

## Lecture 2: Review of thermodynamics and intro to statistical mechanics

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### 1 Suggested reading

- *Molecular Driving Forces* – Dill and Bromberg: Chapters 1, 2, 3, 5, 6, & 10

### 2 Thermodynamics

In this course, we are not always intent on rigorously deriving or proving any thermodynamic relations, leaving that for proper thermodynamics or statistical mechanics courses. Instead, we are interested in developing physical intuition and simple models grounded in thermodynamic principles for the problems that we address. That is, we want to understand the physical system and be able to make appropriate *assumptions* as needed.

Thermodynamics is a useful toolset for reasoning about energies and entropies. It allows us to predict the likelihood of atoms and molecules to react; to adsorb, diffuse, or partition; to dissolve or change phase; and to alter their shape or bonding arrangement. Recall, the **first law of thermodynamics**:  $dU = dq - dw$  and the **second law of thermodynamics**:  $dS \geq 0$ . At the simplest level, thermodynamics can be thought of as these two laws and some calculus.

A **thermodynamic system** is a collection of matter in any form, separated from its surroundings by real or imaginary boundaries. How the system is defined will depend on the problem that we want to solve. Boundaries are key as they define what comes in and goes out. At that point, we need to do some bookkeeping, accounting for energy and matter exchange across the boundaries or for changes in volume. Many times these systems contain **subsystems** that are also defined by real or imaginary boundaries.

Within these systems we have **extensive** and **intensive** properties. An extensive property  $X$  is the sum of the same property in each of the subsystems  $X_1 + X_2 + X_3 + \dots$ . That is extensive properties increase with the system size. On the other hand, intensive properties are independent of the system size. Temperature  $T$ , pressures  $p$ , and concentrations  $[N_i]$  are intensive properties. Extensive properties include volume  $V$ , number of atoms or molecules  $N_i$ , internal energy  $U$ , and entropy  $S$ . In thermodynamics, each extensive property is related to an intensive property. We will see these *conjugate pairs* below in the discussion of thermodynamic driving forces.

The study of thermal and chemical equilibrium is governed by the **second law of thermodynamics** or entropy maximization. In words, this is the assertion that the equilibrium observable state (**macrostate**) of an *isolated* system is that state that can occur in the largest number of different ways (**microstates**). Or, when given the choice from all observable macrostates the isolated system at equilibrium will choose the macrostate that has the most representative microstates. We can write down a **fundamental thermodynamic equation for entropy** as a multivariate expression of extensive properties:

$$S = S(U, V, \{N_i\})$$

This is just a mathematical form to say that the entropy is dependent on  $U, V, N_1, N_2, N_3, \dots$  and that each of these are independent of one another. Traditionally, thermodynamics is discussed by writing down a multivariate **fundamental thermodynamic equation for energy**:

$$U = U(S, V, \{N_i\})$$

We can also compose an equation for **free energy**, such as the Helmholtz Free Energy:  $F = U - TS$ . This is more applicable for ‘real’ systems (non-isolated systems) that we encounter in the world around us and we define equilibrium as the minimum free energy – for this to occur the system will tend toward low energy *and* high entropy. Thus, there is an interplay between the energy of the system and the entropy of the system, which we will explore throughout this course. At high temperatures, entropy dominates. At low temperatures, energy dominates. Note, this is also entropy maximization if you construct a *closed* system by placing the ‘real’ system in a reservoir: say a test-tube in a water bath.

### 3 Thermodynamic driving forces

The fundamental definitions of temperature, pressure, and chemical potential are classically based on the form  $U = U(S, V, \{N_i\})$ . The microscopic origin of these properties are better understood in terms of entropy and so we will often alternate between  $U = U(S, V, \{N_i\})$  and  $S = S(U, V, \{N_i\})$  in this course.

In general, systems will be in equilibrium at extrema in the fundamental thermodynamic equation for energy, entropy, or free energy. As stated above, the tendency toward maximum entropy  $S$  (or maximum microstate multiplicity  $W$ ) presides of the study of thermal and chemical equilibrium. Thus, we are often interested in calculating small changes in this parameter as we deviate a system from its current state. Therefore, we calculate  $dS$  (or in the case of minimizing  $U$ ,  $dU$ ). We will also see that the partial differentials of these multivariate equations can be considered as thermodynamic driving forces (connected to intensive physical properties) that push a system toward equilibrium.

