



STATISTICAL MECHANICS

Based on CHEM_ENG 404 at Northwestern University



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1 A BRIEF REVIEW OF CLASSICAL THERMODYNAMICS

1.1 PRELUDE

This section on classical thermodynamics is not meant to be a thorough review. It does not cover much of the underlying theory. It simply provides a refresher of content typically covered in a standard undergraduate thermodynamics course and is used just to provide context for the statistical mechanical content discussed in later sections.

1.2 TERMINOLOGY

In order to accurately and precisely discuss various aspects of thermodynamics, it is essential to have a well-defined vernacular. As such, a list of some foundational concepts and their definitions are shown below. Other terms will be defined as they are introduced.

- **Universe** – all measured space
- **System** – space of interest
- **Surroundings** – the space outside the system
- **Boundary** – what separates the system from the surroundings
- **Open System** – a system that can have both mass and energy flowing across the boundary
- **Isolated System** – a system that can have neither mass nor energy flowing across the boundary
- **Closed System** – a system that can have energy but not mass flowing across the boundary
- **Extensive Property** – a property that depends on the size of the system
- **Intensive Property** – a property that does not depend on the size of the system
- **State** – the condition in which one finds a system at any given time (defined by its intensive properties)
- **Process** – what brings the system from one state to another
- **State Function** – a quantity that depends only on the current state of a system
- **Path Function** – a quantity that depends on the path taken
- **Adiabatic Process** – a process that has no heat transfer ($Q = 0$)
- **Rigid System** – a system that does not allow for mechanical work ($W = 0$)
- **Permeable System** – a process that does not allow for species transport
- **Isothermal Process** – a process that has a constant temperature ($\Delta T = 0$)
- **Isobaric Process** – a process that has a constant pressure ($\Delta P = 0$)
- **Isochoric Process** – a process that has a constant volume ($\Delta V = 0$)
- **Isenthalpic Process** – a process that has a constant enthalpy ($\Delta H = 0$)
- **Isentropic Process** – a process that has a constant entropy ($\Delta S = 0$)
- **Diathermal Process** – a process that allows heat transfer ($Q \neq 0$)
- **Moveable System** – a system that allows for mechanical work ($W \neq 0$)
- **Impermeable System** – a system that does not allow species transport
- **Mechanical Equilibrium** – no pressure difference between system and surroundings
- **Thermal Equilibrium** – no temperature difference between system and surroundings
- **Chemical Equilibrium** – no tendency for a species to change phases or chemical react
- **Thermodynamic Equilibrium** – a system that is in mechanical, thermal, and chemical equilibrium
- **Phase Equilibrium** – a system with more than one phase present that is in thermal and mechanical equilibrium between the phases such that the phase has no tendency to change
- **Chemical Reaction Equilibrium** – a system undergoing chemical reactions with no more tendency to react

1.3 ZEROETH LAW OF THERMODYNAMICS

The zeroth law of thermodynamics states: if two systems are separately in thermal equilibrium with a third, then they must also be in thermal equilibrium with each other. This is a seemingly trivial statement but is one that must be set for the rest of thermodynamics to rigorously hold true. It essentially defines an operational definition of temperature (i.e. the thing that must be the same between the three systems for them to be in thermal equilibrium).

1.4 FIRST LAW OF THERMODYNAMICS

1.4.1 DEFINITION OF INTERNAL ENERGY

The first law of thermodynamics states that the total quantity of energy in the universe is constant (in other words, energy cannot be created or destroyed, although it can change forms). That being said, it is not convenient to consider the entire universe when doing a thermodynamic calculation. We can break this statement down into the region we are interested in (i.e. the system) and the rest of the universe (i.e. the surroundings). This allows us to restate the first law of thermodynamics as: the energy change of the system must equal the energy transferred across its boundaries from the surroundings. Energy can be transferred as heat, Q , or by work, W , for a closed system. Written mathematically then,

$$\Delta U = Q + W,$$

where ΔU is a state function we call the change in internal energy (of the system). In differential form, this is

$$dU = \delta Q + \delta W,$$

where the δ operator is used in place of the d operator to denote an inexact differential (i.e. the differential change of a path function).

1.4.2 HEAT AND WORK

Heat, Q , is defined as the amount of energy transferred to a system via a temperature gradient. All other forms of energy transfer are considered work, denoted W . Work can be supplied by many means, but the most common in chemical systems is via external pressure over a volume change such that

$$W = - \int P dV.$$

This is often referred to as PV (or mechanical) work. In this context, a positive value of W is defined as the energy transferred from the surroundings to the system. The same sign-convention is chosen for heat.

1.4.3 DEFINITION OF ENTHALPY

For mechanical work, we know that $\delta W = -P dV$, so

$$dU = \delta Q - P dV.$$

At constant pressure, $P dV = d(PV)$, so we can then state

$$dU = \delta Q_p - d(PV),$$

where the subscript on heat denotes constant pressure. Solving for δQ_p ,

$$\delta Q_p = d(U + PV).$$

This $U + PV$ term will appear frequently in thermodynamics and refers to a quantity called enthalpy, H , defined as

$$H \equiv U + PV.$$

This means that at constant P , $dH = \delta Q_P$. In addition, at constant V , no work is done, so $dU = \delta Q_V$. Enthalpy and internal energy therefore each describe how heat changes a system in different conditions. They differ in value because at constant P , some heat will go into performing work instead.

1.4.4 DEFINITION OF HEAT CAPACITY

The heat capacity, C , is defined as the ratio of heat added to the corresponding temperature rise,

$$C \equiv \frac{\delta Q}{dT}.$$

More often, the heat capacity at a constant set of conditions is defined for a given substance. For instance, since $\delta Q = \partial U$ at constant volume, the constant volume heat capacity, C_V , is

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_V.$$

Similarly, since $\delta Q = \partial H$ at constant pressure, the constant pressure heat capacity, C_P , is

$$C_P \equiv \left(\frac{\partial H}{\partial T} \right)_P.$$

It should be noted that $C_P > C_V$ since – for a given δQ – some of that heat must go into work, causing a smaller temperature change.

1.4.5 IDEAL GAS ASSUMPTIONS

For an ideal monatomic gas, it can be shown that

$$U = \frac{3}{2}nRT.$$

and since $H = U + PV$,

$$H = \frac{5}{2}nRT.$$

This then also means that

$$C_V = \frac{3}{2}nR$$

and

$$C_P = \frac{5}{2}nR.$$

As we can see from the above expressions, the following useful relationship exists for ideal gases:

$$C_P - C_V = nR.$$

1.5 CALCULATING FIRST-LAW QUANTITIES IN CLOSED SYSTEMS

1.5.1 STARTING POINT

When calculating first-law quantities in closed systems for reversible processes, it is best to always start with the following three equations, which are always true:

$$W = - \int P dV$$

$$\Delta U = Q + W$$

$$\Delta H = \Delta U + \Delta(PV)$$

If ideal gas conditions can be assumed then, heat capacities are constant and

$$C_p - C_v = nR$$

$$\Delta H = \Delta H(T)$$

$$\Delta U = \Delta U(T)$$

1.5.2 REVERSIBLE, ISOBARIC PROCESS

Since pressure is constant:

$$W = -P\Delta V$$

We then have the following relationships for enthalpy:

$$Q_p = \Delta H$$

$$\Delta H = \int C_p dT$$

$$\Delta H = \Delta U + P\Delta V$$

1.5.3 REVERSIBLE, ISOCHORIC PROCESS

Since volume is constant:

$$W = 0$$

We then have the following relationships for the internal energy:

$$Q_v = \Delta U$$

$$\Delta U = \int C_v dT$$

$$\Delta H = \Delta U + V\Delta P$$

1.5.4 REVERSIBLE, ISOTHERMAL PROCESS

If one is dealing with an ideal gas, ΔU and ΔH are only functions of temperature, so

$$\Delta U = \Delta H = 0$$

Due to the fact that $\Delta U = Q + W$,

$$Q = -W$$

For an ideal gas, integrate the ideal gas law with respect to V to get

$$W = -nRT \ln\left(\frac{V_2}{V_1}\right) = nRT \ln\left(\frac{P_2}{P_1}\right)$$

1.5.5 REVERSIBLE, ADIABATIC PROCESS

By definition the heat exchange is zero, so:

$$Q = 0$$

Due to the fact that $\Delta U = Q + W$,

$$W = \Delta U$$

The following relationships can also be derived for a system with constant heat capacity:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}}$$

$$\left(\frac{P_1}{P_2}\right)^R = \left(\frac{T_1}{T_2}\right)^{C_P}$$

$$P_1 V_1^{C_P/C_V} = P_2 V_2^{C_P/C_V}$$

This means that

$$W = \Delta U = \frac{\Delta(PV)}{C_P/C_V - 1} = \frac{nR\Delta T}{C_P/C_V - 1}$$

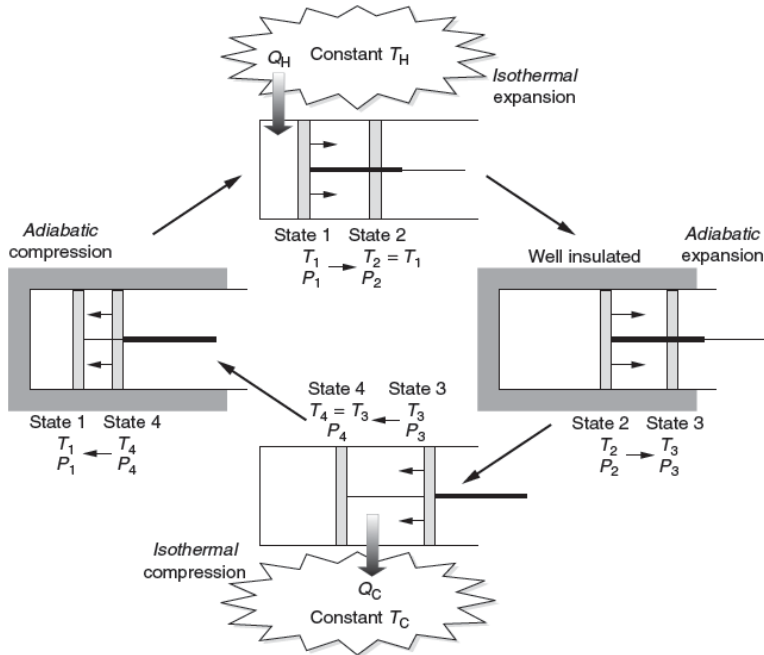
1.5.6 IRREVERSIBLE, ADIABATIC EXPANSION INTO A VACUUM

For this case,

$$Q = W = \Delta U = \Delta H = 0$$

1.6 THE CARNOT CYCLE

A thermodynamic cycle always returns to the same state it was in initially, meaning all state functions are zero for the net cycle. For a Carnot cycle, there are four stages, as outlined in the figure below.



Since all state functions are zero for the net cycle, we know that

$$\Delta U_{\text{cycle}} = \Delta H_{\text{cycle}} = 0$$

Due to the First Law of Thermodynamics,

$$-W_{\text{net}} = Q_{\text{net}}$$

The net work and the net heat can be computed by summing up the individual work and heat from each of the four processes. For a Carnot cycle, there is a negative net work.

The following relationships apply to the Carnot cycle:

$$\frac{P_2}{P_1} = \frac{P_3}{P_4}$$

and

$$\frac{Q_H}{Q_C} = -\frac{T_H}{T_C}$$

The efficiency of the Carnot cycle is defined as

$$\eta \equiv \frac{\text{net work}}{\text{wasted heat}} = \frac{|W_{\text{net}}|}{Q_H} = 1 - \frac{T_C}{T_H}$$

The efficiency of the Carnot cycle run in reverse (i.e. a Carnot refrigerator) is characterized by the coefficient of performance, given by

$$\text{COP} = \frac{Q_C}{|W_{\text{net}}|} = \frac{T_C}{T_H - T_C}$$

1.7 SECOND LAW OF THERMODYNAMICS

Recall that in the equation $dU = \delta Q + \delta W$, we were able to replace δW by a function of only state variables. It would be ideal if the same could be done for δQ so that dU could be calculated from only state functions as well. This can be achieved with the second law of thermodynamics. I will start with the definition and then follow with the mathematical explanation. The second law of thermodynamics states that the entropy, S , of the universe increases for all real, irreversible processes (and does not change for reversible processes). In other words,

$$\Delta S_{\text{univ}} \geq 0,$$

where

$$\Delta S_{\text{univ}} \equiv \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}.$$

However, to understand this law, we must first define entropy, which we can do by finding out the integrating factor to turn δQ into an exact differential. We begin with

$$\delta Q = dU + P dV.$$

Assuming an ideal gas, we can then say

$$\delta Q = \frac{3}{2}nR dT + \frac{nRT}{V} dV.$$

If we were to integrate this expression, we would have an $nRT \ln\left(\frac{V_f}{V_i}\right)$ term on the right-hand side. The factor of T makes this entirely dependent on the path. However, if we divide by T on both sides, we get

$$\frac{\delta Q}{T} = \frac{3}{2}nR \frac{dT}{T} + \frac{nR}{V} dV.$$

Integrating from an initial to final state,

$$\int_i^f \frac{\delta Q}{T} = \frac{3}{2}nR \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right).$$

We then see that $1/T$ is an integrating factor such that $\delta Q/T$ is an exact differential, as it is independent of path now. We can define this exact differential as entropy,

$$dS \equiv \frac{\delta Q}{T}.$$

1.8 CALCULATING SECOND-LAW QUANTITIES IN CLOSED SYSTEMS

1.8.1 REVERSIBLE, ADIABATIC PROCESSES

Since the process is reversible and there is no heat transfer¹,

$$\Delta S = 0, \quad \Delta S_{\text{surr}} = 0, \quad \Delta S_{\text{univ}} = 0$$

1.8.2 REVERSIBLE, ISOTHERMAL PROCESSES

Since temperature is constant,

¹ It will be tacitly assumed any quantity without a subscript refers to that of the system.

$$\Delta S = \frac{Q_{\text{rev}}}{T}$$

If the ideal gas assumption can be made, then $\Delta U = 0$ such that $Q_{\text{rev}} = W_{\text{rev}} = -\int P \, dV$. Plug in the ideal gas law to get

$$\Delta S = -nR \ln\left(\frac{P_2}{P_1}\right)$$

Since all reversible processes have no change in the entropy of the universe (i.e. $\Delta S_{\text{univ}} = 0$), we can say that $\Delta S_{\text{surr}} = -\Delta S$.

