# Stat Mech Notes

Brandon Butler

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# Chapter 1

# Canonical Ensemble

### 1.0.1 Assumptions

- No uncertainty in energy states.

- Each system is a pure system.

- An isolated system is equally likely to be in any available state.

- The average of a property over all available microstates is the macroscopic value.

## 1.1 MicroCanonical

For a system with constant number, volume, and energy, the number of microstates is

$$\Omega = \Omega(N, V, E).$$

Now take an ensemble or collection of systems like this with the number of systems in the ensemble being $A$. Then,

$$E_{tot} = AE$$

$$N_{tot} = AN$$

$$V_{tot} = AV.$$

Since we have no reason to favor one system over the other, we assume each state with the same $N, V, E$ is equally probable. This is known as the principle of equal *a priori* probabilities.

## 1.2 Canonical

### 1.2.1 Deriving the Partition Function

Now lets take a ensemble of systems with the same temperature, volume, and number. The ensemble is put into a heat bath until it is fully equilibrated, and then moved into perfect thermal insulation. The entire ensemble then becomes a system in the microcanonical ensemble.

We know that the system must obey,

$$A = \sum_j a_j$$

$$E_{tot} = \sum_j a_j E_j,$$

where $a_j$ is the occupancy number of state j. We generally do not know the occupancy number of states or number of states, however.

We do know (assumption) that for the microcanonical ensemble each state is equally likely. This means that each state for the entire canonical ensemble is equally likely since the entire canonical ensemble is a system in the microcanonical ensemble; that is all combinations of occupancy numbers is equally likely.

The number of states with distribution $\vec{a}$ of occupancy numbers is given by

$$W(\vec{a}) = \frac{A!}{\prod_j a_j!}.$$

This a multinomial coefficient meaning that at large $A$ it is very sharply peaked; in fact, arbitrarily so at large enough $A$. The probability of being in state j is,

$$P_j = \frac{\sum_a W(\vec{a}) a_j(\vec{a})}{A \sum_a W(\vec{a})} = \frac{\bar{a}_j}{A}.$$

At infinite number of systems in an ensemble, all contributions besides the most common become completely negligible, thus

$$P_j = \frac{\bar{a}_j}{A} = \frac{a_j^*}{A}.$$

We now have a maximization problem (maximizing the weight function $W$) with the following constraints.

$$A = \sum_j a_j$$

$$E_{tot} = \sum_j a_j E_j.$$

Since ln is a monotonic function and, thus, will preserve maxima and minima of inputted functions, $\ln(W(\vec{a}))$ can be maximized instead of $W(\vec{a})$. For further calculations it behooves us to recognize that

$$\ln(W) = \ln(A!) - \sum_j \ln(a_j!).$$

Note the first term is constant and the second is approximately

$$-\sum_j a_j \ln(a_j) + \sum_j a_j = -\sum_j a_j \ln(a_j) + A.$$

Using this we take the partial differential,

$$\frac{\partial(\ln W(\vec{a}) - \alpha \sum_j a_j - \beta \sum_j a_j E_j)}{\partial a_k} = 0,$$

for each $k$ and find,

$$\ln(a_k^*) + \alpha + 1 + \beta E_k = 0$$

or

$$a_k^* = e^{-\alpha'} e^{-\beta E_k}, \text{where} \alpha' = \alpha + 1.$$

Summing over all $(a_j^*)$ gives,

$$A = e^{-\alpha'} \sum_j e^{-\beta E_j}.$$

Finally,

$$P_j = \frac{e^{-\alpha'} e^{-\beta E_k}}{e^{-\alpha'} \sum_j e^{-\beta E_j}} = \frac{e^{-\beta E_k}}{\sum_j e^{-\beta E_j}}.$$

We call the denominator $Q$ and label it the partition function. We now show the ensemble energy and some of its derivatives.

### 1.2.2   Finding $\beta$

$$\bar{E} = \frac{\sum_j E_j e^{-\beta E_j}}{Q}.$$

$$p_j = -\left(\frac{\partial E}{\partial V}\right)_N.$$

$$\bar{p} = -\frac{\sum_j \left(\frac{\partial E}{\partial V}\right)_N e^{-\beta E_j}}{Q}.$$

We can then find,

$$\left(\frac{\partial \bar{E}}{\partial V}\right)_{N,\beta} = -\bar{p} + \beta \overline{Ep} - \beta \bar{E}\bar{p}$$

and

$$\left(\frac{\partial \bar{p}}{\partial \beta}\right)_{N,V} = \bar{E}\bar{p} - \overline{Ep}.$$

Comparing the thermodynamic and ensemble averages we see,

$$\left(\frac{\partial \bar{E}}{\partial V}\right)_{N,\beta} + \beta \left(\frac{\partial \bar{p}}{\partial \beta}\right)_{N,V} = -\bar{p},$$

$$\left(\frac{\partial E}{\partial V}\right)_{N,T} - T \left(\frac{\partial p}{\partial T}\right)_{N,V} = -p.$$

One can see from this that $\beta = \frac{k}{T}$. k will be the same for any system as can be seen from a thought experiment where the ensemble consists of two system composites with the same $N, V, T$. They individual systems will be in equilibrium and from prior calculations the partition function and probability functions are completely separable. This requires they have the same constant k.

### 1.2.3 Entropy

Let
$$f = \ln Q.$$

Then,
$$df = \left(\frac{\partial f}{\partial \beta}\right)_{E_j} d\beta + \sum_k \left(\frac{\partial f}{\partial E_k}\right)_{\beta, E_{j \neq k}} dE_k.$$

This derivative is equivalent of slightly changing the volumes of all systems which changes the energy levels (which is nothing but PV work) and slightly change the temperature before isolated the ensemble again.

This becomes with some manipulation,

$$df = -\bar{E}d\beta - \beta \sum_k P_k dE_k$$

$$d(f + \beta\bar{E}) = \beta \left(d\bar{E} - \sum_k P_k dE_k\right).$$

The first term is the change in average system energy, while the second is the average change of energies in corresponding energy levels. The first is a total energy change while the second is average reversible work. Thus, the quantity is the average reversible heat that of system. This requires that $\beta$ is an integrating factor of $f$.

$$d(f + \beta\bar{E}) = \beta q_{rev}$$

$$d\left(f + \frac{\bar{E}}{kT}\right) = \frac{q_{rev}}{kT}.$$

Thermodynamically the left side must be $dS/k$, so finally,

$$dS = \frac{d\bar{E}}{T} + kd(\ln Q).$$

### 1.2.4 Spontaneous Processes

One can think of spontaneous processes as processes that occur because an increase in available states.