First consider  $dS$ :

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V, \{N_i\}} dU + \left(\frac{\partial S}{\partial V}\right)_{U, \{N_i\}} dV + \sum_{j=1}^M \left(\frac{\partial S}{\partial N_j}\right)_{U, V, N_{i \neq j}} dN_j. \quad (1)$$

We can calculate the same for  $dU$ :

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, \{N_i\}} dS + \left(\frac{\partial U}{\partial V}\right)_{S, \{N_i\}} dV + \sum_{j=1}^M \left(\frac{\partial U}{\partial N_j}\right)_{S, V, N_{i \neq j}} dN_j. \quad (2)$$

For now these are just mathematical definitions, based on the chain rule from calculus. However, each of the partial derivatives of  $dU$  corresponds to a measurable physical property: temperature,  $T$ ; pressure,  $p$ ; and the chemical potential of species  $j$ ,  $\mu_j$ . We are perhaps more used to seeing:

$$dU = TdS - pdV + \sum_{j=1}^M \mu_j dN_j. \quad (3)$$

From this we see the relationships between measurable parameters and the partial differentials:

$$T \equiv \left(\frac{\partial U}{\partial S}\right)_{V, \{N_i\}}, \quad p \equiv -\left(\frac{\partial U}{\partial V}\right)_{S, \{N_i\}}, \quad \mu_j \equiv \left(\frac{\partial U}{\partial N_j}\right)_{S, V, N_{i \neq j}}. \quad (4)$$

We can perform the same logic for  $dS$  by rearranging Eq. 3 and we see that:

$$dS = \left(\frac{1}{T}\right) dU + \left(\frac{p}{T}\right) dV - \sum_{j=1}^M \left(\frac{\mu_j}{T}\right) dN_j. \quad (5)$$

and, therefore:

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{V, \{N_i\}}, \quad \frac{p}{T} \equiv \left(\frac{\partial S}{\partial V}\right)_{U, \{N_i\}}, \quad \frac{\mu_j}{T} \equiv -\left(\frac{\partial S}{\partial N_j}\right)_{U, V, N_{i \neq j}}. \quad (6)$$

We can think of the expressions in Eqs. 4 and 6 as **thermodynamic driving forces** that push the system toward maximum entropy or minimum energy. Temperature,  $T$ , describes the tendency of the system for energy exchange. Energy is the capacity of the system to do work and that capacity can flow as heat. Entropy is the tendency of the work capacity, or energy, to flow from one system to another. In this manner, entropy is a kind of potential to transfer energy from one place to another and  $1/T$  is the corresponding thermodynamic driving force. Pressure,  $p$ , is a ‘force’ for changing volume. The chemical potential,  $\mu$ , is a tendency for matter exchange. In each case, this is done by applying the maximum entropy principle ( $dS_{total} = 0$ ) to specify the state of equilibrium. We can exploit this logic to derive simple concepts, such as the ideal gas law, and use lattice models and the tools of statistical mechanics to understand these principles at the molecular scale.

### 4 Statistical mechanics

To gain a better understanding of the essence of *entropy*, we use the tools of **statistical mechanics**. Statistical mechanics takes a probabilistic view of macroscopic systems whereby the macroscopic observable system is viewed in terms of the average properties of a system consisting of a large number of degrees of freedom.

**Macrostate** refers to the observable, equilibrium properties of a system as described by thermodynamics. **Microstate** describes one particular configuration of a system that is consistent with the observable macrostate. Let us consider an ideal gas of a large number of molecules (on the order of  $10^{23}$ ) at a given temperature  $T$  and volume  $V$  as a macrostate. The observable properties say nothing about the relative positions and momenta of the molecules and we can imagine an immense number of ways of arranging them that lead to the same macrostate – each arrangement corresponds to a microstate. We can imagine the molecules in constant flux, sampling many such microstates such that the average properties of the system give the macrostate properties that we observe. We refer to the collection of possible microstates associated with a given macrostate as an **ensemble**. At this scale, we only know that the molecules obey the laws of quantum mechanics and are often in good approximation of classical Newtonian mechanics. Statistical mechanics gives us the tools to explain the macroscale properties, including but not limited to thermodynamic state functions, by applying probability theory to the mechanic equations of motion for a large ensemble of systems of particles. Instead of trying to follow each particle (atom or molecule) and calculating its 6 degrees of freedom (position:  $\vec{x}, \vec{y}, \vec{z}$  and momentum:  $\vec{p}_x, \vec{p}_y, \vec{p}_z$ ) we use the rules of probability to make predictions about possible observable states.