1.8.3 REVERSIBLE, ISOBARIC PROCESSES

Since $\delta Q_P = dH = C_P \, dT$ for isobaric processes,

$$\Delta S = \int \frac{C_P}{T} \, dT$$

Since all reversible processes have no change in the entropy of the universe (i.e. $\Delta S_{\text{univ}} = 0$), we can say that $\Delta S_{\text{surr}} = -\Delta S$.

1.8.4 REVERSIBLE, ISOCHORIC PROCESSES

Since $\delta Q_V = dU = C_V \, dT$ for isochoric processes,

$$\Delta S = \int \frac{C_V}{T} \, dT$$

Since all reversible processes have no change in the entropy of the universe (i.e. $\Delta S_{\text{univ}} = 0$), we can say that $\Delta S_{\text{surr}} = -\Delta S$.

1.8.5 REVERSIBLE PHASE CHANGE AT CONSTANT T AND P

In this case, Q_{rev} is the latent heat of the phase transition. As such,

$$\Delta S = \frac{Q_P}{T} = \frac{\Delta H_{\text{transition}}}{T}$$

Since all reversible processes have no change in the entropy of the universe (i.e. $\Delta S_{\text{univ}} = 0$), we can say that $\Delta S_{\text{surr}} = -\Delta S$.

1.8.6 IRREVERSIBLE PROCESSES FOR IDEAL GASES

A general expression can be written to describe the entropy change of an ideal gas. Two equivalent expressions are:

$$\Delta S = \int \frac{C_V}{T} \, dT + nR \ln\left(\frac{V_2}{V_1}\right)$$

and

$$\Delta S = \int \frac{C_P}{T} \, dT - nR \ln\left(\frac{P_2}{P_1}\right)$$

In order to find the entropy change of the universe, one must think about the conditions of the problem statement. If the real process is adiabatic, then $Q_{\text{surr}} = 0$ and then $\Delta S_{\text{surr}} = 0$ such that $\Delta S_{\text{univ}} = \Delta S$. If

the real process is isothermal, note that $Q = W$ from the First Law of Thermodynamics (i.e. $\Delta U = 0$) and that due to conservation of energy $Q_{\text{surr}} = -Q$. Once Q_{surr} is known, simply use $\Delta S_{\text{surr}} = \frac{Q_{\text{surr}}}{T}$. The entropy change in the universe is then $\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{surr}}$.

If the ideal gas approximation cannot be made, try splitting up the irreversible process into hypothetical, reversible pathways that may be easier to calculate.

1.8.7 ENTROPY CHANGE OF MIXING

If we assume that we are mixing different inert, ideal gases then the entropy of mixing is

$$\Delta S_{\text{mix}} = R \sum n_i \ln \left(\frac{V_f}{V_i} \right)$$

For an ideal gas at constant T and P then

$$\Delta S_{\text{mix}} = -R \sum n_i \ln \left(\frac{P_i}{P_{\text{tot}}} \right) = -R \sum n_i \ln(x_i)$$

where P_i is the partial pressure of species i and x_i is the mole fraction of species i .

1.8.8 EXPANSION INTO A VACUUM

For expansion into a vacuum (otherwise known as a Joule expansion),

$$\Delta S_{\text{sys}} = \Delta S_{\text{univ}} = nR \ln \left(\frac{V_2}{V_1} \right) = -nR \ln \left(\frac{P_2}{P_1} \right)$$

1.9 DERIVED THERMODYNAMIC QUANTITIES

1.9.1 EXACT DIFFERENTIALS

The change in any intensive thermodynamic property of interest, z , can be written in terms of partial derivatives of the two independent intensive properties, x and y as shown below:

$$dz = \left. \frac{\partial z}{\partial x} \right|_y dx + \left. \frac{\partial z}{\partial y} \right|_x dy,$$

When $z(x, y)$ is a smooth function, the mixed derivatives are equal, such that the following (referred to as the Euler reciprocity) holds:

$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}.$$

1.9.2 MATHEMATICAL RELATIONS

The following general relationship are true:

$$\left(\frac{\partial z}{\partial z} \right)_y \left(\frac{\partial z}{\partial x} \right)_z \left(\frac{\partial z}{\partial y} \right)_x = -1.$$

For a function $\phi = \phi(x, y)$ and a given constraint z ,

$$\left(\frac{\partial \phi}{\partial x} \right)_z = \left(\frac{\partial \phi}{\partial x} \right)_y + \left(\frac{\partial \phi}{\partial y} \right)_x \left(\frac{\partial y}{\partial x} \right)_z$$

1.9.3 HOMOGENEOUS FUNCTION THEOREM

A homogeneous function of order k is one where $f(\lambda a, \lambda b, \lambda c) = \lambda^k f(a, b, c)$. Therefore, all extensive variables are homogeneous functions with degree 1. Euler's homogeneous function theorem states that for an arbitrary homogeneous function f with degree $k = 1$,

$$f(\lambda \mathbf{x}) = \lambda f(\mathbf{x})$$

the following must hold

$$f(\mathbf{x}) = \mathbf{x} \cdot \text{grad}(f(\mathbf{x}))$$

Applying this to the definition of entropy, for example, yields

$$S(N, V, U) = (N, V, U) \cdot \text{grad}(S(N, V, U)) = N \left(\frac{\partial S}{\partial N} \right)_{V,U} + V \left(\frac{\partial S}{\partial V} \right)_{N,U} + U \left(\frac{\partial S}{\partial U} \right)_{N,V}$$

1.10 THERMODYNAMIC RELATIONS

The measured properties of a system are P, V, T and composition. The fundamental thermodynamic properties are U and S , as previously discussed. There are also derived thermodynamic properties. One of which is H . There are also two other convenient derived properties: F , which is Helmholtz free energy, and G , which is Gibbs free energy. The derived thermodynamic properties have the following relationships:

$$dH \equiv dU + d(PV) \quad dF \equiv dU - d(TS) \quad dG \equiv dH - d(TS)$$

The fundamental thermodynamic potentials are given by

$$dU = T dS - P dV + \sum_i \mu_i dN_i$$

$$dH = T dS + V dP + \sum_i \mu_i dN_i$$

$$dF = -P dV - S dT + \sum_i \mu_i dN_i$$

$$dG = V dP - S dT + \sum_i \mu_i dN_i$$

With these expressions, one can derive the following relationships:

$$\left(\frac{\partial U}{\partial S} \right)_{V,N} = T \quad \left(\frac{\partial U}{\partial V} \right)_{S,N} = -P$$

$$\left(\frac{\partial H}{\partial S} \right)_{P,N} = T \quad \left(\frac{\partial H}{\partial P} \right)_{S,N} = V$$

$$\left(\frac{\partial F}{\partial T} \right)_{V,N} = -S \quad \left(\frac{\partial F}{\partial V} \right)_{T,N} = -P$$

$$\left(\frac{\partial G}{\partial T} \right)_{P,N} = -S \quad \left(\frac{\partial G}{\partial P} \right)_{T,N} = V$$

$$\left(\frac{\partial S}{\partial V}\right)_{N,U} = \frac{P}{T} \quad \left(\frac{\partial S}{\partial N}\right)_{V,U} = -\frac{\mu}{T}$$

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{V,S,N_{j \neq i}} = \left(\frac{\partial H}{\partial N_i}\right)_{P,S,N_{j \neq i}} = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_{j \neq i}} = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{i \neq j}}$$

The major Maxwell relations are

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

One can also write heat capacities in terms of T and s :

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V \quad C_P = \left(\frac{\partial H}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P$$

It is useful to know the following identities:

$$\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad \kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

where β and κ are the thermal expansion coefficient and isothermal compressibility, respectively. The Gibbs-Helmholtz equations are

$$H = -T^2 \left(\frac{\partial(G/T)}{\partial T}\right)_P = \left(\frac{\partial(G/T)}{\partial(1/T)}\right)_P$$

$$U = -T^2 \left(\frac{\partial(F/T)}{\partial T}\right)_V = \left(\frac{\partial(F/T)}{\partial(1/T)}\right)_V$$

$$G = -V^2 \left(\frac{\partial(F/V)}{\partial V}\right)_T = \left(\frac{\partial(F/V)}{\partial(1/V)}\right)_T$$

2 FUNDAMENTALS OF STATISTICAL MECHANICS

2.1 BRIEF REVIEW OF PROBABILITY

When dealing with mutually exclusive events, the probability of either event happens is given by

$$p_{ij} = p_i + p_j$$

When dealing with independent events, the probability that both occur is given by

$$p_{ij} = p_i p_j$$

The number of arrangements of n objects of which p is one kind, q is another, r is another (and so on) is given by

$$\# \text{ arrangements} = \frac{n!}{p! q! r! \dots}$$

We now consider the number of ways of making a choice if order of choice is important (i.e. a permutation). The number of permutation of r objects out of n total objects is given by

$${}^n P_r = \frac{n!}{(n-r)!}$$

We now consider the number of ways of making a choice if order of choice is *not* important (i.e. a combination). The number of combinations of r objects out of n total objects is given by

$${}^n C_r = \binom{n}{r} = \frac{n!}{r! (n-r)!}$$

2.2 BRIEF OVERVIEW OF AVERAGES: AN EXAMPLE

Consider a model system that has an energy given by $E = \frac{1}{2} kx^2$. Find a distribution for $p(x)$ and use it to calculate $\langle x \rangle$, $\langle x^2 \rangle$, and $\langle E \rangle$.

We know that the probability is defined as

$$p = \frac{e^{-\frac{kx^2}{2k_B T}}}{Z}$$

The partition function here is found by integrating over all x (assume $x \geq 0$) so

$$p = \frac{e^{-\frac{kx^2}{2k_B T}}}{\int_0^\infty e^{-\frac{kx^2}{2k_B T}} dx} = \frac{1}{\sqrt{\frac{2k}{\pi k_B T}}} e^{-\frac{kx^2}{2k_B T}}$$

The value of $\langle x \rangle$ can be found from

$$\langle x \rangle = \int_0^\infty x p(x) dx = \sqrt{\frac{2k_B T}{\pi k}}$$

The value of $\langle x^2 \rangle$ can be found from

$$\langle x^2 \rangle = \int_0^{\infty} x^2 p(x) dx = \frac{k_B T}{k}$$

The value of $\langle E \rangle$ can be found from

$$\langle E \rangle = \left\langle \frac{1}{2} k x^2 \right\rangle = \frac{1}{2} k \langle x^2 \rangle = \frac{1}{2} k_B T$$

2.3 MICROSCOPIC DEFINITION OF ENTROPY

Boltzmann's hypothesis stated that entropy is related to some function of the number of quantum states, W . In other words,

$$S = \phi(W)$$

where $\phi(W)$ is some unknown function of W . To determine this function, we consider the following argument. Imagine two systems, A and B , which are not interacting (and therefore independent of one another). Their entropies are

$$S_A = \phi(W_A)$$

$$S_B = \phi(W_B)$$

as would be expected. Since entropy is an extensive quantity, we can define the total entropy as simply

$$S_{AB} = S_A + S_B$$

Since the two systems are independent, the total number of quantum states is given by

$$W_{AB} = W_A W_B$$

Therefore,

$$\phi(W_{AB}) = \phi(W_A W_B) = \phi(W_A) + \phi(W_B)$$

The solution to the above equation

$$\phi(W) = k_B \ln(W)$$

where k_B is some constant (which we know now to be Boltzmann's constant). As such, we see that

$$S = k_B \ln(W)$$

To illustrate the utility of this equation, consider N non-interacting molecules moving within a volume V . We can imagine specifying the position of each molecule by subdividing the total volume into individual volumes of size ΔV . The number of ways to place a particular molecule in the volume is

$$W = \frac{V}{\Delta V}$$

In words, if this box had a volume of 100 L, and we had partitions of size 10 L, there are then of course 10 ways to place a single molecule in the box. The number of ways of arranging N molecules in the box is

$$W_N = \left(\frac{V}{\Delta V} \right)^N$$

since each molecule goes in independently of the rest. Therefore, the entropy is

$$S = Nk_B \ln\left(\frac{V}{\Delta V}\right)$$

Of course, this is reliant on the arbitrarily defined volume size ΔV . This is not a concern, however, because S is always defined with respect to a given reference state. If we take an entropy change (given the same V), we will find that

$$\Delta S = S_f - S_i = Nk_B \ln\left(\frac{V_f}{V_i}\right)$$

and the arbitrarily defined ΔV term vanishes. We can also get the pressure of the system now because we know that

$$P = T \left(\frac{\partial S}{\partial V}\right)_U = \frac{Nk_B T}{V}$$

which is just the ideal gas law and also gives us a clear definition of Boltzmann's constant by relating the equation to $PV = nRT$. The relationship is simply $k_B = R/N_A$.

2.4 MODELING SPINS ON A LATTICE SITE

Suppose there are N particles placed on lattice sites with each particle having a magnetic moment given by μ . Each particle's spin can be either spin up (i.e. spin $+1/2$) or spin down (i.e. spin $-1/2$). If the spin points up, the particle has an energy given by $-\varepsilon$ (i.e. $-\mu B$) and if the spin points down the particle has an energy of $+\varepsilon$ (i.e. $+\mu B$). If we define the number of particles that are spin-up as n_1 , then the number of particles with spin down is simply $n_2 = N - n_1$. The total energy is then

$$U = -n_1\varepsilon + (N - n_1)\varepsilon = N\varepsilon - 2n_1\varepsilon$$

The number of ways of choosing n_1 spin-up particles out of a total N particles is given by

$$W = \frac{N!}{n_1!(N - n_1)!}$$

The spin system's entropy is then

$$S = k_B \ln(W) = k_B \ln\left(\frac{N!}{n_1!(N - n_1)!}\right)$$

This can be easily evaluated, but the problem is that a large lattice will have large values of $N!$ (and potentially $n_1!$). This can make calculations quite difficult due to the sheer size of these numbers. As such, a useful approximation is known as Stirling's approximation, given by

$$\ln(N!) \approx N \ln(N) - N$$

If we employ this approximation, we get

$$S \approx -Nk_B \left(\left(\frac{n_1}{N}\right) \ln\left(\frac{n_1}{N}\right) + \left(1 - \frac{n_1}{N}\right) \ln\left(1 - \frac{n_1}{N}\right) \right)$$

We know from the equation $U = N\varepsilon - 2n_1\varepsilon$ that we can write

$$\frac{n_1}{N} = \frac{1 - \frac{U}{N\varepsilon}}{2} = \frac{1 - x}{2}$$

where $x \equiv U/N\varepsilon$. This allows us to rewrite the expression for entropy as

$$S \approx -Nk_B \left(\frac{1+x}{2} \ln \left(\frac{1+x}{2} \right) + \frac{1-x}{2} \ln \left(\frac{1-x}{2} \right) \right)$$

We recall that we can define the temperature as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V = \left(\frac{\partial S}{\partial x} \right)_V \frac{dx}{dU} = \left(\frac{\partial S}{\partial x} \right)_V \frac{1}{N\varepsilon}$$

As such,

$$\frac{1}{T} = \frac{k_B}{2\varepsilon} \ln \left(\frac{1-x}{1+x} \right)$$

which is equivalent to saying

$$x = -\tanh \left(\frac{\varepsilon}{k_B T} \right)$$

We can convert this back to be in terms of U to get the equation of state

$$U = -N\varepsilon \tanh \left(\frac{\varepsilon}{k_B T} \right)$$

We know that $U = -n_1\varepsilon + n_2\varepsilon$. As such,

$$n_1 - n_2 = -\frac{U}{\varepsilon}$$

This means that

$$n_1 - n_2 = N \tanh \left(\frac{\varepsilon}{k_B T} \right)$$

This is the difference in populations as a function of measurable parameters. In electromagnetism, there is also the quantity known as magnetization, which is the magnetic moment per unit volume. The magnetization is simply

$$M = \frac{\mu(n_1 - n_2)}{V} = \frac{\mu N}{V} \tanh \left(\frac{\mu B}{k_B T} \right)$$

where B is the magnetic induction field.