We take the known relation,

$$A(N, V, T) = -kT \ln Q(N, V, T).$$

In addition, one can also recognize that a summation over energy levels rather than states can be done.

$$Q = \sum_l \Omega(N, V, E_l)e^{-\beta E_l}.$$

For a spontaneous process we require that or that available states can only be increased,

$$\Omega_2 \geq \Omega_1.$$

Then,

$$Q_2 - Q_1 = \sum_l (\Omega_2 - \Omega_1)e^{-\beta E_l} \geq 0.$$

Finally,

$$\Delta A = A_2 - A_1 = -kT \ln \frac{Q_2}{Q_1} < 0.$$

# Chapter 2

# Other Ensembles and Fluctuations

## 2.1 Grand Canonical Ensemble

The grand canonical ensemble is a collection of systems with the same volume, temperature, and chemical potential. The ensemble can be thought of as a collection of systems which have been equilibriated w.r.t chemical potential and temperature by placing the ensemble in a heat bath and particle bath. The ensemble once equilibriated is then isolated. Each system within the ensemble is free to exchange particles or energy though.

With the concept of the GC ensemble established, these equations are easily acertained.

$$\sum_N \sum_j a_{Nj} = A$$

$$\sum_N \sum_j a_{Nj} E_{Nj} = E_{tot}$$

$$\sum_N \sum_j a_{Nj} N = N_{tot}$$

Note that $a_{Nj}$ is the occupancy number of systems with $N$ particles and the $j$-th energy state. Like the canonical ensemble the GC ensemble is a system in the microcanonical ensembe so we can use the principle of equal *a priori* probabilities to the distributions of occupancy numbers. The number of states given a distribution $a_{Nj}^-$ is

$$W(a_{Nj}^-) = \frac{A!}{\prod_N \prod_j a_{Nj}!}.$$

The solution to maximizing $W$ with the constrants given is nearly identical to the C ensemble method and simply becomes

$$a_{Nj}^* = e^{-\alpha} e^{-\beta E_{Nj}} e^{-\gamma N} \text{ thus,}$$

$$P_{Nj} = \frac{a_{Nj}^*}{A} = \frac{e^{-\alpha} e^{-\beta E_{Nj}} e^{-\gamma N}}{\sum_N \sum_j e^{-\alpha} e^{-\beta E_{Nj}} e^{-\gamma N}}$$

We note that the denominator is a sum of all states with a two biasing factors based on $\beta E_{Nj}$ and $\gamma N$. Like the C ensemble this will be called the partition function of the GC ensemble. We label it $\Xi$.

### 2.1.1 Finding $\beta$ and $\gamma$

Lets think of the GC ensemble as collections of canonical ensembles with varying numbers. Each ensemble is in thermal equilibrium since the entire GC is. If we

suddenly prevent molecular transport. Then $\Xi$ breaks down to

$$\Xi = e^{\gamma N} \sum_j e^{-\beta E_j}, \; \forall N.$$

This is the canonical partition function with an extra constant which can be ignored since this constant in probabilities would be applied to both the numerator and denominator. Thus, $\beta$ must be the same as the canonical ensemble.

$\gamma$ is a little more involved to derive. If we take the full derivative of $\ln \Xi$, we find

$$df = \left( \frac{\partial f}{\partial \beta} \right)_{\gamma, E_{Nj}} d\beta + \left( \frac{\partial f}{\partial \gamma} \right)_{\beta, E_{Nj}} d\gamma + \left( \frac{\partial f}{\partial \gamma} \right)_{\beta, \gamma, E_{N_{ik} \neq Nj}} dE_{Nj}.$$

This ends up being

$$df = -\bar{E} d\beta - \bar{N} \gamma + \beta \bar{p} dV$$
$$d(f + \beta \bar{E} + \gamma \bar{N}) = \beta d\bar{E} + \beta \bar{p} dV + \gamma d\bar{N}.$$

For multicomponent systems this is the enemble equivalent to the differential form of entropy. Then $\gamma$ must be

$$\gamma = -\frac{\mu}{kT}.$$

An important note is that $\gamma$ is essential another energy scale (chemical potential) compared to thermal energy.

### 2.1.2  Other Points

$\Xi$ can be written as,

$$\sum_N Q(N) e^{\beta \mu N}$$

Often times we see $e^{\beta \mu}$ as $\lambda$ which is called the fugacity and is the absolute activity of a state. This can be seen since

$$\mu = kT \ln \lambda$$
$$\Delta \mu = kT \ln(\lambda_2 / \lambda_1)$$

The function $pV$ is the natural thermodynamic function for the GC ensemble. The proof is simple,

$$S = \frac{\bar{E}}{T} - \frac{\bar{N} \mu}{T} + k \ln \Xi$$
$$G = \mu N = E + pV - TS$$
$$pV = \mu N - E + TS = \mu N - E + T(\frac{\bar{E}}{T} - \frac{\bar{N} \mu}{T} + k \ln \Xi)$$

One final note, the summation over $N$ goes to infinity since in the limit of infinite systems there is a nonzero chance of at least one system having infinite particles. However, we will see that practically speaking the summation could be cut off for reasons of fluctuations.

## 2.2 Gibb's Ensemble

Gibb's ensemble is a collection of systems that have been thermally equilibriated and have impermeable but flexible walls. Thus pressure is also equal each system. Number is also fixed by impermeability. $\Delta$ is the standard denotation of the partition function which is,

$$\sum_E \sum_V \Omega(V, E) e^{-\beta E} e^{\beta p V}$$

True to its name the natural thermodynamic function for the Gibb's ensemble is Gibb's energy.

## 2.3 MicroCanonical Ensemble

### 2.3.1 Universality of Microcanonical Ensemble

For each ensemble, when summing over some combination of energy levels, volumes, or number, we find the degeneracy by the microcanonical partition function $\Omega$. Thus all other ensembles can be thought of as deviations from the microcanonical. The exponential terms are biasings based on intensive properties and the sums represent summations over the extensive properties.

### 2.3.2 Boltzman Equation

If we start from the definition of entropy derived from the GC partition function, we find the famous Boltzman equation which is actually on Boltzman's tomb, and gives intuition as to the nature of entropy.

$$S = k \ln \Xi + k \left( \sum_{N,j} \beta E_{Nj} \frac{e^{-\beta E_{Nj}} e^{-\gamma N}}{\Xi} + \sum_{N,j} \gamma \frac{N e^{-\beta E_{Nj}} e^{-\gamma N}}{\Xi} \right)$$

$$S = k \ln \Xi + k \sum_{N,j} (\beta E_{Nj} + \gamma N) \frac{e^{-\beta E_{Nj}} e^{-\gamma N}}{\Xi}$$