There are several key assumptions that the rules of statistical mechanics are built on. First, we assert that macroscopic systems are composed of molecules that obey quantum mechanical or classical equations of motion. Second, we assume that the systems we study are **ergodic**, meaning that the time average of the microstates is equivalent to the ensemble average:  $\langle X \rangle = \bar{X}$ . Stated another way, this means that provided infinite time the system will visit all possible microstates.

For now we will restrict our discussion to a specific ensemble known as the **microcanonical ensemble**. Here, we assume that we know the macrostate possesses a given fixed internal energy  $U$ . Thus, for a microstate to be consistent with the macrostate, it must also have the same internal energy  $U$ . Since all microstates have the same energy, **the central postulate of statistical mechanics is that all microstates are equally probable**. This is also called the assumption of equal *a priori* equilibrium probabilities. This is to say that if we have a collection of particles (atoms or molecules) of some fixed energy, then any time we take an image of a microstate, all possible positions and momenta that together are consistent with the fixed internal energy  $U$  will be equally likely. We can express this mathematically:

$$p(\mu)_U = \frac{1}{\Omega(U)}, \quad (7)$$

where  $\mu$  is a given microstate and  $\Omega(U)$  is the total number of microstates with internal energy  $U$ . This states simply that the probability of any given microstate is equal.

We now introduce a general definition of the entropy of a system, Gibbs' coarse-grained entropy, based on the probability distribution of microstates for that system:

$$S = - \sum_{i=1}^M p(i) \ln p(i) \quad (8)$$

This is the generalized entropy for any probability distribution, applied to the probability distribution from Eq. 7, we see:

$$S = - \sum_{\mu=1}^{\Omega} p(\mu) \ln p(\mu) \quad (9)$$

$$= - \sum_{\mu=1}^{\Omega} \frac{1}{\Omega(U)} \ln \frac{1}{\Omega(U)} \quad (10)$$

$$= - \ln \frac{1}{\Omega(U)} \quad (11)$$

$$= \ln \Omega(U). \quad (12)$$

This is a reformulation of the classic definition of entropy postulated by Ludwig Boltzmann, and inscribed on his tombstone:

$$S = k_B \ln W \quad (13)$$

where  $k_B$  is the Boltzmann constant,  $\sim 1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$ , and provides the proper units on entropy. Eq. 13 states that as we increase the number of microstates (or multiplicity  $W$ ) in a system, the entropy

increases. Also, it states that the entropy can never be negative. From these postulates, and Eq. 13, all we need to do is some clever counting to calculate entropy and find those systems that have maximum multiplicity  $W$  as these will have maximum entropy! This is true for the microcanonical ensemble discussed here and demonstrated below. We will also discuss and explore the implications of statistical mechanics on other ensembles in future lectures.

As an aside, to my knowledge the form of  $S = k_B \ln W$  while rigorously tested and confirmed has no *a priori* proof. However, some simple logic allows us to understand why it should take the logarithmic form. Consider a system with two subsystems  $A$  and  $B$  having multiplicities  $W_A$  and  $W_B$ . The multiplicity of the total system will be the product  $W = W_A W_B$ . We require that entropy is extensive, meaning that  $S = S_A + S_B$ . The logarithm function satisfies this requirement: if  $S_A = k_B \ln W_A$  and  $S_B = k_B \ln W_B$  then  $S = k_B \ln W = k_B \ln W_A W_B = k_B \ln W_A + k_B \ln W_B = S_A + S_B$ . This simple argument illustrates why  $S$  should be a logarithmic function of  $W$  but is not a rigorous proof.

## 5 Probability

The concepts that we introduce here – **probability**, **multiplicity**, **combinatorics**, **averages**, and **distribution functions** – provide the foundation for statistical mechanics and calculating entropy.

We define **probability** as follows. If we have in total  $N$  events, measurements, or trials each with  $t$  distinct possible outcomes:  $A, B, C, \dots$  and the number of events for each outcome are  $n_A, n_B, n_C, \dots$  or  $\{n_i\}$ , the probability of each outcome is calculated as:

$$p_i = \frac{n_i}{N}. \quad (14)$$

By definition,

$$\sum_{i=1}^t n_i = N \quad \text{and} \quad \sum_{i=1}^t p_i = 1. \quad (15)$$

Thus, probabilities are in the range of zero to one:  $p_i \in [0, 1]$ . If only one outcome is possible, the event is deterministic and the outcome has a probability of one. If an outcome can never occur, it has a probability of zero.