2.5 MODELING A RUBBER BAND

We now consider a simple model of a rubber band, which we model as a collection of links that lie in the $+z$ or $-z$ direction. The work done on the rubber band when it is extended by an amount $d\ell$ is $F d\ell$, where F is the tension in the band. Therefore, the energy energy is given by

$$dU = T dS + F d\ell$$

From this relation, we can say

$$F d\ell = dU - TdS$$

With $S = k_B \ln(W)$, we can say

$$\frac{F}{T} = -k_B \left(\frac{\partial \ln(W)}{\partial \ell} \right)_U$$

We will define n_+ as the number of links in the $+z$ direction and n_- as the number of links in the $-z$ direction. For a chain of N links, W is given by

$$W = \frac{N!}{n_+! n_-!} = \frac{N!}{n_+! (N - n_+)!}$$

We can then say

$$\ln(W) = \ln(N!) - \ln(n_+!) - \ln((N - n_+)!)$$

which is the following via Stirling's approximation

$$\ln(W) \approx -N \left(\left(\frac{n_+}{N} \right) \ln \left(\frac{n_+}{N} \right) + \left(1 - \frac{n_+}{N} \right) \ln \left(1 - \frac{n_+}{N} \right) \right)$$

The total extension is

$$\ell = (n_+ - n_-)d = (2n_+ - N)d$$

where d is the length of each link. This means we can write an expression

$$\frac{n_+}{N} = \frac{1 + \frac{\ell}{Nd}}{2} = \frac{1 + x}{2}$$

where $x \equiv \ell/Nd$. This makes our expression for $\ln(W)$ become

$$\ln(W) = -N \left(\left(\frac{1+x}{2} \right) \ln \left(\frac{1+x}{2} \right) + \left(\frac{1-x}{2} \right) \ln \left(\frac{1-x}{2} \right) \right)$$

The tension is also rewritten in terms of x as

$$\frac{F}{T} = -k_B \left(\frac{\partial \ln(W)}{\partial x} \right)_U \frac{dx}{d\ell}$$

where $\frac{dx}{d\ell} = 1/Nd$ so

$$\frac{F}{T} = -\frac{k_B}{Nd} \left(\frac{\partial \ln(W)}{\partial x} \right)$$

We can plug in our expression for $\ln(W)$ to get

$$\frac{F}{T} = \frac{k_B}{2d} \ln \left(\frac{1+x}{1-x} \right) = \frac{k_B}{2d} \ln \left(\frac{Nd + \ell}{Nd - \ell} \right)$$

For small values of ℓ/Nd , we get

$$F \approx \frac{k_B T \ell}{Nd^2}$$

Therefore, we see that tension is proportional to $T\ell$. Similarly, for a rubber band under constant tension, the length will decrease upon heating (and vice versa).

3 THE CANONICAL ENSEMBLE

3.1 THE PARTITION FUNCTION

Let us consider a system with multiple energetic states, each occurring with a different probability. We wish to be able to describe the thermodynamic behavior of this system at constant temperature, volume, and number of particles (this is referred to as a canonical ensemble and sometimes an NVT ensemble). The probability of being in a state i out of all possible states j is given by

$$p_i = \frac{W_i}{\sum_j W_j}$$

When dealing with energies, we can say that

$$W_i = e^{-\frac{E_i}{k_B T}}$$

Therefore,

$$p_i = \frac{e^{-\frac{E_i}{k_B T}}}{\sum_j e^{-\frac{E_j}{k_B T}}}$$

We define the partition function of a particle to be

$$Z \equiv \sum_j e^{-\frac{E_j}{k_B T}}$$

such that

$$p_i = \frac{e^{-\frac{E_i}{k_B T}}}{Z}$$

For a system of N distinguishable particles,

$$Z_N = Z^N$$

For a system of N indistinguishable particles,

$$Z_N = \frac{Z^N}{N!}$$

for a large N .

When the probabilities are not equal, the entropy is given by the formula

$$S = -k_B \sum_i p_i \ln(p_i)$$

3.2 THERMODYNAMICS FROM Z

We have that entropy is related to probabilities now. Recall that

$$p_i = \frac{e^{-\frac{E_i}{k_B T}}}{Z}$$

Let's take the natural logarithm of this expression

$$\ln(p_i) = -\frac{E_i}{k_B T} - \ln(Z)$$

Plugging this into the expression for entropy yields

$$S = k_B \sum_i p_i \left(\frac{E_i}{k_B T} + \ln(Z) \right)$$

The average internal energy is defined as

$$\bar{U} = \sum_i p_i E_i$$

so

$$S = \frac{\bar{U}}{T} + k_B \ln(Z)$$

which can be rewritten as

$$\bar{U} - TS = -k_B T \ln(Z)$$

We know that $F = U - TS$, so

$$F = -k_B T \ln(Z)$$

From the previously derived thermodynamic relations relating free energy to P and S ,

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = k_B T \left(\frac{\partial \ln(Z)}{\partial V}\right)_T$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = k_B \left(\frac{\partial (T \ln(Z))}{\partial T}\right)_V$$

$$\bar{U} = F + TS = k_B T^2 \left(\frac{\partial \ln(Z)}{\partial T}\right)_V$$

We can calculate C_V as well

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V = -T \left(\frac{\partial^2 F}{\partial T^2}\right)_V = k_B T \left(\frac{\partial^2 (T \ln(Z))}{\partial T^2}\right)_V$$

Essentially, once we know the partition function, we can calculate entropy and free energy, which make it possible to calculate most other thermodynamic quantities of interest.

3.3 THERMODYNAMICS FROM Z : AN EXAMPLE

Suppose that E_i is a function of V . Show that $P = -N\langle\partial E/\partial V\rangle$. We start with the partition function for N indistinguishable particles,

$$Z = \frac{Z_1^N}{N!} = \frac{\sum_i \exp\left(-\frac{E_i}{k_B T}\right)^N}{N!}$$

The Helmholtz free energy is

$$F_1 = -k_B T \ln(Z) = -k_B T \left(N \ln \left(\sum_i \exp\left(-\frac{E_i}{k_B T}\right) \right) + k_B T (N \ln(N) - N) \right)$$

The pressure is then

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = Nk_B T \left(\frac{\partial \ln \left(\sum_i \exp\left(-\frac{E_i}{k_B T}\right) \right)}{\partial V} \right)_T$$

This is difficult to compute though, so we will use the identity that

$$\frac{\partial \ln(y(x))}{\partial x} = \frac{1}{y(x)} \frac{\partial y(x)}{\partial x}$$

so

$$\begin{aligned} P &= \frac{Nk_B T}{Z} \left(\frac{\partial \left(\sum_i \exp\left(-\frac{E_i}{k_B T}\right) \right)}{\partial V} \right)_T = \frac{Nk_B T}{Z} \left(\sum_i \exp\left(-\frac{E_i}{k_B T}\right) \left(-\frac{1}{k_B T}\right) \left(\frac{\partial E_i}{\partial V}\right)_T \right) \\ &= -\frac{N}{Z} \left(\sum_i \exp\left(-\frac{E_i}{k_B T}\right) \left(\frac{\partial E_i}{\partial V}\right)_T \right) \end{aligned}$$

We note that

$$p_i = \frac{\exp\left(-\frac{E_i}{k_B T}\right)}{Z}$$

so

$$P = -N \sum_i p_i \left(\frac{\partial E_i}{\partial V}\right)_T = -N \left\langle \frac{\partial E}{\partial V} \right\rangle$$

3.4 TRANSLATIONAL PARTITION FUNCTION

Recall from quantum mechanics the particle in a box solution to the Schrodinger wave equation,

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2mL^2}$$

We can write the partition function for one particle in the box as the following

$$Z_1 = \sum_{n=1}^{\infty} e^{-\frac{E_n}{k_B T}} = \sum_{n=1}^{\infty} e^{-\gamma n^2} \approx \int_0^{\infty} e^{-\gamma n^2} dn = \frac{L}{\lambda_D}$$

where

$$\gamma \equiv \frac{1}{k_B T} \frac{\hbar^2 \pi^2}{2mL^2}$$

$$\lambda_D = \left(\frac{2\pi \hbar^2}{mk_B T} \right)^{\frac{1}{2}}$$

This only applies for sufficiently small γ for the summation to be computed as an integral. The λ_D term is known as the thermal de Broglie wavelength.

To scale this up to a 3D particle in a box, the energy term is modified to become

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

such that the partition function for a single particle in the 3D box becomes

$$Z_1 = L^3 \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}} = \frac{L^3}{\lambda_D^3}$$

It is important to note that this is the translational partition function for a molecule. In other words,

$$Z_{\text{trans}} = V \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}} = \frac{V}{\lambda_D^3}$$

where V is L^3 for a box. From this, all other thermodynamic quantities can be derived. For instance,

$$F_1 = -k_B T \ln(Z_1) = -k_B T \left(\ln(V) + \frac{3}{2} \ln \left(\frac{mk_B T}{2\pi \hbar^2} \right) \right)$$

However, if we want to write the Helmholtz free energy for an N particle system (where all particles are indistinguishable), we cannot simply multiply F_1 by N . We need to instead use the statement that for large N , $Z_N = (Z_1)^N / N!$ for N indistinguishable particles.

3.5 ROTATIONAL PARTITION FUNCTION

The rotational partition function comes from the rigid rotor quantum mechanical model, which has energy levels of

$$E_\ell = \frac{\hbar^2 \ell(\ell + 1)}{2I}$$

where I is the moment of inertia and ℓ is the rotational quantum number. The moment of inertia is defined as

$$I = \sum_i m_i r_i^2$$

where r_i is the distance of an atom i from the axis of rotation. For a diatomic molecule, the moment of inertia can be conveniently expressed as

$$I = \frac{m_1 m_2}{m_1 + m_2} d^2 = \mu d^2$$

where μ is the reduced mass and d is the distance between the two atoms. For a linear, symmetric molecule (e.g. CO₂), the moment of inertia is $I = 2m_O r_{CO}^2$, where m_O is the mass of the oxygen atom and r_{CO} is the C-O bond length. For a triatomic molecule, such as the D-D-H transition state, the moment of inertia would approximately be $I = m_D r_{DD}^2 + m_H r_{HD}^2$ (this assumes the center of the molecule is the center of mass, which is a fairly reasonable approximation). With this definition, the rotational partition function is

$$Z_{\text{rot}} = \sum_{\ell=0}^{\infty} (2\ell + 1) e^{-\frac{\hbar^2 \ell(\ell+1)}{2Ik_B T}} = \sum_{\ell=0}^{\infty} (2\ell + 1) e^{-\frac{B\ell(\ell+1)}{k_B T}}$$

where B is the rotational constants defined as

$$B \equiv \frac{\hbar^2}{2I}$$

For $B \ll k_B T$ (the “high temperature limit”), we can approximate the summation as an integral to get

$$Z_{\text{rot}} \approx \int_0^{\infty} (2\ell + 1) e^{-\frac{B\ell(\ell+1)}{k_B T}} d\ell = \frac{k_B T}{B}$$

Technically though, this formula needs to take into account the symmetry of the molecule and therefore should be

$$Z_{\text{rot}} \approx \frac{k_B T}{\sigma B}$$

where σ is the symmetry number (the number of ways a molecule can be oriented in indistinguishable ways).

For nonlinear molecules in the high temperature limit, the equation becomes

$$Z_{\text{rot}} \approx \frac{\sqrt{\pi}}{\sigma} \left(\frac{k_B T^3}{ABC} \right)^{\frac{1}{2}}$$

where A , B , and C are the three rotational constants (one for each spatial dimension, resulting from the different moments of inertia that exist in each dimension).

If we are instead operating in the regime of $B \gg k_B T$ (the “low temperature limit”), we cannot approximate the sum as an integral. However, we can truncate the series without loss of significant accuracy. As such,

$$Z_{\text{rot}} \approx 1 + 3e^{-\frac{\hbar^2}{Ik_B T}} + \dots$$

In either limit, we can use this definition of the rotational partition function to find the Helmholtz free energy and therefore obtain the other thermodynamic parameters of interest.

3.6 VIBRATIONAL PARTITION FUNCTION

The vibrational energy levels come from the harmonic oscillator quantum mechanical model, described by

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right)$$

where ω is the angular frequency and n is the vibrational quantum number. The partition function is then

$$Z_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\frac{\hbar\omega(n+\frac{1}{2})}{k_B T}} = \frac{e^{-\frac{\hbar\omega}{2k_B T}}}{1 - e^{-\frac{\hbar\omega}{k_B T}}}$$

In the low temperature limit of $\hbar\omega \gg k_B T$, we must use this form of the vibrational partition function. In the high temperature limit of $\hbar\omega \ll k_B T$, we can approximate the partition function as simply $k_B T / \hbar\omega$.

The aforementioned discussion is only valid for a system with one vibrational mode. More complicated systems can have multiple vibrational modes such that it is more accurate to say

$$Z_{\text{vib}} = \prod_j \frac{e^{-\frac{\hbar\omega_j}{2k_B T}}}{1 - e^{-\frac{\hbar\omega_j}{k_B T}}}$$

3.7 ELECTRONIC PARTITION FUNCTION

The electronic partition function can be described by

$$Z_{\text{el}} = \sum_i g_i e^{-\frac{E_i}{k_B T}}$$

where g_i is the degeneracy and E_i is the electronic energy above the ground state.

