) \frac{\partial^n}{\partial x_{i_1} \dots \partial x_{i_n}} P(\vec{x}(t), t | \vec{x}'(t), t) \right] W(\vec{x}'(t), t) d\vec{x}' , \end{aligned} \quad (3.2.14)$$

where the convention of summation over the indices i_1, i_2, \dots, i_n is implied. Noting that

$$P(\vec{x}(t), t | \vec{x}'(t), t) = \delta(\vec{x}(t) - \vec{x}'(t)) = \delta(x_1(t) - x'_1(t)) \dots \delta(x_N(t) - x'_N(t)) , \quad (3.2.15)$$

we obtain

$$\begin{aligned} W(\vec{x}(t + \tau), t + \tau) = W(\vec{x}(t), t) + \int \left[\sum_{n=1}^{\infty} \frac{1}{n!} (x_{i_1}(t + \tau) - x_{i_1}(t)) \dots \right. \\ \left. (x_{i_n}(t + \tau) - x_{i_n}(t)) \frac{\partial^n}{\partial x_{i_1} \dots \partial x_{i_n}} \delta(\vec{x}(t) - \vec{x}'(t)) \right] W(\vec{x}'(t), t) d\vec{x}' , \end{aligned} \quad (3.2.16)$$

or

$$\begin{aligned} W(\vec{x}(t + \tau), t + \tau) = W(\vec{x}(t), t) + \int \left[\sum_{n=1}^{\infty} \frac{1}{n!} (x'_{i_1}(t + \tau) - x'_{i_1}(t)) \dots \right. \\ \left. (x'_{i_n}(t + \tau) - x'_{i_n}(t)) \frac{\partial^n}{\partial x'_{i_1} \dots \partial x'_{i_n}} \delta(\vec{x}(t) - \vec{x}'(t)) \right] W(\vec{x}'(t), t) d\vec{x}' . \end{aligned} \quad (3.2.17)$$

By successively integrating by parts, we can move the derivatives off of the delta functions:

$$\begin{aligned} W(\vec{x}(t + \tau), t + \tau) = W(\vec{x}(t), t) + \int \delta(\vec{x}(t) - \vec{x}'(t)) \left[\sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial x'_{i_1} \dots \partial x'_{i_n}} \right. \\ \left. (x'_{i_1}(t + \tau) - x'_{i_1}(t)) \dots (x'_{i_n}(t + \tau) - x'_{i_n}(t)) \right] W(\vec{x}'(t), t) d\vec{x}' . \end{aligned} \quad (3.2.18)$$

Equation (3.2.18) integrates to

$$W(\vec{x}(t + \tau), t + \tau) = W(\vec{x}(t), t) + \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial x_{i_1} \dots \partial x_{i_n}} [(x_{i_1}(t + \tau) - x_{i_1}(t)) \dots (x_{i_n}(t + \tau) - x_{i_n}(t)) W(\vec{x}(t), t)] , \quad (3.2.19)$$

or in the limit $\tau \rightarrow 0$,

$$\frac{\partial}{\partial t} W(\vec{x}, t) = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial x_{i_1} \dots \partial x_{i_n}} \left[\lim_{\tau \rightarrow 0} \left(\frac{1}{\tau} [x_{i_1}(t + \tau) - x_{i_1}(t)] \dots [x_{i_n}(t + \tau) - x_{i_n}(t)] \right) W(\vec{x}(t), t) \right] . \quad (3.2.20)$$

Defining the Kramers-Moyal coefficients [4] as

$$D_{i_1 \dots i_n}^{(n)} = \frac{1}{n!} \lim_{\tau \rightarrow 0} \left(\frac{1}{\tau} [x_{i_1}(t + \tau) - x_{i_1}(t)] \dots [x_{i_n}(t + \tau) - x_{i_n}(t)] \right) , \quad (3.2.21)$$

We obtain the Fokker-Planck equation for $W(\vec{x}, t)$:

$$\frac{\partial}{\partial t} W(\vec{x}, t) = \sum_{n=1}^{\infty} (-1)^n \frac{\partial^n}{\partial x_{i_1} \dots \partial x_{i_n}} \left[D_{i_1 \dots i_n}^{(n)} W(\vec{x}(t), t) \right] . \quad (3.2.22)$$

In the following section we evaluate the Kramers-Moyal expansion coefficients for a nonlinear N -dimensional stochastic differential equation.