Recall that,

$$\frac{a^*_{Nj}}{A} = \frac{e^{-\beta E_{Nj}} e^{-\gamma N}}{\Xi}$$

and

$$\ln \frac{a^*_{Nj}}{A} = \ln a^*_{Nj} - \ln A = \ln \left( e^{-\beta E_{Nj}} e^{-\gamma N} \right) - \ln \Xi$$

$$= -(\beta E_{Nj} + \gamma N + \ln \Xi)$$

Thus,

$$S = k \ln \Xi - k \sum_{Nj} \left( \ln a^*_{Nj} - \ln \Xi + \ln A \right) \frac{a^*_{Nj}}{A}$$

$$= k \ln A - \frac{k}{A} \sum_{N,j} a^*_{Nj} \ln a^*_{Nj}$$

This is for each system in the GC ensemble. The entire entropy is then,

$$S = kA \ln A - k \sum_{N,j} a^*_{Nj} \ln a^*_{Nj}$$

$$= k \ln \frac{A}{\sum_{N,j} a^*_{Nj} \ln a^*_{Nj}}$$

$$= k \ln W(\vec{a_{Nj}})$$

$$= k \ln \Omega.$$

## 2.4 Fluctuations

For the assumption that large systems only assume states in their ensemble average, fluctuations around the mean must be small. If they were not, then statistical mechanics would predict that we should observe macroscopic fluctuations in state. Two canonical ways of showing that fluctuations are indeed small (as compared to the mean) the energy of the canonical and number of the grand canonical ensemble will be shown. The most important equation when dealing with fluctuations or second moments around the mean is,

$$\sigma^2_M = \overline{\left( M - \bar{M} \right)^2} = \overline{M^2} - \bar{M}^2$$

### 2.4.1 Energy Fluctuations

For the canonical ensemble $\overline{E^2}$ is

$$\sum_j E_j^2 P_j = \frac{1}{Q} \sum_j E_j^2 e^{-\beta E_j}$$

$$= \frac{-1}{Q} \frac{\partial}{\partial \beta} \sum_j E_j e^{-\beta E_j}$$

The last sum is just the average energy without the partition function's normalization, so

$$\overline{E^2} = \frac{-1}{Q} \frac{\partial}{\partial \beta} (\bar{E} Q).$$

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Via product rule we get

$$\overline{E^2} = -\frac{\partial \bar{E}}{\partial \beta} - \bar{E}\frac{\partial \ln Q}{\partial \beta}$$

$$= kT^2\frac{\partial \bar{E}}{\partial \beta} + \bar{E}^2.$$

Finally, via the definition of the varience,

$$\sigma_E^2 = kT^2\left(\frac{\partial \bar{E}}{\partial T}\right)_{N,V} \qquad\qquad = kT^2C_v$$

Compared to the average energy then the average fluctuations are,

$$\frac{\sigma_E}{\bar{E}} = \frac{(kT^2C_v)^{\frac{1}{2}}}{\bar{E}}$$

For an ideal gas $\bar{E}$ scales as $O(NkT)$ while $C_v$ scales as $O(Nk)$. Thus the fluctuations are proportional to $O(N^{\frac{1}{2}})$ and in a large system are very small. It is worth noting the same result can be achieved from a Taylor expansion of the probability distribution around $\bar{E}$.

### 2.4.2 Density Fluctuations

For the GC ensemble we shall look at number fluctuations. The fluctuations are

$$\sum_{N,j} N^2 P_{Nj} = \frac{1}{\Xi}\sum_{N,j} N^2 e^{-\beta E_{Nj}}e^{-\gamma N} = \frac{-1}{\Xi}\frac{\partial}{\partial \gamma}\sum_{Nj} Ne^{-\beta E_{Nj}}e^{-\gamma N}$$

$$= \frac{-1}{\Xi}\frac{\partial}{\partial \gamma}(\bar{N}\Xi)$$

$$= \frac{\partial \bar{N}}{\partial \gamma} - \bar{N}\frac{\partial \ln \Xi}{\partial \gamma}$$

$$= kT\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{V,T} + \bar{N}^2$$

This looks very similar to the canonical example and should because it is analogous. All we need now is the thermodynamic relationship,

$$\left(\frac{\partial \mu}{\partial N}\right)_{V,T} = -\frac{V^2}{N^2}\left(\frac{\partial p}{\partial \mu}\right)_{N,T}.$$

The fluctuations are,

$$\sigma_N = \left(\frac{\bar{N}^2 kT\kappa}{V}\right)^{\frac{1}{2}}$$

$$\frac{\sigma_N}{\bar{N}} = \left(\frac{kT\kappa}{V}\right)^{\frac{1}{2}}.$$

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Here $\kappa$ is the isothermal compressibility which is $\frac{1}{p}$ for the ideal gas. Then the fluctuations for the ideal gas is once again the property to the $\frac{-1}{2}$. Furthermore, like before the Taylor expansion can be performed to get similar results.

For number fluctuation, this has measurable effects on the Raleigh scattering. The functions make it so that the scattering is a function of wavelength to the $-4$th. Therefore, in our atmosphere, blue light gets scattered much more and the sky is blue and sunsets are red.

# Chapter 3

# Boltzman, Fermi-Dirac, and Bose-Einstein Statistics

When we wish to decouple a system into non-interacting parts, different statistics apply based on the underlying physics of the system. Three major types of statistics exist with respect to molecular systems: Boltzmann, Fermi-Dirac, and Bose-Einstein. To be exact Boltzmann statistics is the limit of the other two at sufficiently high T.

- Fermi-Dirac

  – Occurs when the exchange of basis particles is antisymmetric with respect to the wave function.

  – Example fermions are electrons which the extrapolation of the Fermi-Dirac statistics is the Pauli exclusion principle.

- Bose-Einstein

  – For systems where the exchange of basis particles is symmetric with respect to the wave function, Bose-Einstein statistics apply.

  – Examples are protons and neutrons.

- Boltzmann

  – The high temperature limit of the other two.

  – Ends up being the classical approximation of the quantum mechanical equations.

## 3.1 Boltzmann Statistics

### 3.1.1 Hamiltonian Decoupling

If a multiparticle system is dilute enough the interactions between particles is negligible, and the system can be treated as a $N$ independent body problem. Even in liquids and solids convenient "basis particles" can be chosen so the system is modeled by a $N$ independent body system. In these cases where interactions can be ignored, the Hamiltonian can be decoupled.

$$\mathcal{H} = \sum_{i=1}^{N} \mathcal{H}_i$$

In addition, for individual molecules if the individual modes of molecular energy are decoupled,

$$\mathcal{H}_i = \sum_{m \in M} \mathcal{H}_i^m,$$

where $M$ is the set of all decoupled energy modes.

### 3.1.2 Partition Function Decoupling

We now consider a $N$ distinguishable, independent, body system. Then,

$$\mathcal{Q}(N, V, T) = \sum_j e^{-\beta E_j} = \sum_{j,k,\ldots} e^{-\beta \cdot (\epsilon_j^a + \epsilon_k^b + \epsilon_l^c + \ldots)}$$
$$= q_a q_b q_c \ldots$$

Here we see the canonical partition function becomes $N$ individual particle partition functions. Since the particles are identical, we have

$$q(V, T) = \sum_j e^{-\beta \epsilon_j}$$
$$\mathcal{Q} = q^N.$$

This equation is only true in a distinguishable system though which in molecular systems in rarely the case. Including distinguishably leads to some problems. Consider, two equivalent energy states,

$$E_{tot} = \epsilon_i^a + \epsilon_j^b + \epsilon_j^c + \ldots$$
$$E_{tot} = \epsilon_j^a + \epsilon_i^b + \epsilon_j^c + \ldots \quad .$$

In fact, there are $N$ such equivalent arrangements. However, in the case that all individual energies are different, there are $N!$ combinations. The problem, thus, is that different energy combinations have differing numbers of equivalent arrangements. This would imply that a simple divisor cannot be applied to reduce the number of configurations of a distinguishable system to a indistinguishable one.