Consider the event of a single roll of a Würfel with six sides. The probability that a 6 is rolled is  $1/6$  as there are  $N = 6$  possible outcomes with  $n_6 = 1$  of them is a 6. But suppose we roll the Würfel four times. We may want to calculate the probability that we roll a 6 every time. Or we may want to calculate the probability that we roll one 2 followed by two 4's followed by one 2. Or we may want to calculate the probability that we roll two 4's and two 5's in any order. The rules of probability and **combinatorics** provide the tools to calculate these probabilities. First we need to define certain aspects of the events.

The outcomes  $A, B, C, \dots$  are considered **mutually exclusive** if the occurrence of one precludes the occurrence of all the others. For example, with the Würfel 2 and 4 are mutually exclusive as only one number can appear face up for each roll. The outcomes  $A, B, C, \dots$  are considered **collectively exhaustive** if they comprise all possible outcomes for the event, trial, or measurement and no other possible outcomes exist. For example,  $\{1, 2, 3, 4, 5, 6\}$  is the collectively exhaustive set of outcomes for the roll of the Würfel, as long as we discount any of the rare times that it might end up on a side. Events are **independent** if the outcomes of each is unrelated or not correlated with the outcome of any other event. That is, there is no information transfer from event to event. Assuming that no one has manipulated the Würfel, each roll is independent of all past rolls.

The **multiplicity** of events is the total number of ways in which different outcomes can occur. If the number of outcomes of type  $X$  is  $n_X$  and the number of outcomes of type  $Y$  is  $n_Y$ , then the total number of possible combinations of outcomes is the multiplicity

$$W = n_X n_Y \quad (16)$$

In the case where we have multiple subsystems  $1, 2, 3, \dots$  with multiplicities  $W_1, W_2, W_3, \dots$  we can calculate the multiplicity of the total system:

$$W = W_1 W_2 W_3 \dots \quad (17)$$

The **rules of probability** allow us to calculate the probabilities of combinations of events. One such case is the probability that outcome  $A$  OR outcome  $B$  will occur in a given event. If the outcomes  $A, B, C, \dots$  are mutually exclusive, then the probability of observing  $A$  OR  $B$  ( $A \cup B$ ) is,

$$p(A \cup B) = p_A + p_B. \quad (18)$$

This is often stated as the *addition rule* and requires that the outcomes are mutually exclusive.

Another such case is the probability that outcome  $A$  AND outcome  $B$  occur in successive events. If the outcomes  $A, B, C, \dots$  are independent, then the probability of observing  $A$  AND  $B$  in successive events ( $A \cap B$ ) is,

$$p(A \cap B) = p_A p_B. \quad (19)$$

This is often stated as the *multiplication rule* and requires that the outcomes are independent. A more general form can be constructed in cases where the outcomes are not independent and occur with a **conditional probability**. The conditional probability  $p(B|A)$  is the probability of outcome  $B$ , given that outcome  $A$  has occurred. In this case,

$$p(A \cap B) = p(B|A)p_A = p(A|B)p_B. \quad (20)$$

Eq. 20 is more commonly referred to as Bayes' rule. Importantly, Bayes' rule reduces to Eq. 19 in the case of independence, *i.e.*,  $p(B|A) = p_B$ .

The addition rule can also be generalized for outcomes that are not mutually exclusive:

$$p(A \cup B) = p_A + p_B - p(A \cap B). \quad (21)$$

Again Eq. 21 reduces to Eq. 18 in the case where  $A$  and  $B$  are mutually exclusive, *i.e.*,  $p(A \cap B) = 0$ .

**Combinatorics** allows us to count events. This process is central to statistical mechanics and will be the basis of calculating *entropy*. Combinatorics is the study of the composition of a series of events as opposed to following the direct sequence of events. For example, we can contrast the following two curiosities. First: What is the probability of the specific sequence of four coin flips  $HTTH$ , (where  $H$  refers to head and  $T$  refers to tails and where  $p_H = p_T = 1/2$ )? Second: What is the probability of two H's and two T's in any order? The first is addressed by Eq. 19 and  $p(HTTH) = p_H p_T p_T p_H = (1/2)^4 = 1/16$ . The second is answered by counting the number of sequences with two H's and two T's:  $HTTH$ ,  $HHTT$ ,  $HTHT$ ,  $THHT$ ,  $THTH$ , and  $TTHH$ . Thus, the probability of observing two H's and two T's is  $6/16$  or  $3/8$ .