3.3 Brownian Motion of Several Particles

Consider the general nonlinear Langevin equation for several variables $\vec{\chi}(t) = \chi_1(t), \chi_2(t) \dots \chi_N(t)$:

$$\dot{\chi}_i = h_i(\vec{\chi}(t), t) + g_{ij}(\vec{\chi}(t), t) \Gamma_j(t) \quad (3.3.23)$$

where $\Gamma_j(t)$ are uncorrelated white noise processes distributed according to:

$$\langle \Gamma_i(t) \rangle = 0 \quad , \quad \langle \Gamma_i(t_1) \Gamma_j(t_2) \rangle = 2\delta_{ij} \delta(t_1 - t_2) . \quad (3.3.24)$$

In Equation (3.3.23) we use the Einstein convention of summation over repeated indices. Thus the matrix g_{ij} describes the covariance structure of the random forces acting on $\vec{\chi}(t)$.

Equation (3.3.23) has the general solution:

$$\chi_i(t + \tau) - \chi_i(t) = \int_t^{t+\tau} [h_i(\vec{\chi}(t'), t') + g_{ij}(\vec{\chi}(t'), t') \Gamma_j(t')] dt' \quad (3.3.25)$$

We can expand this integral by expanding the functions h_i and g_{ij}

$$\begin{aligned} h_i(\vec{\chi}(t'), t') &= h_i(\vec{\chi}(t), t') + [\chi_k(t') - \chi_k(t)] \cdot \frac{\partial}{\partial \chi_k} h_i(\vec{\chi}(t), t') + \dots \\ g_{ij}(\vec{\chi}(t'), t') &= g_{ij}(\vec{\chi}(t), t') + [\chi_k(t') - \chi_k(t)] \cdot \frac{\partial}{\partial \chi_k} g_{ij}(\vec{\chi}(t), t') + \dots \end{aligned} \quad (3.3.26)$$

and inserting these expansions into Equation (3.3.25):

$$\begin{aligned} \chi_i(t + \tau) - \chi_i(t) &= \int_t^{t+\tau} h_i(\vec{\chi}(t'), t') dt' + \int_t^{t+\tau} [\chi_k(t') - \chi_k(t)] \cdot \frac{\partial}{\partial \chi_k} h_i(\vec{\chi}(t), t') dt' + \dots \\ &+ \int_t^{t+\tau} g_{ij}(\vec{\chi}(t), t') \Gamma_j(t') dt' + \int_t^{t+\tau} [\chi_k(t') - \chi_k(t)] \cdot \frac{\partial}{\partial \chi_k} g_{ij}(\vec{\chi}(t), t') \Gamma_j(t') dt' + \dots \end{aligned} \quad (3.3.27)$$

We can expand the $[\chi_k(t') - \chi_k(t)]$ terms in the above equation and recursively using Equation (3.3.27):

$$\begin{aligned} \chi_k(t + \tau) - \chi_k(t) &= \int_t^{t+\tau} h_k(\vec{\chi}(t'), t') dt' + \int_t^{t+\tau} [\chi_l(t') - \chi_l(t)] \cdot \frac{\partial}{\partial \chi_l} h_k(\vec{\chi}(t), t') dt' + \dots \\ &+ \int_t^{t+\tau} g_{kl}(\vec{\chi}(t), t') \Gamma_l(t') dt' + \int_t^{t+\tau} [\chi_l(t') - \chi_l(t)] \cdot \frac{\partial}{\partial \chi_l} g_{kl}(\vec{\chi}(t), t') \Gamma_l(t') dt' + \dots \end{aligned} \quad (3.3.28)$$