Despite this fact, we can still often make the approximation of dividing the distinguishable partition function by $N!$. At room temperature ($m = 10^{-22}g$, $a = 10$cm), the number of energy states available to a particle in a box is $O(10^{30})$. This number signifies that in all but extremely dense systems at around room temperature or even colder is much greater than the number of particles, so it is unlikely that any two particles adopt the same energy, so

$$\mathcal{Q} = \frac{q^N}{N!},$$

is an excellent approximation for all but 'the lightest molecules at very low temperatures.'

### 3.1.3 Getting Molecular Properties

Since we now are dealing with individual molecular partition functions, we can get averages of molecular properties. The probability of being in state $j$ is

$$\pi_j = \frac{e^{-\beta \epsilon_j}}{q}.$$

Any mechanical properties is then,

$$\bar{M} = \sum_j M_j \pi_j.$$

The parallelism to the ensembles already mentioned is not an accident as Boltzmann's original examination of statistical mechanics used a system of molecules in thermal equilibrium as his start. In fact, we could from *a priori* principles derive the previous two equations.

## 3.2 Fermi-Dirac and Bose-Einstein Statistics

### 3.2.1 Common Derivation

Derivation of the exact distribution of states in an independent system obeying either Fermi-Dirac or Bose-Einstein statistics is most readily done in the grand canonical ensemble. We let $E_j(N, V)$ be the energy available to a $N$ body system, $\epsilon_k$ the molecular quantum states, and $n_k$ the occupancy number of a molecular quantum state. Thus it follows,

$$E_j = \sum_k \epsilon_k n_k$$

$$N = \sum_k n_k.$$

From here, we take the $\Xi$ and find its form on a molecular basis.

$$\Xi = \sum_N \lambda^N \sum_j e^{-\beta E_j} = \sum_N \lambda^N \sum_{n_k \in S} e^{-\beta \cdot \sum_i \epsilon_i n_i},$$

where $S$ is the set of all occupancies numbers that obeys $\sum_k n_k = N$. Some more manipulation leads to,

$$\Xi = \sum_{N=0}^{\infty} \sum_{n_k \in S} \lambda^{\sum_i n_i} e^{-\beta \cdot \sum_i \epsilon_i n_i}$$

$$= \sum_{N=0}^{\infty} \sum_{n_k \in S} \prod_k (\lambda e^{-\beta \epsilon_k})^{n_k}.$$

We have moved $\lambda$ into the second summation which just distributes $\lambda^N$ to each term. We then isolated $n_k$ by using a series product. From here, we must notice that since $N \to \infty$, every distribution of $n_k \in \mathbb{N}$ compatible with the occupancy number requirements of the given statistics will be summed over. Thus each $n_k$ will vary over all its possible values in combination with every other occupancy

number. The knowledge allows us to write the previous equation as,

$$\Xi = \sum_{n_1}^{\max(n_1)} \sum_{n_2}^{\max(n_2)} \sum_{n_3}^{\max(n_3)} \cdots \prod_k (\lambda e^{-\beta \epsilon_k})^{n_k}$$

or

$$\Xi = \sum_{n_1}^{\max(n_1)} (\lambda e^{-\beta \epsilon_1})^{n_1} \sum_{n_2}^{\max(n_2)} (\lambda e^{-\beta \epsilon_2})^{n_2} \cdots \quad .$$

This is simple the product of $N$ terms so we have,

$$\Xi = \prod_k \sum_{n_k}^{\max(n_k)} (\lambda e^{-\beta \epsilon_k})^{n_k}$$

### 3.2.2  Fermi-Dirac

For Fermi-Dirac statistics each state is either uniquely occupied or not occupied at all. Therefore, the summation above expands to two terms for occupied and unoccupied states.

$$\Xi = \prod_k (1 + \lambda e^{-\beta \epsilon_k}).$$

### 3.2.3  Bose-Einstein

In the case of Bose-Einstein statistics each state can be occupied any number of times without restriction. This becomes,

$$\Xi = \prod_k \sum_{n_k}^{\infty} (\lambda e^{-\beta \epsilon_k})^{n_k}$$

$$= \prod_k \sum_{i_k}^{\infty} x^{i_k}$$

$$= \prod_k (1 + x)^{-1} \quad \text{for } x < 1$$

$$= \prod_k (1 + \lambda e^{-\beta \epsilon_k})^{-1}$$

The last two lines uses the result from the geometric series. One way to write this result is,

$$\Xi_{BE}^{FD} = \prod_k (1 + \lambda e^{-\beta \epsilon_k})^{\pm 1}.$$

From here we note that,

$$\ln \Xi = \sum_k \ln (1 \pm \lambda e^{-\beta \epsilon_k}).$$

Thus $\bar{E}$ can be calculated by first noting,

$$\bar{n}_k = \frac{\lambda e^{-\beta\epsilon_k}}{1 \pm \lambda e^{-\beta\epsilon_k}}$$

then,

$$\bar{E} = \sum_k \bar{n}_k \epsilon_k = \sum_k \frac{\epsilon_k \lambda e^{-\beta\epsilon_k}}{1 \pm \lambda e^{-\beta\epsilon_k}}.$$

By allowing $T \to \infty$ or $\frac{N}{V} \to 0$, $\lambda \to 0$ which means $\bar{n}_k \to 0$. This can be shown to make both Fermi-Dirac and Bose-Einstein statistics go to the Boltzmann limit.

# Chapter 4

# The Monotonic Ideal Gas

## 4.1 The Monotonic Ideal Gas

This chapter will concern gases that are sufficiently dilute as to have negligible interactions with other particles. In addition, these molecules will be monotonic i.e. only consist of one atom. Therefore, no rotational or vibrational energy will be taken into consideration. Furthermore, we will assume that the partition function of a molecule can be decoupled into its individual energy modes.

Assumptions

- Gas is dilute enough to neglect individual particle interactions.

- Individual energy modes in the atom are decoupled.