These problems are tractable for coins flips or Würfel rolls with small  $N$ . However, most physical systems of interest are composed of extremely large numbers of atoms or molecules and we need to generalize our ability to count! For this we use the math of **permutations** and **combinations**. In the example above, if each coin is distinguishable – say by using coins of different values – there would be  $W = N! = 24$  permutations for each outcome. However, in general one coin is **indistinguishable** from another coin of the same value and if we use four coins of the same value we can only distinguish  $H$  from  $T$ . Throughout this course, in general, items of the same character will be treated as *indistinguishable*. In this case, the number of permutations is reduced by the fact that we cannot distinguish between the different  $H$ 's and  $T$ 's. In general, for a collection of  $N$  objects (or events) with  $t$  categories, of which  $n_i$  objects in each category are *indistinguishable* from each other but distinguishable from the objects in the other categories, the number of permutations  $W$  is

$$W = \frac{N!}{n_A! n_B! n_C! \dots n_t!}. \quad (22)$$

The *multiplicity* is also written as  $\Omega$  and we will likely use the terms interchangeably in this course.

If there are only two categories, as in the case for a coin flip or in the case of success / failure, the permutations for  $n$  successes out of  $N$  events is

$$W(n, N) = \binom{N}{n} = \frac{N!}{n!(N-n)!}. \quad (23)$$

As an aside, the notation  $N!$ , read  $N$  factorial, is the product of the integers from 1 to  $N$

$$N! = N(N-1)(N-2) \dots 1. \quad (24)$$

By definition,  $0! \equiv 1$ .

It is often convenient to combine  $W(n, N)$  with  $p_n$  to generate a function from which we can calculate **averages** and visualize **distributions**. We consider here the **binomial distribution** by combining Eq. 23 with Eq. 19:

$$P(n, N) = p^n (1 - p)^{N-n} \frac{N!}{n!(N-n)!} \tag{25}$$

where  $p$  is the probability of ‘success’. As expected the average value for the distribution  $\langle n \rangle = Np$ . What happens to this distribution in the limit of large  $N$ ?

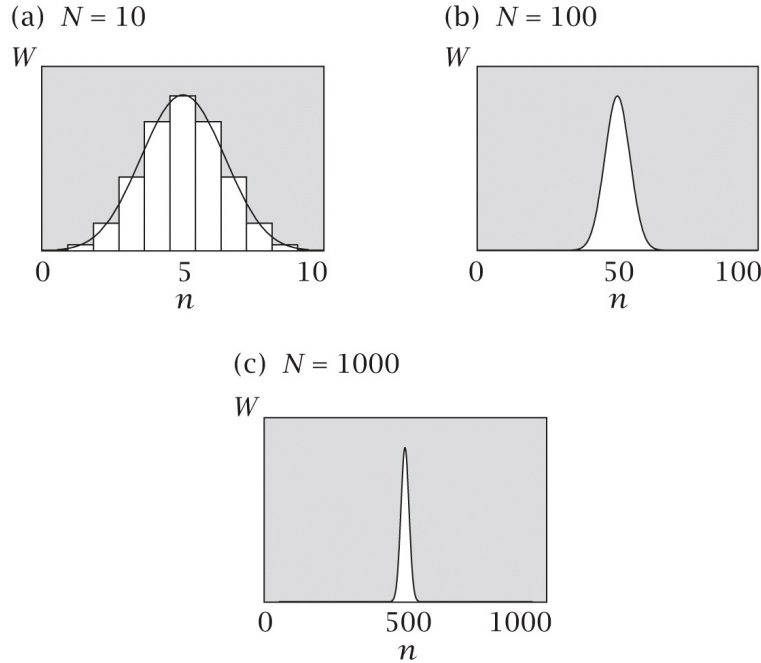


Figure 2.6 Molecular Driving Forces 2/e (© Garland Science 2011)

First observation: the probability distribution rapidly collapses on the condition that maximizes  $W$ . We will see that this is equivalent to maximizing entropy! Second, we can approximate the binomial distribution as a continuous function, the Gaussian function, for sufficiently large  $N$ . Let us define  $q = 1 - p$  and then solve for  $\bar{n}$ . We can do this more easily by taking the derivative of the  $\ln P(n, N)$  and setting it to 0.