3.8 FACTORIZING THE PARTITION FUNCTION

Since the total energy of a molecular system is the sum of translation, rotational, vibrational, and electronic components, we can then say that the molecular partition function is the product of all the individual components. In other words,

$$Z_1 = Z_{\text{trans}} Z_{\text{vib}} Z_{\text{rot}} Z_{\text{el}}$$

The partition functions derived in the previous sections are only applicable to a single molecule. If we wish to scale the system up to N indistinguishable molecules, the partition function is simply

$$Z_N = \frac{(Z_{\text{trans}})^N}{N!} Z_{\text{vib}}^N Z_{\text{rot}}^N Z_{\text{el}}^N$$

With this, the free energy can be written as

$$F = -k_B T \ln(Z_N) = -Nk_B T (\ln(Z_{\text{trans}}) + \ln(Z_{\text{rot}}) + \ln(Z_{\text{el}}) - \ln(N!))$$

We then see that when the energies can be added, the partition functions can be multiplied, and the free energies of each component can be added (and therefore so can other thermodynamic functions).

3.9 FLUCTUATIONS IN THE CANONICAL ENSEMBLE

In the canonical ensemble, which has a constant N, V, T in each system, the energy of each system can fluctuate around the average value. We wish to describe the size of these fluctuations. If we define our internal energy as $U \equiv \langle E \rangle$, then we can state

$$U = \sum_i E_i p_i = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

where $\beta \equiv 1/k_B T$. We can then state that

$$\left(\frac{\partial U}{\partial \beta}\right)_V = \frac{-\sum_i E_i^2 e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} + \left(\frac{(\sum_i E_i e^{-\beta E_i})^2}{(\sum_i e^{-\beta E_i})^2}\right)$$

We immediately can recognize that

$$\frac{-\sum_i E_i^2 e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = -\langle E^2 \rangle$$

$$\left(\frac{(\sum_i E_i e^{-\beta E_i})^2}{(\sum_i e^{-\beta E_i})^2}\right) = \langle E \rangle^2$$

such that

$$\langle E^2 \rangle - \langle E \rangle^2 = -\left(\frac{\partial U}{\partial \beta}\right)_V$$

We can substitute back in for β to get

$$\left(\frac{\partial U}{\partial \beta}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial \beta}\right) = \left(\frac{\partial U}{\partial T}\right)_V (-k_B T^2) = C_V (-k_B T^2)$$

such that

$$\langle E^2 \rangle - \langle E \rangle^2 = C_V k_B T^2$$

We then see that C_V is an entity that can describe the fluctuations in energy of the canonical ensemble.

4 HAMILTONIAN MECHANICS

4.1 FORMALISM

We are often used to dealing with Newtonian mechanics, where momentum is related to force via

$$\dot{p} \equiv \frac{dp}{dt} = F$$

If the force is a function of the three spatial variables, then this is a set of second order differential equations in those coordinates whose solution is a function of time. For N particles, there are $3N$ second order differential equations with $6N$ initial conditions. To simplify this formalism, we can make use of Lagrangian and Hamiltonian mechanics. In Lagrangian mechanics, we let T be the kinetic energy of a particle. In Cartesian coordinates,

$$T(\dot{x}, \dot{y}, \dot{z}) = \frac{m}{2} (\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$$

We also deal with a potential energy, denoted V . Newton's equation of motion can be written as

$$m\ddot{x} = -\frac{\partial V}{\partial x}$$

with analogous equations in y and z . Now, we introduce a new function called the Lagrangian:

$$L(x, y, z, \dot{x}, \dot{y}, \dot{z}) \equiv T(\dot{x}, \dot{y}, \dot{z}) - V(x, y, z)$$

The generalized momentum is then

$$\frac{\partial L}{\partial \dot{x}} = \frac{\partial T}{\partial \dot{x}} = m\dot{x} = p_x$$

The generalized force is then

$$\frac{\partial L}{\partial x} = -\frac{\partial V}{\partial x}$$

Newton's equations can therefore be written as

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{x}} \right) = \frac{\partial L}{\partial x}$$

We now wish to introduce transformed coordinates so that we are not restricted to the Cartesian system. Let us consider q_1 , q_2 , and q_3 as the transformed spatial coordinates. If we use this, then Lagrange's equations become

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) = \frac{\partial L}{\partial q_j}$$

where $j = 1, 2, 3$. For N particles, there are still $3N$ second order differential equations and $6N$ initial conditions, but the equations have the same form in any coordinate system. To simplify the second order differential equations to a set of first order differential equations, we must introduce the Hamiltonian approach.

Let us define a generalized momentum by

$$p_j = \frac{\partial L}{\partial \dot{q}_j}$$

where $j = 1, 2, \dots, 3N$. Then we can define the Hamiltonian function for a system containing one particle (for simplicity) as

$$H(p_1, p_2, p_3, q_1, q_2, q_3) = \sum_{j=1}^3 p_j \dot{q}_j - L(\dot{q}_1, \dot{q}_2, \dot{q}_3, q_1, q_2, q_3)$$

We can write the kinetic energy as

$$T = \sum_{j=1}^{3N} a_j(q_1, q_2, \dots, q_{3N}) \dot{q}_j^2$$

where a_j are functions of the generalized coordinates. If the potential energy is a function only of the generalized coordinates, then p_j can be defined by

$$p_j = \frac{\partial L}{\partial \dot{q}_j} = \frac{\partial T}{\partial \dot{q}_j} = 2a_j \dot{q}_j$$

This then lets us write that

$$H = T + V$$

such that the Hamiltonian is just the sum of the kinetic and potential energies. If the Lagrangian is not an explicit function of time, then the time-derivative of the Hamiltonian is zero. Let us begin with the definition of H

$$dH = \sum_j \dot{q}_j dp_j + \sum_j p_j d\dot{q}_j - \sum_j \frac{\partial L}{\partial \dot{q}_j} d\dot{q}_j - \sum_j \frac{\partial L}{\partial q_j} dq_j$$

We can use the previously derived equations to then state

$$dH = \sum_j \dot{q}_j dp_j + \sum_j \dot{p}_j dq_j$$

The total derivative of the Hamiltonian is

$$dH = \sum_j \left(\frac{\partial H}{\partial p_j} \right) dp_j + \sum_j \left(\frac{\partial H}{\partial q_j} \right) dq_j$$

Therefore, comparing the last two equations it is clear to see that

$$\frac{\partial H}{\partial p_j} = \dot{q}_j$$

and

$$\frac{\partial H}{\partial q_j} = -\dot{p}_j$$

with $j = 1, 2, \dots, 3N$ for N particles. The last two expressions are Hamiltonian's equations of motions. For N particles, there are $6N$ first order differential equations and $6N$ initial conditions. In particular, the Hamiltonian equations of motion describe the motion of a particle through a phase space composed of p_j and q_j coordinates. For a classical continuous system, the canonical partition function for one particle is

$$Z_1 = \frac{1}{h^3} \iiint dp_i dp_j dp_k \iiint dq_i dq_j dq_k \exp\left(-\frac{H}{k_B T}\right)$$

Here, the i, j, k subscripts are used to represent three spatial coordinates in a given coordinate system. Note that if we are dealing with a system that is in less than three dimensions, the volume integral (and the number of derivative terms) would change accordingly. In addition, recall that q is just a generalized position variable. So, if we are operating in Cartesian coordinates, the above is simply

$$Z_1 = \frac{1}{h^3} \iiint dp_x dp_y dp_z \iiint dx dy dz \exp\left(-\frac{H}{k_B T}\right)$$

4.2 PRACTICE PROBLEMS

4.2.1 CLASSICAL SPRING MODEL

Consider a one-dimensional spring, whose Hamiltonian can be expressed as

$$H = \frac{p^2}{2m} + \frac{cq^2}{2}$$

Find the partition function of one particle whose energy follows this expression.

We start with the classical, continuous partition function for one particle

$$Z_1 = \frac{1}{h^3} \iiint dp_i dp_j dp_k \iiint dq_i dq_j dq_k \exp\left(-\frac{H}{k_B T}\right)$$

We are only operating in one dimension, so we can more simply say

$$Z_1 = \frac{1}{h} \int dp \int dq \exp\left(-\frac{H}{k_B T}\right)$$

Plugging in the Hamiltonian,

$$Z_1 = \frac{1}{h} \int dp \int dq \exp\left(-\frac{\frac{p^2}{2m} + \frac{cq^2}{2}}{k_B T}\right)$$

We can split up the exponential into parts

$$Z_1 = \frac{1}{h} \int \left(-\frac{p^2}{2k_B T}\right) dp \int \exp\left(-\frac{cq^2}{2k_B T}\right) dq$$

This has the solution

$$Z_1 = \sqrt{\frac{2\pi k_B T}{c}} \sqrt{2\pi m k_B T} = 2\pi k_B T \sqrt{\frac{m}{c}}$$

4.2.2 CLASSICAL IDEAL GAS

Consider an ideal gas consisting of N particles that obey classical statistics. The energy of a particle is ε and is proportional to the magnitude of the momentum, p , via $\varepsilon = c|p|$. Find the equation of state and energy of the gas. Consider the particles as structureless.

Let us first begin with one particle. If the particle is structureless, we are only considering translational contributions to the partition function. We start with the classical, continuous partition function for one particle

$$Z_1 = \frac{1}{h^3} \iiint dp_i dp_j dp_k \iiint dq_i dq_j dq_k \exp\left(-\frac{H}{k_B T}\right)$$

We recognize that we are dealing in three dimensions, so these integrals will be triple integrals. We also know that the Hamiltonian is a representation of the energy, so we can substitute in ε for H . This allows us to then say

$$Z_1 = \frac{1}{h^3} \iiint dp_x dp_y dp_z \iiint dx dy dz \exp\left(-\frac{\varepsilon}{k_B T}\right)$$

Since the momentum and position variables can fluctuate from $-\infty$ to $+\infty$, those are the bounds of the triple integral in the dp_i terms. For the spatial triple integral, we can simply recognize that integrating over the three spatial coordinates is the volume of the system, V , so

$$Z_1 = \frac{V}{h^3} \iiint_{-\infty}^{\infty} dp_x dp_y dp_z \exp\left(-\frac{\varepsilon}{k_B T}\right)$$

Plugging in for the energy

$$Z_1 = \frac{V}{h^3} \iiint_{-\infty}^{\infty} dp_x dp_y dp_z \exp\left(-\frac{c|p|}{k_B T}\right)$$

To evaluate this integral, we transform it into spherical coordinates in momentum space

$$Z_1 = \frac{V}{h^3} \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \exp\left(-\frac{cr}{k_B T}\right) r^2 \sin\theta \, dr d\theta d\phi$$

since $|p| = \sqrt{p_x^2 + p_y^2 + p_z^2} = r$. This can be integrated to yield

$$Z_1 = \frac{8\pi V}{h^3} \left(\frac{k_B T}{c}\right)^3$$

Scaling this up to N particles,

$$Z_N = \frac{Z_1^N}{N!} = \frac{1}{N!} \left(\frac{8\pi V}{h^3} \left(\frac{k_B T}{c}\right)^3\right)^N$$

The free energy is

$$\begin{aligned}
F &= -k_B T \ln(Z_N) = -k_B T \ln\left(\frac{1}{N!} \left(\frac{8\pi V}{h^3} \left(\frac{k_B T}{c}\right)^3\right)^N\right) = -k_B T \left(N \ln\left(\frac{8\pi V}{h^3} \left(\frac{k_B T}{c}\right)^3\right) - \ln(N!)\right) \\
&= -k_B T N \left(\ln\left(8\pi \frac{V}{N}\right) + 3 \ln\left(\frac{k_B T}{hc}\right) + 1\right)
\end{aligned}$$

We can then note that

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{k_B T N}{V} = \frac{nRT}{V}$$

which is the ideal gas law. To find the energy of the gas, note that

$$U = F + TS$$

Therefore, we first need the entropy. This is

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = k_B T N \left(\ln\left(8\pi \frac{V}{N}\right) + 3 \ln\left(\frac{k_B T}{hc}\right) + 1\right) + 3k_B N$$

Therefore,

$$U = 3k_B T N = 3nRT$$

We do not get the typical answer for an ideal gas of $U = \frac{3}{2}nRT$ since the Hamiltonian does not have three quadratic terms (it only has one – the one for the translational component).

5 CHEMICAL EQUILIBRIUM

5.1 CONDITIONS OF CHEMICAL EQUILIBRIUM

We now consider a simple equilibrium reaction of $A \leftrightarrow B$, such as isomerization or the folding of a protein. We know from kinetics that

$$K = \frac{[B]_{eq}}{[A]_{eq}}$$

where K is the chemical equilibrium constant. We wish to relate chemical equilibrium to chemical potential. At constant T and V ,

$$dF = -SdT - PdV + \mu_A dn_A + \mu_B dn_B$$

becomes

$$dF = \mu_A dn_A + \mu_B dn_B$$

If we define ξ as the extent of reaction such that $d\xi = -dn_A = +dn_B$, then

$$dF = (\mu_B - \mu_A)d\xi$$

such that

$$\left(\frac{\partial F}{\partial \xi}\right)_{T,V} = \mu_B - \mu_A$$

At equilibrium, we know that the derivative must be zero, and therefore equilibrium in this system is defined as being when $\mu_A = \mu_B$. We could have repeated the same procedure constant T and P . As such,

$$dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B$$

becomes

$$dG = \mu_A dn_A + \mu_B dn_B$$

such that

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \mu_B - \mu_A$$

We can also determine that the chemical potential of a species i by

$$\mu_i = \mu_i^\circ + k_B T \ln\left(\frac{p_i}{P}\right)$$

5.2 CALCULATING EQUILIBRIUM CONSTANTS

This is effectively a mini-summary of Sections 3.4-3.8. From kinetics, we know that we can express the equilibrium constant as

$$K_C = \exp\left(-\frac{\Delta U}{k_B T}\right) \prod_i Z_i^{\nu_i}$$

where ΔU represents the energy change of the reaction. Note that if you have bond dissociation energies (BDE), that $\Delta U = \text{BDE}_{\text{bonds broken}} - \text{BDE}_{\text{bonds formed}}$ in order for the sign convention to work out since BDEs are tabulated as positive quantities.

We recall that the partition function can be factorized, so each species' partition function is the product of the various components. Recalling from before, the translational partition function per unit volume is

$$\frac{Z_{\text{trans}}}{V} = \frac{1}{\lambda_D^3} = \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}}$$

In calculating K , you must use Z_{trans}/V to get the units correct. Common values of Z_{trans}/V are about 10^{24} cm^{-3} .