## 4.2 The Individual Molecular Partition Functions

First we must assess the different modes of energy that a molecule can carry. Since there are no interactions, there is no potential energy in the system unless a body force were to be acting on the entire system. The only available modes for storing energy into the system are then,

1. Translational

2. Electronic

3. Nuclear.

The partition functions are then,

$$q_{mol} = q_{trans}q_{elec}q_{nucl}$$

$$\mathcal{Q} = \frac{q_{mol}^N}{N!}$$

$$\mathcal{Q} = \frac{(q_{trans}q_{elec}q_{nucl})^N}{N!}.$$

### 4.2.1 Translational Partition Functions

We begin with the exploration of the translational partition function. From one of the first problems solved in quantum mechanics, the particle in an infinite potential box, we know,

$$\epsilon_{n_x,n_y,n_z} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2).$$

From here we can directly plug in $\epsilon$ into $q_{trans}$.

$$\begin{aligned} q_{trans} &= \sum_{j,k,l} e^{-\beta(\epsilon_{n_x}+\epsilon_{n_y}+\epsilon_{n_z})} \\ &= \sum_i e^{-\beta\epsilon_{n_i}} \sum_j e^{-\beta\epsilon_{n_j}} \sum_l e^{-\beta\epsilon_{n_l}} \\ &= \left( \sum_{i=0}^{\infty} e^{-\beta\epsilon_{n_l}} \right)^3 \\ &= \left( \sum_{i=0}^{\infty} \exp\left( -\frac{\beta h^2 n^2}{8ma^2} \right) \right)^3 \end{aligned}$$

*This summation cannot be expressed exactly analytically.* However, the density of available states is so large, that the available energy level can be treated as continuous which means the summation can be approximated by an integral. The difference between two energy levels is given by,

$$\Delta = \frac{\beta h^2 (n_x+1)^2}{8ma^2} - \frac{\beta h^2 n_x^2}{8ma^2} = \frac{\beta h^2 (2n_x+1)}{8ma^2}.$$

At $T = 300K$, $m = 10^{-22}$, and $a = 10cm$, $\Delta$ is on the order of $(2n_x+1) \cdot 10^{-20}$. For these conditions $n_x \approx 10^{10}$. As one can see then the approximation is a very good one.

Thus, $q_{trans}$ becomes,

$$\left( \int_0^{\infty} e^{-\beta h^2 n^2/8ma^2} \mathrm{d}n \right)^3 = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V.$$

$V$ represents the volume or $a^3$. This result follows that the integrand and lower limit of the integral forms the error function. Another way to come to this result is to use the density of states approximation where the density of transitional energy levels is,

$$\omega(\epsilon)\mathrm{d}\epsilon = \frac{\pi}{4} \left( \frac{8ma^2}{h^2} \right)^{3/2} \epsilon^{1/2} \mathrm{d}\epsilon.$$

Some observations are worth noting. First that the average momentum $p$ is $(mkT)^{1/2}$. This comes from equating the translational energy stated above using an ensemble average and the momentum form of translational energy. From here, we can see that $q_{trans}$ is,

$$\frac{V}{(h/p)^3} = \frac{V}{\Lambda^3}.$$

$\Lambda$ is simple the DeBroglie wavelength.

### 4.2.2 Electronic Partition Functions

For the electronic energy we use energy levels so that,

$$q_{elec} = \sum_i \omega_i e^{-\beta \epsilon_i}.$$

We then fix the ground state energy to zero which gives us,

$$q_{elec} = \omega_1 + \sum_{i=2} \omega_i e^{-\beta \Delta \epsilon_{1i}}.$$

The argument in the exponential is usually large since the energy difference is on the order of electron volts. Specific cases like the halogen series require more than just the first term, however. Regardless, the sum converges quickly and energy levels of available states for many atoms and materials have been tabulated. The following is usually enough,

$$q_{elec} = \omega_1 + \omega_2 e^{-\beta \Delta \epsilon_{12}}.$$

### 4.2.3 Nuclear Partition Functions

While there are excited nuclear states to access them requires temperatures of $10^{10} K$. Thus only the ground state degeneracy matters and

$$q_{nucl} = \omega_1.$$

For most cases the nuclear partition function is just omitted.

## 4.3 Thermodynamic Relations with the Ideal Gas

Taking the definition of the Helmholtz energy in terms of the canonical ensemble we have for the monotonic ideal gas,

$$A(N, V, T) = -kT \ln \mathcal{Q}$$

$$= -kT \ln \left[ \left( \frac{V}{\Lambda^3} \right)^N (\omega_1 + \omega_2 e^{-\beta \Delta \epsilon_{12}})^N \frac{1}{N!} \right]$$

$$= -NkT \ln \frac{V}{\Lambda^3} - NkT \ln (\omega_1 + \omega_2 e^{-\beta \Delta \epsilon_{12}}) + NkT \ln N - NkT$$

$$= NkT \left( -\ln \frac{V}{\Lambda^3} - \ln (\omega_1 + \omega_2 e^{-\beta \Delta \epsilon_{12}}) + \ln N - 1 \right).$$

The electronic term is small so,

$$A \approx -NkT \left( \ln \frac{V}{\Lambda^3} - \ln N + 1 \right)$$

or

$$A \approx -NkT \left( \ln \frac{V}{N\Lambda^3} + 1 \right).$$

At this point it is helpful to note that,

$$\ln \mathcal{Q} = N \left( \ln \frac{V}{N\Lambda^3} (\omega_1 + \omega_2 e^{-\beta \Delta \epsilon_{12}}) + 1 \right).$$

Pressure is given by,

$$p = kT \left( \frac{\partial \ln \mathcal{Q}}{\partial T} \right)_{N,V} = \frac{NkT}{V}.$$

Energy is,

$$E = kT^2 \left( \frac{\partial \ln \mathcal{Q}}{\partial T} \right)_{N,V} = \frac{3}{2} NkT + \frac{N \omega_2 \Delta \epsilon_{12} e^{-\beta \Delta \epsilon_{12}}}{q_{elec}}$$

Entropy is,

$$S = \frac{E}{T} - \frac{A}{T}$$

$$S = \frac{3}{2} Nk + \frac{N \omega_2 \Delta \epsilon_{12} e^{-\beta \Delta \epsilon_{12}}}{q_{elec} T} - NkT \left( -\ln \frac{V}{\Lambda^3} - \ln (\omega_1 + \omega_2 e^{-\beta \Delta \epsilon_{12}}) + \ln N - 1 \right)$$

$$= Nk \left( \frac{5}{2} + \ln \frac{V}{N\Lambda^3} \right) + Nk \ln(\omega_1 + \omega_2 e^{-\beta \Delta \epsilon_{12}}) + \frac{N \omega_2 \Delta \epsilon_{12} e^{-\beta \Delta \epsilon_{12}}}{q_{elec}}$$

$$= Nk \left( \frac{5}{2} + \ln \frac{V}{N\Lambda^3} \right) + S_{elec}.$$

Using,

$$\mu(T, p) = -kT \left( \frac{\partial \ln \mathcal{Q}}{\partial N} \right)_{V,T},$$

one can similarly find the chemical potential. The procedure is the same for all thermodynamic properties.