$$\ln P(n, N) = \ln p^n q^{N-n} \frac{N!}{n!(N-n)!} \tag{26}$$

$$= n \ln p + (N - n) \ln q + \ln N! - \ln n! - \ln(N - n)! \tag{27}$$

$$\approx n \ln p + (N - n) \ln q + N \ln N - N - n \ln n + n - (N - n) \ln(N - n) + (N - n) \tag{28}$$

$$\frac{\partial \ln P(n, N)}{\partial n} = \ln p - \ln q - \ln n + \ln(N - n) \tag{29}$$

$$= \ln \frac{p(N - n)}{nq} = 0 \quad \text{at maximum} \tag{30}$$

$$\therefore \bar{n}q = p(N - \bar{n}) \tag{31}$$

$$\bar{n} = \frac{Np}{p + q} = Np. \tag{32}$$

NB: In this derivation, we used Stirling’s approximation:  $\ln x! = x \ln x - x$ . We will employ this throughout the course. Next, we can take a Taylor’s series approximation about the most probable value,  $\bar{n}$ :

$$\ln P(n, N) = \ln P(\bar{n}, N) + \frac{\partial}{\partial n} \ln P(n, N)|_{n=\bar{n}}(n - \bar{n}) + \frac{1}{2!} \frac{\partial^2}{\partial n^2} \ln P(n, N)|_{n=\bar{n}}(n - \bar{n})^2 + \dots \tag{33}$$

From Eq. 29:

$$\frac{\partial^2}{\partial^2 n} \ln P(n, N) = -\frac{1}{n} - \frac{1}{N-n} \tag{34}$$

$$= -\frac{1}{Np} - \frac{1}{N-Np} \text{ evaluated at } \bar{n} \tag{35}$$

$$= -\frac{1}{N} \left( \frac{1}{p} + \frac{1}{1-p} \right) \tag{36}$$

$$= -\frac{1}{N} \left[ \frac{1}{p(1-p)} \right] = \boxed{-\frac{1}{Npq}} \tag{37}$$

Back to the Taylor's series:

$$\ln P(n, N) = \ln P(\bar{n}, N) - \frac{1}{2} \frac{1}{Npq} (n - Np)^2. \tag{38}$$

Exponentiate to solve for  $P(n, N)$ :

$$P(n, N) = P(\bar{n}, N) \cdot e^{-\frac{(n-Np)^2}{2Npq}}. \tag{39}$$

Determine the normalization constant by integrating over all space and knowing that the  $\int_{-\infty}^{\infty} P(n, N) = 1$ . This results in:

$$P(n, N) = \frac{1}{\sqrt{2\pi Npq}} \cdot e^{-\frac{(n-Np)^2}{2Npq}}. \tag{40}$$

Note that this is the form of a Gaussian distribution with the mean  $\bar{n}$  and variance  $\sigma^2$  embedded into the equation with  $\bar{n} = Np$  and  $\sigma^2 = Npq$ . This implies that the fraction of likely outcomes decreases as  $N$  increases. The ratio of likely outcomes to total outcomes scales as  $\frac{\sqrt{N}}{N}$ . Again, this is pushing toward maximizing  $W$  and entropy!

## 6 Simple lattice models

Statistical mechanics often employs simple models and counting to predict equilibrium behavior. One such model landscape that is employed are **lattice models**, which will be used several times in this course. A lattice model considers atoms and molecules as hard spheres and space as a collection of sphere-sized bins, which are artificial, mutually exclusive, and collectively exhaustive units of space. Each lattice site is either occupied or not and no two atoms or molecules can reside in the same lattice site. Very simple this illustrates the concept that atoms or molecules are located in different places in space and that no two particles can be in the same place at the same time.

Lattice models can be very helpful in understanding simple thermodynamic concepts. For example, we can ask why an ideal gas exerts pressure? Imagine an ideal gas of  $N$  atoms or molecules that are free to distribute throughout a large or small volume,  $V$ . The tendency to spread out or pressure is often described by mechanics as a result of the atoms or molecules smashing into the side walls of the enclosed volume. However, we can also employ the concepts of multiplicity to understand pressure as the gas will seek to maximize the multiplicity (or entropy). Consider a simplified case of  $N = 3$  atoms or molecules placed into three 'volumes':  $V_A = 5, V_B = 4$ , and  $V_C = 3$ .