The rotational partition function is different depending on the shape of the molecule. For a linear molecule,

$$Z_{\text{rot}} = \frac{8\pi^2 I k_B T}{\sigma h^2} = \frac{T}{\sigma \theta_{\text{rot}}}$$

where θ_{rot} is the rotational “temperature”. For a nonlinear molecule

$$Z_{\text{rot}} = \frac{8\pi^2 (8\pi^3 I_1 I_2 I_3)^{\frac{1}{2}} (k_B T)^{\frac{3}{2}}}{h^3 \sigma}$$

In these equations, σ represents the symmetry number and is determined by the number of spatial orientations of the subject molecule that are identical. For easy reference, it is a value of 2 for linear molecules with a center of symmetry and 1 for linear molecules without a center of symmetry. The quantity I is the moment of inertia, and for the nonlinear case they are the three principal moments. The moment of inertia is defined as

$$I = \sum_i m_i r_i^2$$

where r is the distance to the axis of rotation. For a diatomic molecule, the moment of inertia is $I = \mu R^2$ where μ is the reduced mass and R is the distance between the two atoms. For a linear, symmetric molecule like CO_2 , the moment of inertia is $I = 2m_{\text{O}}r_{\text{CO}}^2$, where m_{O} is the mass of the oxygen atom and r_{CO} is the C-O bond length. For a triatomic linear molecule, such as a D-D-H transition state, the moment of inertia would approximately be $I = m_{\text{D}}r_{\text{DD}}^2 + m_{\text{H}}r_{\text{HD}}^2$ (this assumes the center of the molecule is the center of mass, which is a reasonable approximation). The value of Z_{rot} is unitless and approximately $10^2 - 10^4$ for linear molecules and $10^3 - 10^6$ for nonlinear molecules.

The vibrational partition function is given by

$$Z_{\text{vib}} = \prod_i^n \left(1 - \exp\left(-\frac{h\nu_i}{k_B T}\right) \right)^{-1} = \prod_i^n \left(1 - \exp\left(-\frac{\theta_{\text{vib}}}{T}\right) \right)^{-1}$$

where n is the degrees of vibrational freedom, ν_i is the vibrational frequency from IR or Raman spectroscopy, and θ_{vib} is the vibrational “temperature”. The value of Z_{vib} is unitless and approximately 1 to 10. Note that spectra normally yield wavenumbers with units of inverse length. To convert a wavenumber $\tilde{\nu}$ to frequency, use $\nu_i = c\tilde{\nu}_i$.

Finally, the electronic partition function is given by

$$Z_{el} = \sum_i g_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right)$$

where g_i is the degeneracy and ε_i is the electronic energy above the ground state.

5.3 GRAND CANONICAL ENSEMBLE

5.3.1 DEFINITION

In the canonical ensemble, we assumed constant NVT conditions. We now wish to consider the case where we can let the number of particles fluctuate, which is at constant μ VT conditions instead.

The probability to find a member of the ensemble that contains N particles and is in an energy state $E_i(N, V)$ is given by

$$P_i = \frac{e^{-\frac{(E_i - \mu N)}{k_B T}}}{\Xi}$$

where Ξ is the grand canonical partition function, given by

$$\Xi = \sum_{\text{states}} e^{-\frac{(E - \mu N)}{k_B T}}$$

It is important to note that this sum is over all possible microstates. That includes all combinations of energy levels and N . As such, the grand canonical partition function (for one type of particle) can be restated as

$$\Xi = \sum_N \sum_i e^{-\frac{(E_i - \mu N)}{k_B T}}$$

where the inner sum is over all possible energy states, and the outer sum is overall possible number of particles. Since the exponential can be split into the product of two exponentials, it is also worthwhile to note that

$$\Xi = \sum_N Z_N e^{\frac{\mu N}{k_B T}}$$

5.3.2 CONNECTION TO THERMODYNAMICS

We recall that the entropy is given by

$$S = -k_B \sum_i p_i \ln(p_i)$$

Plugging in our probability expression gets us

$$S = \frac{\bar{U}}{T} - \frac{\mu \bar{N}}{T} + k_B \ln(\Xi)$$

Therefore, we define a new state function called the grand potential that is

$$\Phi \equiv \bar{U} - TS - \mu \bar{N}$$

The definition implies that

$$d\Phi = d\bar{U} - d(\mu\bar{N}) - d(TS)$$

If we note that

$$dU = TdS - PdV + \mu dN$$

then

$$d\Phi = -PdV - \bar{N}d\mu - SdT$$

This allows us to state that

$$S = -\left(\frac{\partial\Phi}{\partial T}\right)_{V,\mu} = k_B \left(\frac{\partial(T \ln(\Xi))}{\partial T}\right)_{V,\mu}$$

$$P = -\left(\frac{\partial\Phi}{\partial V}\right)_{T,\mu} = k_B T \left(\frac{\partial(\ln(\Xi))}{\partial V}\right)_{T,\mu}$$

$$\bar{N} = -\left(\frac{\partial\Phi}{\partial\mu}\right)_{T,V} = k_B T \left(\frac{\partial(\ln(\Xi))}{\partial\mu}\right)_{T,V}$$

It is also clear from our definition of the grand canonical partition function and grand potential that

$$\Phi = -k_B T \ln(\Xi)$$

$$PV = k_B T \ln(\Xi)$$

6 THERMODYNAMICS OF BIOPOLYMERS

6.1 MEAN SIZE OF RANDOM WALK MACROMOLECULE

Let us start by considering a lattice model with a lattice constant determined by ℓ . The value of ℓ represents the distance over which a polymer bends. We can then relate the contour length of the polymer (i.e. the length of the polymer when fully outstretched), L , and the number of steps taken, N , via

$$N = \frac{L}{\ell}$$

The end-to-end distance of the polymer is given by \vec{r} . Let $g_N(\vec{r})$ equal the total number of walks on the lattice that start at the origin and end at \vec{r} . This implies then that $\sum_{\vec{r}} g_N(\vec{r})$ is the total number of possible configurations of the polymer. We will define this as

$$\sum_{\vec{r}} g_N(\vec{r}) = g_{\text{tot}} = \gamma^N$$

It can be shown that that $\gamma = 2$ for 1D, $\gamma = 4$ for 2D, and $\gamma = 6$ for 3D. Before we get Z , let us try to get the size of the polymer, given by $\sqrt{\langle \vec{r}^2 \rangle}$. If we define the position vector as $\vec{r} = \vec{\ell}_1 + \vec{\ell}_2 + \dots + \vec{\ell}_N$ then

$$\langle \vec{r}^2 \rangle = \left\langle \left(\sum_{i=1}^N \vec{\ell}_i \right)^2 \right\rangle = \left\langle \sum_{i=1}^N \sum_{j=1}^N \vec{\ell}_i \cdot \vec{\ell}_j \right\rangle = \sum_{i=1}^N \langle \vec{\ell}_i^2 \rangle + \sum_{i \neq j=1}^N \langle \vec{\ell}_i \cdot \vec{\ell}_j \rangle$$

Since every step is independent of all steps that preceded and follow it, the second term on the right-hand side is zero. In addition, $\langle \vec{\ell}_i^2 \rangle = \ell^2$ since $\vec{\ell}_i = \pm \ell$. Therefore,

$$\langle \vec{r}^2 \rangle = N\ell^2$$

The polymer size, R_0 , is then

$$R_0 = \sqrt{\langle \vec{r}^2 \rangle} = \ell\sqrt{N} = \sqrt{L}\ell$$

6.2 RANDOM WALK: DIFFUSION

Let $p_0(\vec{r}, t)$ be the probability of a diffusing random-walker particle to be a distance \vec{r} at a time t . It can be shown that the probability is

$$p_0 = \frac{e^{-\frac{\vec{r}^2}{4Dt}}}{(4\pi Dt)^{\frac{3}{2}}}$$

To find $\langle \vec{r}^2 \rangle$, we note that the following statement is true (so long as the probability function is normalized such that it has a value of 1 over all space)

$$\langle \vec{r}^2 \rangle = \int_{-\infty}^{\infty} \vec{r}^2 p_0(\vec{r}) d\vec{r}$$

Plugging in our probability

$$\langle \vec{r}^2 \rangle = \int_{-\infty}^{\infty} \vec{r}^2 \frac{e^{-\frac{\vec{r}^2}{4Dt}}}{(4\pi Dt)^{\frac{3}{2}}} d\vec{r}$$

This would be a nightmare to actually integrate. We can note the following identity:

$$\int_{-\infty}^{\infty} e^{-\alpha \vec{r}^2} d\vec{r} = \left(\frac{\pi}{\alpha}\right)^{\frac{3}{2}}$$

To make our exponential in $\langle \vec{r}^2 \rangle$ look like the above integral, we note that $\alpha = 1/4Dt$. Substituting this in yields the following (and I pulled out a constant factor in front of the integral):

$$\langle \vec{r}^2 \rangle = \frac{1}{(4\pi Dt)^{\frac{3}{2}}} \int_{-\infty}^{\infty} \vec{r}^2 e^{-\alpha \vec{r}^2} d\vec{r}$$

This almost looks like the tabulated integral, except for there is an \vec{r}^2 factor inside the integrand as well. We can solve this easily by noting that

$$\vec{r}^2 e^{-\alpha \vec{r}^2} = -\frac{d}{d\alpha} (e^{-\alpha \vec{r}^2})$$

Therefore, we can say

$$\langle \vec{r}^2 \rangle = \frac{1}{(4\pi Dt)^{\frac{3}{2}}} \left(-\frac{d}{d\alpha} \int_{-\infty}^{\infty} e^{-\alpha \vec{r}^2} d\vec{r} \right) = \frac{1}{(4\pi Dt)^{\frac{3}{2}}} \left(-\frac{d}{d\alpha} \left(\frac{\pi}{\alpha}\right)^{\frac{3}{2}} \right) = \frac{1}{(4\pi Dt)^{\frac{3}{2}}} \left(\frac{3\pi^{\frac{3}{2}}}{2\alpha^{\frac{5}{2}}} \right) = 6Dt$$

Therefore, $\sqrt{\langle \vec{r}^2 \rangle} \sim \sqrt{t}$.

6.3 ANALOGY TO POLYMERS

Using the previous solution, we make an analogy to polymers. For diffusion, we dealt with time (t) whereas for polymers we deal with a length scale N (defined by $t/\Delta t$, where Δt is a discrete time step). It can therefore be shown that the size is proportional to \sqrt{N} (instead of \sqrt{t}) for polymers. From our expressions of

$$\langle \vec{r}^2 \rangle = N\ell^2$$

and

$$\langle \vec{r}^2 \rangle = 6Dt$$

we can equate them to yield

$$D = \frac{\ell^2 N}{6t} = \frac{\ell^2}{6\Delta t}$$

For polymers, the probability can be expressed as the following, as discussed in the next section:

$$p = \left(\frac{3}{2\pi N\ell^2}\right)^{\frac{3}{2}} e^{-\frac{3\vec{r}^2}{2N\ell^2}}$$

6.4 ENTROPIC SPRING MODEL

Using the previous Gaussian chain formulation, find the probability that the two ends of a polymer chain are at a distance δ or smaller from each other. To do this, we begin by recalling that

$$p = \left(\frac{3}{2\pi N\ell^2} \right)^{\frac{3}{2}} e^{-\frac{3r^2}{2N\ell^2}}$$

We essentially want to calculate the probability the two ends are within a volume slice of distance δ , so

$$p_0 = \int_0^\pi \int_0^{2\pi} \int_0^\delta r^2 p \sin \theta \, d\theta d\phi dr$$

This becomes

$$p_0 = 4\pi \int_0^\delta r^2 p \, dr$$

or

$$p_0 = 4\pi \left(\frac{3}{2\pi N\ell^2} \right)^{\frac{3}{2}} \int_0^\delta r^2 e^{-\frac{3r^2}{2N\ell^2}} \, dr$$

If we can assume that $\delta \ll \sqrt{N}\ell$, then the exponential is approximately 1 and therefore

$$p_0 = 4\pi \left(\frac{3}{2\pi N\ell^2} \right)^{\frac{3}{2}} \frac{\delta^3}{3} = \left(\frac{6}{\pi N^3} \right)^{\frac{1}{2}} \left(\frac{\delta}{\ell} \right)^3$$

6.5 ENTROPIC RESTORING FORCE

For polymers, the probability of being in a given state is the number of ways to get a given \vec{r} divided by the total number of configurations. We shall denote this as follows

$$p(\vec{r}, t) = \frac{g_N(\vec{r})}{\gamma^N}$$

Therefore, using the identity $N\ell^2 = L\ell$, we can find $g_N(\vec{r})$ to get

$$g_N(\vec{r}) = \frac{\gamma^N 3^{\frac{3}{2}}}{(2\pi L\ell)^{\frac{3}{2}}} e^{-\frac{3r^2}{2N\ell^2}}$$

We can now calculate the force associated with a given end-to-end distance. The Helmholtz free energy is given by

$$F = U - TS$$

where U is just the internal energy of the system, which is a constant. Since

$$S = k_B \ln(g_N(\vec{r}))$$

we get

$$F = U - k_B T \ln(g_N(\vec{r}))$$

Since U is a constant, we can say

$$F = \text{const} + \frac{3k_B T}{2L\ell} \vec{r}^2 = \left(\text{const} + \frac{1}{2}\right) \kappa \vec{r}^2$$

where κ is the entropic spring constant given by

$$\kappa = \frac{3k_B T}{L\ell}$$

The restoring force for a stretched polymer is driven by entropy.