# Chapter 5

# Ideal Diatomic Gas

## 5.1 Introduction

An ideal diatomic gas has two more means of storing energy compared to the monotonic case: vibrational and rotational. Strictly speaking vibrational and rotational modes are coupled and rotational-electronic and are coupled. However, there are cases where this can be ignored and others where reality requires a more nuanced quantum mechanic approach. One important assumption we will be making is the **Born-Oppenheimer approximation**. This simply states that electronic movement occurs on a timescale where nuclei are effectively stationary. Therefore, we can solve the Schrödinger equation for the electrons with stationary nuclei and for nuclei in an electron cloud. The interatomic interactions determined by the electron cloud often is difficult to solve so empirical and semi-empirical potentials like **Moore** or **Leonard-Jones** are often used. Figure 5.1 shows an experimentally determined interatomic potential with a dashed line representing the Moore's potential.
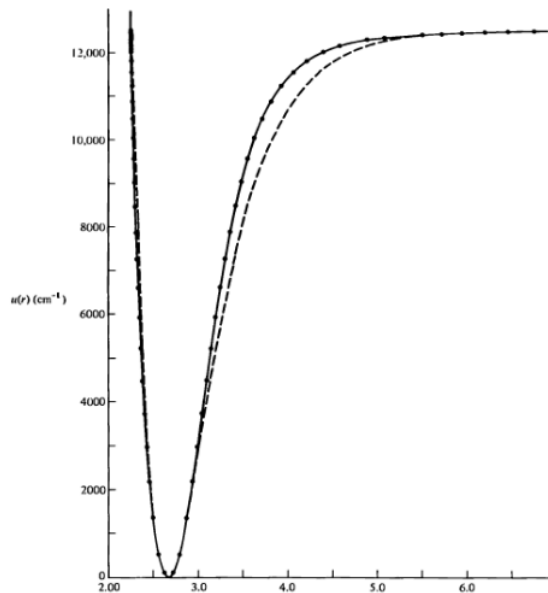


Figure 5.1: Interatomic potential of a diatomic species.

## 5.2 Rigid Rotor Harmonic Oscillator

For a diatomic atom, we first notice we can define translational movement as that movement with respect to the center of mass, thus the Hamiltonian becomes

$$\mathcal{H} = \mathcal{H}_{trans} + \mathcal{H}_{int},$$

where the second term is the energy from the relative motion of the two masses. This relative motion is clearly either rotational or vibrational. Technically the rotational energy is effected by the current interatomic distance; however, in most cases the changing of the effective radius is not consequential.

**Proof** If we let $u(r)$ represent the interatomic potential, then a Taylor series around the current distance, $R$, is,

$$u(r) = u(R) + (r - R)\left(\frac{\partial u}{\partial r}\right)_{r=R} + \frac{1}{2}(r - R)^2\left(\frac{\partial^2 u}{\partial r^2}\right)_{r=R}$$
$$= u(R) + \frac{1}{2}k(r - R)^2.$$

The second steps substitutes the second derivative for $k$. The reason we can drop the linear term stems from the fact that in most cases the interatomic distance is very close to the potential minimum. At the minimum, the first derivative goes to zero. Therefore, if $k$ or the second derivative is large then the bond is stiff and distance will not fluctuate much. *Note:* that $k$ is similar to Hooke's constant.

We can then state,
$$\mathcal{H}_{int} = \mathcal{H}_{rot} + \mathcal{H}_{vib}.$$

Of course, the above is equivalent to,

$$q_{int} = q_{rot}q_{vib}.$$

This approximation is known as the rigid rotor harmonic oscillator approximation. The approximation allows vibrational-rotational decoupling.

## 5.3  Vibrational Partition Function

### 5.3.1  Energy Levels and Spectra

For a quantum harmonic oscillator, the energies are given by

$$\epsilon_{vib} = h\nu(n + \frac{1}{2}).$$

*Note:* that the degeneracy of each level is one, so each state is its own level. $\nu$ is given by,

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}.$$

The selection rules for vibrational transitions is that transitions can only occur between energy adjacent states or $\Delta n = \pm 1$. Taking the above equation

for $\epsilon_{vib}$, and finding the energy difference between adjacent levels gives

$$\Delta\epsilon = \epsilon_{n+1} - \epsilon_n$$
$$= \nu h((n+3/2) - (n+1/2)) = \nu h(1)$$

$\nu$ then is,

$$\nu = \frac{\Delta\epsilon}{h} = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}.$$

This gives the spectra for vibrational transitions. For there to be radiation, a changing dipole in the molecule must exist. Using this equation, $k$ can be found for different diatomic molecules. *Note,* the vibrational spectra consists of one line. One other quick fact is that for a given electronic state there is an vibrational energy $D_o$ that corresponds to a disassociating molecule. Figure 5.2 shows the potential the vibrational mode operates in with some common quantities: $D_o$ represents the dissociation energy for the molecule, $D_e$ represents the depth of the potential well, the top function represents the first excited electronic state.
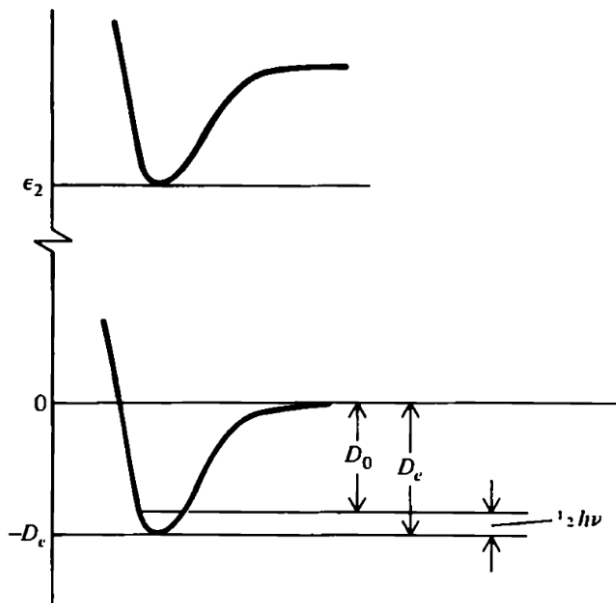


Figure 5.2: Electronic potentials for the ground and first excited state with relevant quantities marked.

## 5.3.2   Deriving the Partition Function

In order to derive the partition function, a zero state energy must be assigned. Two possibilities exist 0 or $h\nu/2$. The book uses the latter and so shall I. The

derivation of the vibrational partition function goes as follows,

$$q_{vib} = \sum_n e^{-\beta\epsilon_n}$$

$$= \sum_n e^{-\beta h\nu(n+1/2)} = \sum_n e^{-\beta h\nu n}e^{-\beta h\nu/2}$$

$$= e^{-\beta h\nu/2}\sum_{n=0}^{\infty} e^{-\beta h\nu n}$$

$$= \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \qquad e^{-\beta h\nu} < 1.$$

The first step follows by definition. The second is just the expansion and simplification of $\epsilon_{vib}$. The third is just taking the constant out of the sum. The fourth step involves seeing that the sum is a geometric series if $e^{-\beta h\nu} < 1$. The partition function here is exact given the constraint, but we can still take a high temperature limit using an integral. This then is,

$$q_{vib} = e^{-\beta h\nu/2}\int_{n=0}^{\infty} e^{-\beta h\nu n}\mathrm{d}n = \frac{kT}{h\nu}.$$

### 5.3.3   Properties of Vibrational Mode

We will look at level occupancy and average vibrational energy. The average energy given by the exact partition function is,

$$E_v = NkT^2\frac{\mathrm{d}\ln q_v}{\mathrm{d}T} = NkT^2\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{h\nu}{2kT} - \ln\left(1 - e^{-h\nu/kT}\right)\right)$$

$$= \frac{Nk\Theta}{2} + Nk\Theta\frac{e^{-\Theta/T}}{1 - e^{-\Theta/T}} = Nk\Theta\left(\frac{1}{2} + \frac{1}{e^{\Theta/T} - 1}\right).$$

Where, $\Theta = h\nu/k$. For the high temperature limit, we have,

$$E_v = NkT^2\frac{\mathrm{d}\ln q_v}{\mathrm{d}T} = NkT^2\frac{\mathrm{d}}{\mathrm{d}T}\left(\ln\frac{T}{\Theta}\right) = NkT.$$

The specific heat in this case is simply $Nk$ since $C_v$ is the derivative of energy with respect to temperature.