To compute $\langle \chi_i(t + \tau) - \chi_i(t) \rangle$ in the limit $\tau \rightarrow 0$, we insert Equation (3.3.28) into Equation (3.3.27), average over trajectories, and retain terms of first order:

$$\langle \chi_i(t + \tau) - \chi_i(t) \rangle = \tau h_i(\vec{\chi}(t), t) + \int_t^{t+\tau} \int_t^{t'} \left[\frac{\partial}{\partial \chi_k} g_{ij}(\vec{\chi}(t), t') \right] g_{kl}(\vec{\chi}(t), t'') 2\delta_{jl} \delta(t' - t'') dt'' dt' + \dots \quad (3.3.29)$$

where terms of order τ^2 are not shown. To evaluate the integral in Equation (3.3.29), we use the identity:

$$\int_t^{t'} g_{kl}(\vec{\chi}(t), t) 2\delta_{jl} \delta(t' - t'') dt'' = g_{kj}(\vec{\chi}(t), t), \quad (3.3.30)$$

and we get:

$$D_i^{(1)} = h_i(\vec{\chi}(t), t) + g_{kj}(\vec{\chi}(t), t) \frac{\partial}{\partial \chi_k} g_{ij}(\vec{\chi}(t), t) \quad (3.3.31)$$

for the drift coefficients.

Evaluating $\langle [\chi_i(t + \tau) - \chi_i(t)] \cdot [\chi_j(t + \tau) - \chi_j(t)] \rangle$, the only term that survives averaging and the limit $\tau \rightarrow 0$ is

$$\begin{aligned} \langle [\chi_i(t + \tau) - \chi_i(t)] \cdot [\chi_k(t + \tau) - \chi_k(t)] \rangle &= \\ \int_t^{t+\tau} \int_t^{t'} g_{ij}(\vec{\chi}(t), t') g_{kl}(\vec{\chi}(t), t'') 2\delta_{jl} \delta(t' - t'') dt'' dt' &= 2\tau g_{ij}(\vec{\chi}(t), t) g_{kj}(\vec{\chi}(t), t) \end{aligned} \quad (3.3.32)$$

and

$$D_{ij}^{(2)} = g_{ik}(\vec{\chi}(t), t) g_{jk}(\vec{\chi}(t), t). \quad (3.3.33)$$

All higher-order coefficients are zero:

$$D_{i_1 \dots i_n}^{(n)} = \frac{1}{n!} \lim_{\tau \rightarrow 0} \langle [\chi_{i_1}(t + \tau) - \chi_{i_1}(t)] \dots [\chi_{i_n}(t + \tau) - \chi_{i_n}(t)] \rangle = 0, \quad n \geq 3. \quad (3.3.34)$$

The Fokker-Planck equation corresponding to Equation (3.3.23) is:

$$\begin{aligned} \frac{\partial W(\vec{x}(t), t)}{\partial t} &= \frac{\partial}{\partial x_i} \left[- \left(h_i(\vec{x}(t), t) + g_{kj}(\vec{x}(t), t) \frac{\partial}{\partial x_k} g_{ij}(\vec{x}(t), t) \right) W(\vec{x}(t), t) \right] \\ &+ \frac{\partial^2}{\partial x_i \partial x_j} [g_{ik}(\vec{x}(t), t) g_{jk}(\vec{x}(t), t) W(\vec{x}(t), t)]. \end{aligned} \quad (3.3.35)$$