6.6 FORCE AS A FUNCTION OF EXTENSION

We can use the machinery of statistical mechanics, in particular the canonical ensemble, to determine the force and other macroscopic properties. Recall that the canonical partition function is

$$Z = \sum_n e^{-\frac{E_n}{k_B T}}$$

For this discussion, we will rearrange our definition of Z to instead read

$$Z = \sum_E g_N(E) e^{-\frac{E}{k_B T}}$$

This is now a sum over all allowable energies, and $g_N(E)$ is the energy level degeneracy (known as the density of states). If E is thought of as the work done to move one end of the polymer to move it from the origin to a position \vec{r} , then

$$E = -\vec{F} \cdot \vec{r}$$

Plugging this in yields

$$Z = \sum_{\vec{r}} g_N(\vec{r}) e^{\frac{\vec{F} \cdot \vec{r}}{k_B T}}$$

We recognize that we can substitute in κ into $g_N(\vec{r})$, remembering that equivalence $N\ell = L$. As such,

$$g_N(\vec{r}) = \frac{\gamma^N 3^{\frac{3}{2}}}{(2\pi L\ell)^{\frac{3}{2}}} e^{-\frac{3\vec{r}^2}{2N\ell^2}} = \frac{\gamma^N 3^{\frac{3}{2}}}{(2\pi L\ell)^{\frac{3}{2}}} e^{-\frac{3\vec{r}^2}{2L\ell}} = \frac{\gamma^N 3^{\frac{3}{2}}}{(2\pi L\ell)^{\frac{3}{2}}} e^{-\frac{1\kappa\vec{r}^2}{2k_B T}}$$

Plugging in for g_N yields

$$Z = \sum_{\vec{r}} \frac{\gamma^N 3^{\frac{3}{2}}}{(2\pi L\ell)^{\frac{3}{2}}} e^{-\frac{1\kappa\vec{r}^2}{2k_B T}} e^{\frac{\vec{F} \cdot \vec{r}}{k_B T}} = \text{const} \cdot \sum_{\vec{r}} e^{-\frac{1\kappa\vec{r}^2}{2k_B T} + \frac{\vec{F} \cdot \vec{r}}{k_B T}}$$

Converting this to an integral in the continuum limit,

$$Z = \text{const} \cdot \int_{-\infty}^{\infty} e^{-\frac{1}{2} \frac{\kappa \vec{r}^2}{k_B T} + \frac{\vec{F} \cdot \vec{r}}{k_B T}} d\vec{r}$$

Let us assume that \vec{F} only acts in the \hat{x} direction. As such, $F_y = F_z = 0$. Then, if we write the integral in Cartesian coordinates (and noting $\vec{F} = F_x \hat{x} \equiv F$)

$$Z = \text{const} \cdot \left(\int_{-\infty}^{\infty} e^{-\frac{1}{2} \frac{\kappa x^2}{k_B T} + \frac{Fx}{k_B T}} dx \int_{-\infty}^{\infty} e^{-\frac{1}{2} \frac{\kappa y^2}{k_B T}} dy \int_{-\infty}^{\infty} e^{-\frac{1}{2} \frac{\kappa z^2}{k_B T}} dz \right)$$

This can be integrated by using the following identity (in addition to the one already mentioned before):

$$\int_{-\infty}^{\infty} e^{-\alpha x^2 + \beta x} dx = \sqrt{\frac{\pi}{\alpha}} e^{\frac{\beta^2}{4\alpha}}$$

Employing this identity yields

$$Z = \text{const} \cdot \left(\left(\frac{2\pi k_B T}{\kappa} \right)^{3/2} e^{\frac{F^2}{2\kappa k_B T}} \right)$$

We now wish to obtain an expression for $\langle x \rangle$. To do so, we note that

$$\langle x \rangle = k_B T \frac{\partial \ln(Z)}{\partial F}$$

To see why this is true takes a bit of foresight. The following is a brief explanation. Recall that the average value of a function ξ is going to have the form

$$\langle \xi \rangle = \frac{\int \xi e^{-\frac{E(\xi)}{k_B T}}}{\int e^{-\frac{E(\xi)}{k_B T}}}$$

We want to find an expression that has this form. We begin with our expression of the partition function in its integral formulation:

$$Z = \text{const} \cdot \left(\int_{-\infty}^{\infty} e^{-\frac{1}{2} \frac{\kappa x^2}{k_B T} + \frac{Fx}{k_B T}} dx \int_{-\infty}^{\infty} e^{-\frac{1}{2} \frac{\kappa y^2}{k_B T}} dy \int_{-\infty}^{\infty} e^{-\frac{1}{2} \frac{\kappa z^2}{k_B T}} dz \right)$$

Now, we take the derivative with respect to F and divide by Z to get

$$\frac{1}{Z} \frac{\partial Z}{\partial F} = \frac{1}{Z} \left[\text{const} \cdot \frac{1}{k_B T} \int_{-\infty}^{\infty} x e^{-\frac{1}{2} \frac{\kappa x^2}{k_B T} + \frac{Fx}{k_B T}} dx \int_{-\infty}^{\infty} e^{-\frac{1}{2} \frac{\kappa y^2}{k_B T}} dy \int_{-\infty}^{\infty} e^{-\frac{1}{2} \frac{\kappa z^2}{k_B T}} dz \right]$$

We see that the integral in the x direction now has an x term multiplied by an exponential. That looks just like the expression for the definition of the average value I quoted above! This means that

$$\langle x \rangle \sim \frac{1}{Z} \frac{\partial Z}{\partial F}$$

or put another way

$$\langle x \rangle \sim \frac{\partial \ln(Z)}{\partial F}$$

with the constant of proportionality being $k_B T$. It is important to note that we do not include the lumped constant term in the expression for $\langle x \rangle$ since it is also present in Z and will therefore cancel. We now calculate $\langle x \rangle$.

$$\ln(Z) = \ln(\text{const}) + \frac{3}{2} \ln\left(\frac{2\pi k_B T}{\kappa}\right) + \frac{F^2}{2\kappa k_B T}$$

Therefore,

$$\frac{\partial \ln(Z)}{\partial F} = \frac{F}{\kappa k_B T}$$

This then means

$$\langle x \rangle = k_B T \frac{\partial \ln(Z)}{\partial F} = \frac{F}{\kappa} = \frac{1}{3} \frac{L\ell}{k_B T} F$$

Therefore, if we plot $\langle x \rangle$ as a function of F , it will be a line with a slope of one-third. While this is true experimentally for small to moderate values of F , the polymer obviously cannot extend infinitely – it must level off at high F and approach the contour length. This is where the following models come into play.

6.7 FREELY JOINTED CHAIN

In the freely jointed chain model, we model a polymer by discrete segments connected by hinges. We shall discretize the polymer curve with tangents, each with a length \vec{t}_j . The absolute value of the tangent vector is equal to the persistence length, $|\vec{t}_j| = \ell$. We begin by writing the partition function for the system. We only include the configurational part (i.e. any factors of $1/h$ and any momentum integral terms will be neglected) because we really care about ratios of partition functions, and constants will cancel. The energy is now

$$E = -\vec{F} \cdot \sum_{j=1}^N \vec{t}_j$$

The configurational partition function is then

$$Z = \int d\Omega_1 \int d\Omega_2 \dots \int d\Omega_N e^{\frac{\vec{F} \cdot \sum_{j=1}^N \vec{t}_j}{k_B T}}$$

where

$$\int d\Omega_i = \int_0^{2\pi} d\phi_j \int_0^\pi d\theta_j \sin(\theta_j)$$

To explain what's going on here, we are doing our position integrals over a spherical coordinate space, but only the angular terms matter since each chain is assumed to have the same length. The exponential in the definition of the canonical partition function usually contains the negative of the Hamiltonian. In this case,

the energy is simply (negative of the) force times the distance, which is now this tangent vector. We can note that from the definition of the dot product,

$$\vec{F} \cdot \vec{t}_j = F\ell \cos(\theta_j)$$

This then means we can rewrite the partition function as

$$Z = \int d\Omega_1 \int d\Omega_2 \dots \int d\Omega_N e^{\frac{F \sum_{j=1}^N \ell \cos(\theta_j)}{k_B T}}$$

We can rewrite this without the summation in the exponential by the following (since sums in an exponential can be rewritten as the product of exponentials):

$$Z = \prod_{j=1}^N \int d\Omega_j e^{\frac{F\ell \cos(\theta_j)}{k_B T}}$$

Substituting in for our generalized angular coordinates yields

$$Z = \prod_{j=1}^N \left[\int_0^{2\pi} d\phi_j \int_0^\pi d\theta_j \sin(\theta_j) e^{\frac{F\ell \cos(\theta_j)}{k_B T}} \right]$$

That is going to get messy, so let's evaluate Z_1 ($N = 1$) first (or we could note that the two integrals yield constant terms, so we just raise their product to the power of N in the end). That is,

$$Z_1 = \int_0^{2\pi} d\phi_j \int_0^\pi d\theta_j \sin(\theta_j) e^{\frac{F\ell \cos(\theta_j)}{k_B T}}$$

The integral over $d\phi_j$ is just 2π , so that can be factored out. The right integral is a bit harder, but can be done out via u -substitution to yield

$$\int_0^\pi d\theta_j \sin(\theta_j) e^{\frac{F\ell \cos(\theta_j)}{k_B T}} = \frac{2k_B T}{F\ell} \sinh\left(\frac{F\ell}{k_B T}\right)$$

Therefore,

$$Z_1 = \frac{4\pi k_B T}{F\ell} \sinh\left(\frac{F\ell}{k_B T}\right)$$

Scaling this up to N (distinguishable) chains yields

$$Z = \left(\frac{4\pi k_B T}{F\ell} \sinh\left(\frac{F\ell}{k_B T}\right) \right)^N$$

If we are stretching the polymer in the \hat{x} direction, we now wish to find $\langle x \rangle$ again, so we can use the result from before that

$$\langle x \rangle = k_B T \frac{\partial \ln(Z)}{\partial F}$$

If we really want to prove this to ourselves though, we begin with our partition function in integral form as

$$Z = \int d\Omega_1 \int d\Omega_2 \dots \int d\Omega_N e^{\frac{F \sum_{j=1}^N \ell \cos(\theta_j)}{k_B T}}$$

Then we realize that if take a derivative with respect to F and then divide by Z we get the following

$$\frac{1}{Z} \frac{\partial Z}{\partial F} = \frac{1}{Z} \left[\int d\Omega_1 \int d\Omega_2 \dots \int d\Omega_N \frac{\sum_{j=1}^N \ell \cos(\theta_j)}{k_B T} e^{\frac{F \sum_{j=1}^N \ell \cos(\theta_j)}{k_B T}} \right]$$

That looks like an average of the position and supports the conclusion that

$$\langle x \rangle = k_B T \frac{\partial \ln(Z)}{\partial F}$$

We start with

$$\ln(Z) = N \ln \left(\frac{4\pi k_B T}{F\ell} \sinh \left(\frac{F\ell}{k_B T} \right) \right)$$

We then note that

$$\frac{d}{d\xi} \ln \left(\frac{\alpha \sinh(\beta\xi)}{\beta\xi} \right) = \beta \coth(\beta\xi) - \frac{1}{\xi}$$

To use this identity, we note that $\alpha = 4\pi$, $\beta = \ell/k_B T$ and $\xi = F$ such that $\langle x \rangle$ becomes

$$\langle x \rangle = N\ell \left(\coth \left(\frac{F\ell}{k_B T} \right) - \frac{k_B T}{F\ell} \right)$$

We know that $L = N\ell$, so

$$\langle x \rangle = L \left(\coth \left(\frac{F\ell}{k_B T} \right) - \frac{k_B T}{F\ell} \right)$$

We want to understand the limiting behavior. At $\xi \rightarrow 0$, $\coth(\xi) \rightarrow \frac{1}{\xi} + \frac{1}{3}\xi + O(\xi^2)$. Therefore, at the limit of $F \rightarrow 0$ we get

$$\langle x \rangle = L \left(\frac{k_B T}{F\ell} + \frac{1}{3} \frac{F\ell}{k_B T} - \frac{k_B T}{F\ell} \right)$$

or

$$\frac{\langle x \rangle}{L} = \frac{1}{3} \frac{F\ell}{k_B T}$$

so the initial slope is still one-third, which is good. At $\xi \rightarrow \infty$, $\coth(\xi) \rightarrow 1$, so if we let $F \rightarrow \infty$, then $\langle x \rangle \rightarrow L$, and therefore the polymer length approaches the contour length at high force, which is also good. Experimentally, this is pretty good, but there is another improvement we need to make. At high force, the value of $\langle x \rangle$ should decay as $1/\sqrt{F}$, not $1/F$. As such, we go to the next more complicated model.

6.8 WORM-LIKE CHAIN

In the worm-like chain model, we no longer let $|\vec{t}_j| = \ell$ but instead some microscopic length scale a such that $|\vec{t}_j| = a$, such that $a \ll \ell$. We also add resistance to bending, such that the tangents want to be parallel. The energy function is now the same as the freely jointed chain but with an energy “bonus” for chains in the same direction (and penalty if not parallel):

$$E = -\tilde{K} \sum_{j=1}^{N-1} \vec{t}_j \cdot \vec{t}_{j+1} - \vec{F} \cdot \sum_{j=1}^N \vec{t}_j$$

with $\tilde{K} > 0$ so that the tangents want to align locally. We then note that

$$-\tilde{K} \sum_{j=1}^{N-1} \vec{t}_j \cdot \vec{t}_{j+1} = \frac{1}{2} \tilde{K} \sum_{j=1}^{N-1} (\vec{t}_{j+1} - \vec{t}_j)^2 - N\tilde{K}$$

such that

$$E = \frac{1}{2} \tilde{K} \sum_{j=1}^{N-1} (\vec{t}_{j+1} - \vec{t}_j)^2 - N\tilde{K} - \vec{F} \cdot \sum_{j=1}^N \vec{t}_j$$

We note that $(\vec{t}_{j+1} - \vec{t}_j)^2$ looks like a derivative term. It looks like $\left(\frac{d\vec{t}}{dj}\right)^2$, where j is just a counting variable so its finite difference is 1. If we define an arc length, s , that describes each chain, then we can write \vec{t} in terms of s instead of in j . It can then be noted that $a = ds/dj$ and $\vec{t} = a\vec{n}$. As such, we will say

$$(\vec{t}_{j+1} - \vec{t}_j)^2 = \left(\frac{d\vec{t}}{dj}\right)^2 = \left(\frac{d\vec{t}}{ds} \frac{ds}{dj}\right)^2 = a^2 \left(\frac{d\vec{t}}{ds}\right)^2 = a^4 \left(\frac{d\vec{n}}{ds}\right)^2$$

Plugging this into the energy expression yields

$$E = \frac{1}{2} \tilde{K} \sum_{j=1}^N a^4 \left(\frac{d\vec{n}}{ds}\right)^2 - N\tilde{K} - \vec{F} \cdot \sum_{j=1}^N \vec{t}_j$$

We now convert our sum into an integral in the continuum limit via the following thought process. We start by noting that since Δj is 1,

$$\sum_j f = \int f dj$$

Then we know that $a = ds/dj$, so $dj = 1/a ds$. As such,

$$\sum_j f = \int f dj = \frac{1}{a} \int f ds$$

Plugging this in yields,

$$E = \frac{1}{2} \tilde{K} \frac{1}{a} \int_0^L a^4 \left(\frac{d\vec{n}}{ds}\right)^2 ds - N\tilde{K} - \vec{F} \cdot \int_0^L \vec{n}(s) ds$$