The fraction of molecules in a given energy state are,

$$f_n = \frac{e^{-\beta h\nu(n+1/2)}}{q_{vib}}.$$

Therefore the fraction of molecules in an excited state are,

$$f_{n>0} = \frac{\sum_{n=1}^{\infty} e^{-\beta h\nu(n+1/2)}}{q_{vib}} = 1 - f_0 = \frac{e^{-\beta h\nu/2}}{q_{vib}} = 1 - (1 - e^{-\beta h\nu}) = e^{-\beta h\nu}.$$

The solution comes from the fact that the fraction in a excited state is the inverse of the fraction in the ground state.

## 5.4 Rotational Partition Function

### 5.4.1 Energy States and Spectra

For a rigid rotor the energy states and degeneracy are given by,

$$\epsilon_j = \frac{\hbar^2 J(J+1)}{2I}$$
$$\omega_j = 2J + 1.$$

Here, $I$ is the moment of inertia, which is $\mu r_e^2$ for the diatomic case. $\mu$ is the reduced mass of the molecule.

The transition rules for rotational energy are that the transition must be adjacent like the vibrational modes and the molecule must have a permanent dipole moment. The electromagnetic spectra that comes from the rotational energy is then given by taking the different in adjacent energy levels like before.

$$\Delta\epsilon = \epsilon_{j+1} - \epsilon_j = \frac{\hbar^2}{2I}((J+1)(J+2) - J(J+1)) = \frac{\hbar^2}{I}(J+1)$$
$$\nu = \frac{\Delta\epsilon}{h} = \frac{h}{4\pi^2 I}(J+1)$$

To get the final form, $\hbar$ was expanded to $h/2\pi$. What this says is unlike vibrational energy, rotational energy transitions emit multiple wavelengths. *Note:* we will set the rotational ground energy to zero.

### 5.4.2 Deriving the Rotational Partition Function

### 5.4.3 Heteronuclear Derivation

For reasons of wavefunction symmetry under the exchange of particles we must separate the heteronuclear and homonuclear cases. We begin by examining the heteronuclear.

By definition,

$$q_{rot} = \sum_{J=0}^{\infty} (2J+1)e^{-\beta \bar{B} J(J+1)}.$$

The variable $\bar{B}$ is $h/8\pi^2 Ic$ where c is the speed of light. Then, $\epsilon_J = \bar{B}J(J+1)$. We can further define $\Theta_r$ to be $\bar{B}/k$ which is a rotational temperature. In order to write the summation in terms of a integral we require that the difference between adjacent values be small. This is fulfilled if $\Theta_r/k(J+1)$ is small which is true at small $J$. By the time large $J$ are reached the contributions become

negligible though, so we can just take the integral.

$$q_{rot} = \int_0^\infty (2J+1)e^{-\Theta_r J(J+1)/T} \mathrm{d}J$$

$$= \int_0^\infty e^{-\Theta_r J(J+1)/T} \mathrm{d}[J(J+1)] = \left[\frac{T}{\Theta_r}e^{-\Theta_r J(J+1)/T}\right]_0^\infty = \frac{T}{\Theta_r}$$

$$= \frac{8\pi^2 I k T}{h^2}.$$

The second line recognizes that a change of variable can drastically simplify the integral. For cases where the above is a bad approximation say $\Theta_r > 0.7T$, the summation can be expanded to 4 terms with good accuracy. Of course higher order approximations can be taken.

The two approximation, however, leave an intermediate gap. The solution is to use a Euler-MacLaurin summation formula approximation. This is given by

$$\sum_{n=a}^b f(n) = \int_a^b f(n)\mathrm{d}n + \frac{1}{2}[f(b)+f(a)] + \sum_{j=1}^\infty (-1)^j \frac{B_j}{(2j)!}[f^{(2j-1)}(a) - f^{(2j-1)}(b)],$$

where $B_j$ is the $j$-th Bernoulli number and the last bracketed term uses the $(2j-1)$-th derivative. This give for the rotational partition function,

$$q_{rot} = \frac{T}{\Theta_r}\left(1 + \frac{1}{3}\left(\frac{\Theta_r}{T}\right) + \frac{1}{15}\left(\frac{\Theta_r}{T}\right)^2 + \frac{1}{315}\left(\frac{\Theta_r}{T}\right)^3 + \cdots\right).$$

### 5.4.4 Heteronuclear Thermodynamics

The ensemble rotational energy in the high temperature limit is,

$$E_r = NkT^2\left(\frac{\partial \ln q_{rot}}{\partial T}\right) = NkT^2\left(\frac{\partial}{\partial T}\right)(\ln T - \ln\Theta_r) = NkT.$$

This means that $C_v$ like in the vibrational case is $Nk$. The fraction of molecules in a particular vibrational state can be taken just like the rotational state, but since it is an identical procedure it is not shown here. However, an important feature of rotational energy levels is that the most occupied level at room temperature is an excited state. The most occupied level can be derived by taking the derivative of the occupancy fraction,

$$\frac{\mathrm{d}f_J}{\mathrm{d}J} = \frac{\mathrm{d}}{\mathrm{d}J}\left(\frac{N_J}{N}\right) = \frac{\mathrm{d}}{\mathrm{d}J}\left(\frac{(2J+1)e^{-\Theta_r J(J+1)/T}}{q_{rot}}\right),$$

and setting it equal to zero.

## 5.4.5 Homonuclear Derivation

*Note:* The homonuclear case can be approximated by

$$q_{rot,homo} = \frac{q_{rot,heter}}{2}.$$

This deals with the fact that in the homonuclear case a two-fold symmetry exists perpendicular to the interatomic axis. This prevents the over counting of states. This factor of 2 can be generalized to a factor $\sigma$ which is called the symmetry number and represents the number of indistinguishable rotational states or the number or rotational symmetries.

However, this will not work at low temperatures since homonuclear diatomic molecules must obey certain wavefunction symmetries when an exchange of nuclei is performed. This symmetry depends on the spins of the nuclei. If the spins are integers the wavefunction is symmetric; otherwise, the wavefunction is anti-symmetric with respect to exchange.