3.4 Fluctuation-Dissipation and Brownian Dynamics

To examine how the fluctuation-dissipation theorem arises for the general nonlinear Langevin equation, we first examine the simple one-dimensional problem described by:

$$\begin{aligned} \dot{\chi} &= h(\chi, t) + g(\chi, t)\Gamma(t) \\ \langle \Gamma(t_1)\Gamma(t_2) \rangle &= 2\delta(t_1 - t_2). \end{aligned} \quad (3.4.36)$$

If the systematic term is proportional to the gradient of a potential, $h = -D\beta\nabla U$, then the Fokker-Planck equation is expressed as:

$$\frac{\partial W(x, t)}{\partial t} = \frac{\partial}{\partial x} [D\beta(\nabla U)W] + \frac{\partial^2}{\partial x^2} [g^2 W]. \quad (3.4.37)$$

If we further assume that $W \sim e^{-\beta U}$ at equilibrium, then

$$\frac{d}{dx} \left[-D\beta \left(\frac{dU}{dx} \right) e^{-\beta U} \right] = \frac{d^2}{dx^2} [g^2 e^{-\beta U}]. \quad (3.4.38)$$

It is straightforward to show that this condition is satisfied if $g = D^{1/2}$, which is the fluctuation-dissipation theorem for this one-dimensional Brownian motion.

This relationship generalizes for the following N -dimensional case:

$$\dot{\chi}_i = \beta D_{ij} f_j + g_{ij} \Gamma_j(t) \quad (3.4.39)$$

$$\langle \Gamma_i(t_1) \Gamma_j(t_2) \rangle = 2\delta_{ij} \delta(t_1 - t_2) \quad (3.4.40)$$

$$f_j = \frac{d}{d\chi_j} U(\vec{\chi}(t), t), \quad (3.4.41)$$

to

$$g_{ik} g_{jk} = D_{ij}. \quad (3.4.42)$$

In the above equations, $U(\vec{\chi}(t), t)$ is the potential energy function, and D_{ij} is the frictional interaction matrix which determines the hydrodynamic interactions between the particles in the system. Thus the covariance structure of the random forcing is proportional to the hydrodynamic interaction matrix. Given a diffusional matrix D_{ij} , generation of the random force vector requires the calculation of g_{ik} , the factorization of D_{ij} . In fact, for Brownian dynamics simulations, this factorization represents the computational bottleneck that demands the majority of CPU resources.

Problems

1. (Brownian Motion) Consider the coupled Langevin equations:

$$M\ddot{\vec{x}} + Z\dot{\vec{x}} = -\nabla U + H\vec{\Gamma}(t),$$

where M is a diagonal matrix of particle masses, Z is the non-diagonal *frictional interaction matrix*, and the noise term Γ is correlated according to:

$$\langle \Gamma(t_1)\Gamma^T(t_2) \rangle = 2I\delta(t_1 - t_2),$$

where I is the identity matrix. The fluctuation-dissipation theorem tells us that:

$$H^T H = kTZ.$$

- (a) Brownian Motion If we ignore inertia in the above system we get

$$\dot{\vec{x}} = -\frac{1}{kT}D\nabla U + G\vec{\Gamma}(t)$$

where $D = kTZ^{-1}$ is the diffusion matrix. Show that $G^T G = D$. Given a diffusion matrix D , how would you calculate its factor G ?

- (b) Brownian Dynamics Algorithm Under what circumstances do you think the inertial system will reduce to the over-damped (non-inertial) system? Assuming that the random and systematic forces remain constant over a time step of length Δt , find an expression for $\vec{v}(t + \Delta t)$ in terms of $\vec{v}(t)$. [Hint: The equations can be decoupled by considering the eigen decomposition of $A = M^{-1}Z$. Proceed by finding a matrix-vector equivalent to Equation (3.1.3).] Show that under a certain highly-damped limit, this expression reduces to the Brownian equation

$$\vec{v}(t) = \frac{D}{kT} [\text{systematic force} + \text{random force}].$$

2. (Numerical Methods) Devise a numerical propagation scheme for the Brownian equation.

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