If we define $K \equiv \tilde{K}a^3$ then

$$E = \frac{1}{2}K \int_0^L \left(\frac{d\vec{n}}{ds} \right)^2 ds - N\tilde{K} - \vec{F} \cdot \int_0^L \vec{n}(s) ds$$

The energy is now a function of \vec{n} , which is a function of s , so E is said to be a functional. Although it is not obvious yet, we can simply drop the $N\tilde{K}$ term since it is a constant, and it will be divided out at a later point. With this adjustment,

$$E = \frac{1}{2}K \int_0^L \left(\frac{d\vec{n}}{ds} \right)^2 ds - \vec{F} \cdot \int_0^L \vec{n}(s) ds$$

We can split this up into a bending and a force component, where $E = E_{\text{bending}} + E_{\text{force}}$ with

$$E_{\text{bending}} = \frac{1}{2}K \int_0^L \left(\frac{d\vec{n}}{ds} \right)^2 ds$$

and

$$E_{\text{force}} = -\vec{F} \cdot \int_0^L \vec{n}(s) ds$$

We consider pulling the polymer in the \hat{z} direction such that \vec{F} is parallel to \hat{z} . We note that \vec{n} is a unit vector (whose magnitude must be unity). As such, we can write it as a function of its components as follows:

$$\vec{n}(s) = \begin{pmatrix} n_x(s) \\ n_y(s) \\ \sqrt{1 - n_x^2 - n_y^2} \end{pmatrix}$$

We consider for the remainder of the derivation large forces only (since this is the regime we wish to make more accurate – the one-third slope at the low-force regime is already accurate). We note that the following Taylor expansion:

$$\sqrt{1 - \xi} \approx 1 - \frac{1}{2}\xi + O(\xi^2)$$

We apply this expansion to our expression for $\vec{n}(s)$, letting $\xi = n_x^2 + n_y^2$ and keeping only the first two terms, to arrive at

$$\vec{n}(s) \approx \begin{pmatrix} n_x(s) \\ n_y(s) \\ 1 - \frac{1}{2}(n_x^2 + n_y^2) \end{pmatrix}$$

We want to get the derivative term in our E_{bending} expression. As such,

$$\left(\frac{d\vec{n}}{ds}\right)^2 = \left(\frac{dn_x}{ds}\right)^2 + \left(\frac{dn_y}{ds}\right)^2 + O(n_x^4 + n_y^4)$$

which we will simplify to just

$$\left(\frac{d\vec{n}}{ds}\right)^2 = \left(\frac{dn_x}{ds}\right)^2 + \left(\frac{dn_y}{ds}\right)^2$$

This then makes E_{bending} become

$$E_{\text{bending}} = \frac{1}{2}K \int_0^L \left[\left(\frac{dn_x}{ds}\right)^2 + \left(\frac{dn_y}{ds}\right)^2 \right] ds$$

The E_{force} term can be expressed now with our expression for $\vec{n}(s)$ as follows, noting that we only need the n_z term if we note we are pulling in the \hat{z} direction only:

$$E_{\text{force}} = -\vec{F} \cdot \int_0^L \left[1 - \frac{1}{2}(n_x^2 + n_y^2) \right] ds = -FL + \frac{1}{2}F \int_0^L [n_x^2 + n_y^2] ds$$

This means

$$E = \frac{1}{2}K \int_0^L \left[\left(\frac{dn_x}{ds}\right)^2 + \left(\frac{dn_y}{ds}\right)^2 \right] ds + \frac{1}{2}F \int_0^L [n_x^2 + n_y^2] ds - FL$$

The $-FL$ term is a constant that will be also be cancelled later on. We now have an expression for the energy that we can use to find the partition function.

Since E is a function of \vec{n} , which is a function of s , we must perform a path integral, denoted by a \mathcal{D} operator, when evaluating the partition function (which is shown below for reference):

$$Z = \int e^{-\frac{E[\vec{n}(s)]}{k_B T}} \mathcal{D}[\vec{n}(s)]$$

This is going to be very difficult to compute, and so before we tackle it, we must convert our energy expression to Fourier space. Returning to our energy expression, we can write $n_x(s)$ (or $n_y(s)$ for that matter) as

$$n_x(s) = \frac{1}{L} \sum_q e^{iqs} \hat{n}_x(q)$$

for $0 \leq s \leq L$. We now assume periodic boundary conditions, such that $n_x(s) = n_x(s + L)$. This turns out to be a rather reasonable assumption. This then means that

$$\frac{1}{L} \sum_q e^{iqs} \hat{n}_x(q) = \frac{1}{L} \sum_q e^{iq(s+L)} \hat{n}_x(q)$$

For this to be true, $e^{iqL} = 1$. Therefore,

$$q = \frac{2\pi}{L}m$$

where $m = 0, \pm 1, \pm 2, \dots$. We recognize that a constraint on $n_x(s)$ is that it must be real, such that $n_x(s) = n_x^*(s)$, where the asterisk denotes the complex conjugate. Therefore,

$$\frac{1}{L} \sum_q e^{iqs} \hat{n}_x(q) = \frac{1}{L} \sum_q e^{-iqs} \hat{n}_x^*(q)$$

This then implies that $q = -q$ such that $\hat{n}_x(q) = \hat{n}_x^*(-q)$. With these expressions, we can plug in our prior expression of $n_x(s)$ into the integral in the bending energy term, which as a reminder is

$$E_{\text{bending}} = \frac{1}{2}K \int_0^L \left[\left(\frac{dn_x}{ds} \right)^2 + \left(\frac{dn_y}{ds} \right)^2 \right] ds$$

We now claim that

$$\left(\frac{dn_x}{ds} \right)^2 = \left[\left(\frac{iq}{L} \right) \sum_q e^{iqs} \hat{n}_x(q) \right] \left[\left(\frac{ik}{L} \right) \sum_k e^{iks} \hat{n}_x(k) \right]$$

Then

$$\int_0^L \left(\frac{dn_x}{ds} \right)^2 ds = -\frac{1}{L^2} \sum_q \sum_k qk \int_0^L e^{i(q+k)s} ds \hat{n}_x(q) \hat{n}_x(k)$$

We note that

$$\int_0^L e^{i(q+k)s} ds = L\delta_{q+k,0}$$

The notation $\delta_{q+k,0}$ means it has a value of 1 when $q = -k$ and 0 when $q \neq -k$. Therefore, we can write our double-sum in terms of just one sum as follows, plugging in $k = -q$. Our expression is now the following (the $\delta_{q+k,0}$ converts the double sum to a single sum and kills off the exponential)

$$\int_0^L \left(\frac{dn_x}{ds} \right)^2 ds = \frac{1}{L} \sum_q q^2 \hat{n}_x(q) \hat{n}_x(-q)$$

We then note that

$$\hat{n}_x(q) \cdot \hat{n}_x^*(q) = (\text{Re}(\hat{n}_x))^2 + (\text{Im}(\hat{n}_x))^2 \equiv |\hat{n}_x(q)|^2$$

From the result of the periodic boundary condition, we can also state this is

$$\hat{n}_x(q) \cdot \hat{n}_x(-q) = |\hat{n}_x(q)|^2$$

We can now use this to state

$$\int_0^L \left(\frac{dn_x}{ds} \right)^2 ds = \frac{1}{L} \sum_q q^2 |\hat{n}_x(q)|^2$$

This mean our bending term is the following, when we plug in the above term (and repeat the process for n_y):

$$E_{\text{bending}} = \frac{1}{2} \frac{K}{L} \sum_q q^2 \left(|\hat{n}_x(q)|^2 + |\hat{n}_y(q)|^2 \right)$$

We now wish to find the force term, which we recall was:

$$E_{\text{force}} = -FL + \frac{1}{2} F \int_0^L (n_x^2 + n_y^2) ds$$

We note that

$$n_x^2 = \frac{1}{L^2} \left[\sum_q e^{iqs} \hat{n}_x(q) \right] \left[\sum_k e^{iks} \hat{n}_x(k) \right]$$

Then

$$\int_0^L n_x^2 ds = \frac{1}{L^2} \sum_q \sum_k \int_0^L e^{i(q+k)s} ds \hat{n}_x(q) \hat{n}_x(k)$$

This again can be simplified via the delta function such that

$$\int_0^L n_x^2 ds = \frac{1}{L} \sum_q |\hat{n}_x(q)|^2$$

Therefore,

$$E_{\text{force}} = -FL + \frac{1}{2} \frac{F}{L} \sum_q \left(|\hat{n}_x(q)|^2 + |\hat{n}_y(q)|^2 \right)$$

Our total energy expression is then

$$E = \frac{1}{2} \frac{K}{L} \sum_q q^2 \left(|\hat{n}_x(q)|^2 + |\hat{n}_y(q)|^2 \right) + \frac{1}{2} \frac{F}{L} \sum_q \left(|\hat{n}_x(q)|^2 + |\hat{n}_y(q)|^2 \right) - FL$$

This can be rewritten as

$$E = \frac{1}{2L} \sum_q \left((kq^2 + F) |\hat{n}_x(q)|^2 + (kq^2 + F) |\hat{n}_y(q)|^2 \right) - FL$$

We now have an energy expression we can use to evaluate the partition function that is now written in Fourier space. Our partition function once again is

$$Z = \int e^{-\frac{E[\vec{n}(s)]}{k_B T}} \mathcal{D}[\vec{n}(s)]$$

In Fourier space, we can rewrite the path integral as

$$\int \mathcal{D}[\vec{n}(s)] = \int_{-\infty}^{\infty} d[\text{Re}(\hat{n}_x(q))] \int_{-\infty}^{\infty} d[\text{Im}(\hat{n}_x(q))] \int_{-\infty}^{\infty} d[\text{Re}(\hat{n}_y(q))] \int_{-\infty}^{\infty} d[\text{Im}(\hat{n}_y(q))]$$

We then use this to write our partition function as

$$Z = \prod_{q \geq 0} \int_{-\infty}^{\infty} d[\text{Re}(\hat{n}_x(q))] \int_{-\infty}^{\infty} d[\text{Im}(\hat{n}_x(q))] \int_{-\infty}^{\infty} d[\text{Re}(\hat{n}_y(q))] \int_{-\infty}^{\infty} d[\text{Im}(\hat{n}_y(q))] e^{-\frac{E_q}{k_B T}}$$

where the product over $q \geq 0$ is to prevent double-counting. Note that I have written E_q instead of E , which is what allows me to introduce the product notation.

We want to find the average extension length, $\langle r \rangle$, if we pull in the \hat{z} direction. As such,

$$\langle r \rangle = \hat{z} \langle \sum_{j=1}^N \vec{t}_j \rangle$$

We note from before that $\vec{t} = a\vec{n}$ and that $\sum_j f \approx 1/a \int f ds$, so

$$\langle r \rangle = \langle \int_0^L n_z(s) ds \rangle = \int_0^L \langle n_z(s) \rangle ds$$

For large F , $\langle n_z(s) \rangle$ is mostly independent of s so

$$\langle r \rangle = L \langle n_z \rangle$$

We can plug in our expression for n_z to get

$$\frac{\langle r \rangle}{L} = \left\langle \sqrt{1 - n_x^2 - n_y^2} \right\rangle \approx 1 - \frac{1}{2} (\langle n_x^2 \rangle + \langle n_y^2 \rangle)$$

We need to evaluate $\langle n_x^2 \rangle$ and $\langle n_y^2 \rangle$. We start by noting that

$$\langle n_x^2(s) \rangle = \frac{1}{L^2} \sum_q \sum_k e^{i(q+k)s} \langle \hat{n}_x(q) \hat{n}_x(k) \rangle$$

We're a step closer, but we *now* need to evaluate $\langle \hat{n}_x(q) \hat{n}_x(k) \rangle$. I will temporarily switch to a notation of q_1 and q_2 instead of q and k . As such,

$$\langle \hat{n}_x(q_1) \hat{n}_x(q_2) \rangle = \frac{\int e^{-\frac{E[\vec{n}(s)]}{k_B T}} \hat{n}_x(q_1) \hat{n}_x(q_2) \mathcal{D}[\vec{n}(s)]}{\int e^{-\frac{E[\vec{n}(s)]}{k_B T}} \mathcal{D}[\vec{n}(s)]}$$

This integral can be written out as follows

$$\begin{aligned} & \langle \hat{n}_x(q_1) \hat{n}_x(q_2) \rangle \\ &= \frac{\prod_{q \geq 0} \int_{-\infty}^{\infty} d[\text{Re}(\hat{n}_x(q))] \int_{-\infty}^{\infty} d[\text{Im}(\hat{n}_x(q))] \int_{-\infty}^{\infty} d[\text{Re}(\hat{n}_y(q))] \int_{-\infty}^{\infty} d[\text{Im}(\hat{n}_y(q))] \hat{n}_x(q_1) \hat{n}_x(q_2) e^{-\frac{E_q}{k_B T}}}{\prod_{q \geq 0} \int_{-\infty}^{\infty} d[\text{Re}(\hat{n}_x(q))] \int_{-\infty}^{\infty} d[\text{Im}(\hat{n}_x(q))] \int_{-\infty}^{\infty} d[\text{Re}(\hat{n}_y(q))] \int_{-\infty}^{\infty} d[\text{Im}(\hat{n}_y(q))] e^{-\frac{E_q}{k_B T}}} \end{aligned}$$

It may not be immediately clear how to simplify this further. However, let us have a brief side-thought. In general, if we wanted to calculate a function $\langle x^2 \rangle$ and we had $E_q(x^2 + y^2 + z^2)$ then we could say

$$\langle x^2 \rangle = \frac{\int dx \int dy \int dz x^2 e^{-\frac{x^2 + y^2 + z^2}{k_B T}}}{\int dx \int dy \int dz e^{-\frac{x^2 + y^2 + z^2}{k_B T}}}$$

However, since the exponential function can be split into three multiplied terms of $e^{-\frac{x^2}{k_B T}} e^{-\frac{y^2}{k_B T}} e^{-\frac{z^2}{k_B T}}$, the y and z terms will cancel such that

$$\langle x^2 \rangle = \frac{\int dx x^2 e^{-\frac{x^2}{k_B T}}}{\int dx e^{-\frac{x^2}{k_B T}}}$$