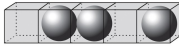
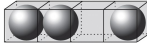

Case	Configuration	Volume
A		5
B		4
C		3

Figure 2.7 Molecular Ordering From 2a (© Garland Science 2011)

We can then calculate the multiplicity based on the assumption that every sequence possible is equally likely (the statistical mechanical approach), no matter how one arranges the vacancies and occupancies:

$$W(N, V) = \binom{V}{N} = \frac{V!}{N!(V - N)!} \tag{41}$$

so that  $W_A(3, 5) = 10$ ,  $W_B(3, 4) = 4$ , and  $W_C(3, 3) = 1$ . The multiplicity increases as the volume increases. That is, if the degree of freedom for the system is its volume, the particles will spread to occupy the largest allowable volume to maximize the multiplicity of the system. This is the basis for the force called *pressure*. This simple model can be used to understand the entropic driving force in pressure and even to derive the ideal and van der Waals gas laws!

In another example, we can ask why molecules diffuse? Here, we can place four white spheres and four black spheres on eight lattice sites. Imagine that we are able to organize the white spheres and black spheres into separate sections of the lattice (see *C* below) and place a perfectly permeable barrier between them. This represents the unmixed case. Now calculate the the multiplicities for the left and right regions. For Case *C*,  $W_{left} = \binom{4}{4}$  and  $W_{right} = \binom{4}{4}$  and from Eq. 17,  $W_C = 1$ . We can do the same for Cases *B* and *A* and see that  $W_B = \binom{1}{4} \cdot \binom{3}{4} = 16$  and  $W_A = \binom{2}{4} \cdot \binom{2}{4} = 36$ .

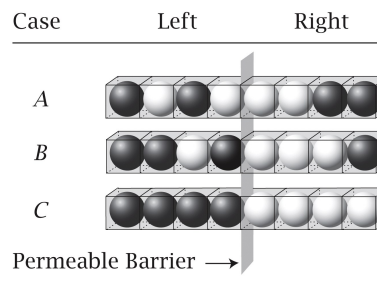


Figure 2.8 Molecular Driving Forces 2nd Edition Gilbert Science 2011

Here, if the degree of freedom is the extent of particle exchange, then the system will have the greatest multiplicity when the ‘concentration’ is uniform throughout. This can be understood as the entropic basis of chemical potential!



As a final example, we can ask why is rubber elastic? This is a simple question that is foundational for this course. When you pull on a rubber, it pulls back. When you push on a rubber, it pushes back. As we will discuss in much more detail, these restorative forces can be understood by the tendency for a polymer chain to adopt the conformation that maximizes its multiplicities. A simple lattice model can be considered where we attach the first monomer to a wall and ‘grow’ a short chain of three monomers. The degree of freedom here is the distance,  $\ell$ , of the end of the chain from the wall in the two-dimensional space. All we need to then do is count the possible conformations for the polymer chain as a function of  $\ell$  in the two-dimensional lattice. As we see  $W(\ell = 1) = 2, W(\ell = 2) = 4,$  and  $W(\ell = 3) = 1$ . Thus, the polymer chain will adopt a conformation with  $\ell = 2$  and if we pull it to  $\ell = 3$  there will be a restoring force that is felt as elasticity!

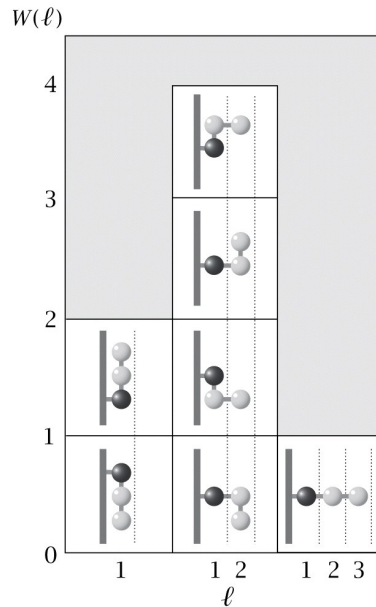


Figure 2.9 Molecular Driving Forces 2/e (© Garland Science 2011)

In these model examples we see that the systems tend toward maximum multiplicity. In all of these examples the energy of the system is fixed and so all we need to do is count multiplicities and find that the system tends to maximize multiplicity, which is directly maximizing the entropy:  $S = k \ln W$ . In later examples, we will also consider the energies of non-ideal systems and derive physical relations from the same simple principles introduced here.