This result can be extended to our worm-like chain problem. We note that our average is just over the q_1 and q_2 dimensions, so can cancel all the integrals that are not those terms. This makes the problem more tractable. When doing this, and plugging in E_q ,

$$\begin{aligned} & \langle \hat{n}_x(q_1) \hat{n}_x(q_2) \rangle \\ &= \frac{\int_{-\infty}^{\infty} d[\text{Re}(\hat{n}_x(q_1))] \int_{-\infty}^{\infty} d[\text{Im}(\hat{n}_x(q_2))] \int_{-\infty}^{\infty} d[\text{Re}(\hat{n}_x(q_1))] \int_{-\infty}^{\infty} d[\text{Im}(\hat{n}_x(q_2))] \hat{n}_x(q_1) \hat{n}_x(q_2) e^{-\frac{(kq_1^2 + F)|\hat{n}_x(q_1)|^2}{2Lk_B T}} e^{-\frac{(kq_2^2 + F)|\hat{n}_x(q_2)|^2}{2Lk_B T}}}{\int_{-\infty}^{\infty} d[\text{Re}(\hat{n}_x(q_1))] \int_{-\infty}^{\infty} d[\text{Im}(\hat{n}_x(q_2))] \int_{-\infty}^{\infty} d[\text{Re}(\hat{n}_x(q_1))] \int_{-\infty}^{\infty} d[\text{Im}(\hat{n}_x(q_2))] e^{-\frac{(kq_1^2 + F)|\hat{n}_x(q_1)|^2}{2Lk_B T}} e^{-\frac{(kq_2^2 + F)|\hat{n}_x(q_2)|^2}{2Lk_B T}}} \end{aligned}$$

We then recall the result of the periodic boundary condition: that $q_1 = -q_2$, which we will just call q . As such, we can simplify the equation further because $\hat{n}_x(q_1) \hat{n}_x(q_2) = \hat{n}_x(q_1) \hat{n}_x(-q_1) = |\hat{n}_x(q)|^2 = (\text{Re}(\hat{n}_x(q)))^2 + (\text{Im}(\hat{n}_x(q)))^2$, and also by only writing our integrals in terms of this general q . Substituting this in

$$\begin{aligned} & \langle \hat{n}_x(q_1) \hat{n}_x(q_2) \rangle \\ &= \frac{\int_{-\infty}^{\infty} d[\text{Re}(\hat{n}_x(q))] \int_{-\infty}^{\infty} d[\text{Im}(\hat{n}_x(q))] \left[(\text{Re}(\hat{n}_x(q)))^2 + (\text{Im}(\hat{n}_x(q)))^2 \right] e^{-\frac{(kq^2 + F) \left[(\text{Re}(\hat{n}_x(q)))^2 + (\text{Im}(\hat{n}_x(q)))^2 \right]}{2Lk_B T}}}{\int_{-\infty}^{\infty} d[\text{Re}(\hat{n}_x(q))] \int_{-\infty}^{\infty} d[\text{Im}(\hat{n}_x(q))] e^{-\frac{(kq^2 + F) \left[(\text{Re}(\hat{n}_x(q)))^2 + (\text{Im}(\hat{n}_x(q)))^2 \right]}{2Lk_B T}}} \end{aligned}$$

This expression can actually be easily evaluated. We note that

$$\frac{\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx}{\int_{-\infty}^{\infty} e^{-\alpha x^2} dx} = \frac{1}{2\alpha}$$

To apply this to our expression, we note the following. In general,

$$\frac{\iint dx dy (x^2 + y^2) e^{-\alpha(x^2+y^2)}}{\iint dx dy e^{-\alpha(x^2+y^2)}} = \frac{2 \iint dx dy x^2 e^{-\alpha x^2} e^{-\alpha y^2}}{\iint dx dy e^{-\alpha x^2} e^{-\alpha y^2}} = \frac{2 \int dx x^2 e^{-\alpha x^2}}{\int dx e^{-\alpha x^2}} = \frac{1}{\alpha}$$

In our expression, $\alpha = \frac{kq^2+F}{2Lk_B T}$, $x = \text{Re}(\hat{n}_x(q))$, and $y = \text{Im}(\hat{n}_x(q))$. Therefore,

$$\langle \hat{n}_x(q_1) \hat{n}_x(q_2) \rangle = \delta_{q_1+q_2,0} \frac{2Lk_B T}{kq^2 + F}$$

Switching back to our q and k nomenclature

$$\langle \hat{n}_x(q) \hat{n}_x(k) \rangle = \delta_{q+k,0} \frac{2Lk_B T}{kq^2 + F}$$

where the $\delta_{q+k,0}$ ensures the periodic boundary condition of $q = -k$. We therefore can finally plug this in to get

$$\langle n_x^2(s) \rangle = \frac{1}{L} \sum_q \frac{2k_B T}{kq^2 + F}$$

For large L , we can convert the summation to an integral. The process to do so is below, noting that $q = 2\pi m/L$ so $\Delta q = 2\pi/L$:

$$\sum_q f = \frac{L}{2\pi} \sum_q f \Delta q = \frac{L}{2\pi} \int f dq$$

to get

$$\langle n_x^2(s) \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{2k_B T}{kq^2 + F} dq$$

Of course, we could repeat this whole procedure for $\langle n_y^2(s) \rangle$. Plugging these two expressions into $\langle r \rangle$ yields

$$\frac{\langle r \rangle}{L} = 1 - \frac{1}{2} \left[\frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{2k_B T}{kq^2 + F} + \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{2k_B T}{kq^2 + F} \right]$$

or

$$\frac{\langle r \rangle}{L} = 1 - \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{2k_B T}{kq^2 + F}$$

This is a contour integral (due to the singularity at $q = \pm i\sqrt{F/k}$). It can be computed, and we arrive at

$$\frac{\langle r \rangle}{L} = 1 - \frac{k_B T}{\sqrt{kF}}$$

for the high force limit of the worm-like chain model.

6.9 1D HARMONIC CHAIN

Consider a one-dimensional harmonic chain of length L , defined with respect to sites that each site a distance ℓ apart. Each particle in the chain (which sit in a potential well $\dots, x_{m-1}, x_m, x_{m+1}, \dots$) is connected to its neighbors by a spring. So, if an actual particle position is $r_m = x_m + u_m$ (where u_m is just defined as the displacement from x_m). The energy is given as

$$E = \frac{B'}{2} \sum_m (u_{m+1} - u_m)^2 + \frac{C'}{2} \sum_m u_m^2$$

We note that in the continuum limit,

$$(u_{m+1} - u_m)^2 = \left(\frac{du}{dm}\right)^2$$

We, however, want to write du/dx instead. So, if we note that $dx/dm = \ell$ then

$$(u_{m+1} - u_m)^2 = \left(\frac{du}{dm}\right)^2 = \left(\frac{du}{dx} \frac{dx}{dm}\right)^2 = \ell^2 \left(\frac{du}{dx}\right)^2$$

Plugging into the left-hand term gets

$$E = \frac{B' \ell^2}{2} \sum_m \left(\frac{du}{dx}\right)^2 + \frac{C'}{2} \sum_m u_m^2$$

We now convert the summations to integrals such that

$$E = \frac{B' \ell}{2} \int_0^L \left(\frac{du}{dx}\right)^2 + \frac{C'}{2\ell} \int_0^L u^2 dx$$

We can define $B \equiv B' \ell$ and $C \equiv C'/\ell$ to get

$$E = \frac{B}{2} \int_0^L \left(\frac{du}{dx}\right)^2 + \frac{C}{2} \int_0^L u^2 dx$$

We define the Fourier variable

$$u = \frac{1}{L} \sum_q e^{iqx} \hat{u}$$

We shall address the left-hand term first. The squared derivative term can be written in terms of Fourier modes as

$$\left(\frac{du}{dx}\right)^2 = \left[\left(\frac{iq}{L}\right) \sum_q e^{iqx} \hat{u}(q) \right] \left[\left(\frac{ik}{L}\right) \sum_k e^{ikx} \hat{u}(k) \right]$$

Then

$$\int_0^L \left(\frac{du}{ds}\right)^2 dx = -\frac{1}{L^2} \sum_q \sum_k qk \int_0^L e^{i(q+k)x} dx \hat{u}(q)\hat{u}(k)$$

We note that

$$\int_0^L e^{i(q+k)x} dx = L\delta_{q+k,0}$$

This kills off one of the summations to lead to

$$\int_0^L \left(\frac{du}{ds}\right)^2 dxs = \frac{1}{L} \sum_q q^2 \hat{u}(q)\hat{u}(-q)$$

From the result of the periodic boundary condition, we can also state that is

$$\hat{u}(q) \cdot \hat{u}(-q) = |\hat{u}(q)|^2$$

We can now use this to state

$$\int_0^L \left(\frac{du}{ds}\right)^2 dxs = \frac{1}{L} \sum_q q^2 |\hat{u}(q)|^2$$

We now do a similar procedure for the right-hand term. We note that

$$u^2 = \frac{1}{L^2} \left[\sum_q e^{iqx} \hat{u}(q) \right] \left[\sum_k e^{ikx} \hat{u}(k) \right]$$

Then

$$\int_0^L u^2 dx = \frac{1}{L^2} \sum_q \sum_k \int_0^L e^{i(q+k)x} dx \hat{u}(q)\hat{u}(k)$$

This again can be simplified via the delta function such that

$$\int_0^L u^2 dx = \frac{1}{L} \sum_q |\hat{u}(q)|^2$$

Therefore,

$$E = \frac{B}{2L} \sum_q q^2 |\hat{u}(q)|^2 + \frac{C}{2L} \sum_q |\hat{u}(q)|^2$$

or

$$E = \frac{1}{2L} \sum_q |\hat{u}(q)|^2 (Bq^2 + C)$$

As in the worm-like chain derivation, we can define the partition function (and therefore the free energy) as

$$Z = \int e^{-\frac{E}{k_B T} \mathcal{D}[u(x)]}$$

This becomes the following in Fourier space

$$Z = \int_{-\infty}^{\infty} d[\text{Re}(\hat{u}(q))] \int_{-\infty}^{\infty} d[\text{Im}(\hat{u}(q))] e^{-\frac{E}{k_B T}}$$

If we wanted to continue as in the worm-like chain derivation, we could find $\langle u^2(x) \rangle$. Taking the result from the worm-like chain derivation,

$$\langle u^2(x) \rangle = \frac{1}{L^2} \sum_q \sum_k e^{i(q+k)x} \langle \hat{u}(q) \hat{u}(k) \rangle$$

We therefore need to evaluate $\langle \hat{u}(q) \hat{u}(k) \rangle$, which can be done via

$$\langle \hat{u}(q) \hat{u}(k) \rangle = \frac{\int e^{-\frac{E}{k_B T} \hat{u}(q) \hat{u}(k) \mathcal{D}[u]} \mathcal{D}[u]}{\int e^{-\frac{E}{k_B T} \mathcal{D}[u]}$$

As we found out in the worm-like chain derivation, this just becomes

$$\langle \hat{u}(q) \hat{u}(k) \rangle = \delta_{q+k,0} \frac{1}{2\alpha} = \delta_{q+k,0} \frac{1}{2 \left(\frac{1}{2L} (Bq^2 + C) \right)} = \delta_{q+k,0} \frac{Lk_B T}{Bq^2 + C}$$

Plugging this in gets

$$\langle u^2(x) \rangle = \frac{1}{L} \sum_q \frac{k_B T}{Bq^2 + C}$$

For large L , we can convert the summation to an integral. We note that $\Delta q = 2\pi/L$, so

$$\langle u^2(x) \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{k_B T}{Bq^2 + C} dq$$

This is a contour integral with a singularity at $q = \pm i\sqrt{C/B}$. As such,

$$\langle u^2(x) \rangle = \frac{k_B T}{2\sqrt{BC}}$$

It is analogous to the worm-like chain solution.

Now let us assume we wish to find the free energy. For this, we go back to

$$Z = \int e^{-\frac{E}{k_B T} \mathcal{D}[u(x)]}$$

We recall that $Z = e^{-\frac{F}{k_B T}}$, so

$$F = -k_B T \ln \left(\int e^{-\frac{E}{k_B T}} \mathcal{D}[u(x)] \right)$$

We recall that

$$E = \frac{1}{2L} \sum_q |\hat{u}(q)|^2 (Bq^2 + C)$$

We must restrict the summation to be $q \geq 0$. We write out E into two parts: one at $q = 0$ and one at $q > 0$ as follows

$$E = \gamma(0) |\hat{u}(0)|^2 + \sum_{q>0} 2\gamma(q) |\hat{u}(q)|^2$$

where

$$\gamma(q) \equiv \frac{Bq^2 + C}{2L}$$

The factor of 2 is included in the right-hand term in the expression for E to account for all values of q . This then means our expression for F becomes

$$F = -k_B T \ln \left(\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{\gamma(0)|\hat{u}(0)|^2}{k_B T}} d[\text{Re}(\hat{u}(0))] d[\text{Im}(\hat{u}(0))] \prod_{q>0} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{2\gamma(q)|\hat{u}(q)|^2}{k_B T}} d[\text{Re}(\hat{u}(q))] d[\text{Im}(\hat{u}(q))] \right)$$

We can note the following integral:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\alpha(x^2+y^2)} = \frac{\pi}{\alpha}$$

Therefore,

$$F = -k_B T \ln \left(\frac{\pi k_B T}{\gamma(0)} \prod_{q>0} \frac{\pi k_B T}{2\gamma(q)} \right)$$

Plugging back in for γ yields

$$F = -k_B T \ln \left(\frac{2\pi k_B T L}{C} \prod_{q>0} \frac{\pi k_B T L}{Bq^2 + C} \right)$$

Therefore,

$$F = -k_B T \left[\ln \left(\frac{2\pi k_B T L}{C} \right) - \sum_{q>0} \ln \left(\frac{\pi k_B T L}{Bq^2 + C} \right) \right]$$

If we want to get the expression for F in the limit of $L \rightarrow \infty$, we can do so. We first note that since $q = 2\pi m/L$, having large L implies that the spacing between q 's is infinitesimal, so we can convert the summation to an integral (as we have done many times before). Therefore, noting that $\Delta q = 2\pi/L$,

$$F = -k_B T \left[\ln \left(\frac{2\pi k_B T L}{C} \right) - \frac{L}{2\pi} \int_{q>0}^{\infty} \ln \left(\frac{\pi k_B T L}{Bq^2 + C} \right) \right]$$

We can set the lower-bound on the integral to be $q \approx 0$ since it will not greatly affect the integral. Therefore,

$$F = -k_B T \left[\ln \left(\frac{2\pi k_B T L}{C} \right) - \frac{L}{2\pi} \int_0^{\infty} \ln \left(\frac{\pi k_B T L}{Bq^2 + C} \right) \right]$$