### Digression on Symmetry Requirements

To determine the individual symmetry contributions of the electronic, translational, vibrational, rotational, and nuclear energies to the wavefunction, we imagine that we take a diatomic molecule and exchange both nuclei along with their electrons. We then flip the electrons again. For molecules where only the ground electronic state is useful and ground state is $\Sigma_g^+$, the electronic wavefunction is symmetric to such operations. The translational and vibration wavefunctions are obviously unaffected by such transformations. This only leaves the nuclear and rotational.

By looking at the rotational wavefunctions for hydrogen, one can see that even $J$ are symmetric to the swap, but odd $J$ are anti-symmetric to it. In addition, for hydrogen, the nuclei spins are $\pm 1/2$. This leads to four spin combinations: three are symmetric and one is anti-symmetric. Since the total wavefunction must be anti-symmetric we must pair symmetric rotational wavefunctions with anti-symmetric nuclear wavefunctions and vice versa. The opposite holds true for integer spin molecules.

For a generic system the number of spin states for a nucleus is $2I + 1$. For a diatomic molecule there are $(2I+1)^2$ states then. The number of antisymmetric states can be calculated using $(2I + 1)(2I)/2$. The number of symmetric is just the total minus the number of antisymmetric wavefunctions. This leads to

- Integral spin

    - Odd J - I(2I+1)
    - Even J - (I+1)(2I+1)

- Half-integral spin

    - Odd J - (I+1)(2I+1)

– Even J - I(2I+1).

One can see that the two are just mirrors of each other. The partition function is then,

$$q_{rot,nucl} = w_{k,even} \sum_{J \ even} (2J+1)e^{-\Theta_r J(J+1)/T} + w_{k,odd} \sum_{J \ odd} (2J+1)e^{-\Theta_r J(J+1)/T},$$

where $w_{k,even/odd}$ represents the appropriate spin weighting. The rotation and nuclear partition functions are then coupled. However, at high temperatures,

$$\sum_{J \ odd} \approx \sum_{J \ even} \approx \frac{1}{2} \sum_{J}.$$

This is just one half of the heteronuclear case. Then all the previous equations apply with the adding factor of 1/2. In this limit, we can separate the partition functions to get,

$$q_{rot} = \frac{T}{2\Theta_r} = \frac{T}{\sigma\Theta_r}$$
$$q_{nucl} = (2I+1)^2.$$

This requires that $\Theta_r < 0.2T$. $\sigma$ is just the symmetry number mentioned previously. When the temperature is not high enough however the coupled partition function must be used. In general, this is only necessary with molecules like hydrogen where $\Theta_r$ is appreciable at gas temperatures. The splitting of $H_2$ into two different types para (parallel spins) and ortho (anti-parallel spins) comes from this weighting. At room temperature $H_2$ is 25% para and 75% ortho. At lower temperatures though this ratio changes as the summations over even and odd $J$'s are not approximately equivalent.

All thermodynamic quantities can be calculated normally and will either not vary in the high temperature limit (as is the case for energy and specific heat) or will vary by factors of $\sigma$. This is also true in the Euler-MacLaurin approximation.

## 5.5 Total Partition Function

The total partition function then becomes at the high temperature limit of the harmonic-oscillator rigid rotor approximation,

$$q = q_{trans} \ q_{rot} \ q_{vib} \ q_{nucl} \ q_{elec}$$
$$= \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V \frac{8\pi^2 IkT}{\sigma h^2} \frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}} \omega_{e1} e^{D_e/kT}.$$

This equation ignores the nuclear partition function.

*Note:* In cases where the ground electronic state is not a $\Sigma$ state, the electronic and nuclear angular momentum must be coupled. At high temperatures compared to $\Theta_r$, they can still be decoupled, however. This means that for all but low temperatures for molecules like NO the previous approach would work.

# Chapter 6

# Classical Mechanics

## 6.1 Formulation of the Classical Partition Function

Quantum mechanics approaches classical mechanics when quantum numbers become sufficiently high. This occurs at relatively high $T$ for a given quantum quantity. This means for many purposes we can begin our derivation from a classical mechanics standpoint and above a certain threshold quantity we achieve accurate results. For instance the translation quantum number at room temperature, $n \approx 10^8$, thus a classical mechanical approximation is very accurate. However, at the same conditions the vibrational quantum number is too low to achieve accurate results using a classical approach.

### 6.1.1 Molecular Partition Function

We know for a quantum mechanical derivation of molecular partition functions we arrive at

$$q_p = \sum_{j \in J} e^{-\beta \mathcal{H}_p},$$

for a particular separable mode of energy $p$. Hence, we assume that for a classical system we take the argument of the summation and integrate over accessible energy levels,

$$q_{p,class} = \int_{\mathcal{H}_p} e^{-\beta \mathcal{H}_p} \mathrm{d}\mathcal{H}_p.$$

The whole molecular partition function is then,

$$q_{class} = \int_{\mathcal{H}} e^{-\beta \mathcal{H}} \mathrm{d}\mathcal{H}$$
$$= \int \cdots \int e^{-\beta \mathcal{H}(\vec{p},\vec{q})} \mathrm{d}\vec{p}\mathrm{d}\vec{q},$$

where the second line takes the Hamiltonian to be a function of coordinates $\vec{q}$ and conjugate momenta $\vec{p}$. The dimensionality of the vectors $q$ and $p$ is simply the dimensionality of the molecule or the number of degrees of freedom that must be satisfied to fully describe the molecule.

**Translational Partition Function**

We know classically the energy of translation is

$$\mathcal{H} = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2).$$

Then, the translational partition function is,

$$q_{trans} = \int \cdots \int \exp\left(-\frac{\beta(p_x^2 + p_y^2 + p_z^2)}{2m}\right) \mathrm{d}p_x \mathrm{d}p_y \mathrm{d}p_z \mathrm{d}x \mathrm{d}y \mathrm{d}z$$

$$= V \iiint \exp\left(-\frac{\beta(p_x^2 + p_y^2 + p_z^2)}{2m}\right) \mathrm{d}p_x \mathrm{d}p_y \mathrm{d}p_z$$

$$= V \left(\int_{-\infty}^{\infty} e^{-\frac{\beta p^2}{2m}} \mathrm{d}p\right)^3$$

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

$$= V(2\pi mkT)^{3/2}.$$

$V$ comes from the lack of spacial dependence so the volume integral evaluates to the volume. The last two lines come from the error function. When we compare this to the classical approximation made in chapter 5,

$$V\left(\frac{2\pi mkT}{h^2}\right)^{3/2},$$

we find that a factor of $h^{-3}$ is missing.

**Rotational Partition Function**

For a classical rigid rotor the Hamiltonian is,

$$\mathcal{H} = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right).$$

The partition function is then,

$$q_{rot} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{2\pi} \int_0^{\pi} e^{-\beta\mathcal{H}} \mathrm{d}p_\theta \mathrm{d}p_\phi \mathrm{d}\phi \mathrm{d}\theta$$

$$= 2\pi \int_{-\infty}^{\infty} e^{-\beta p_\theta^2/2I} \mathrm{d}p_\theta \int_{-\infty}^{\infty} \int_0^{\pi} e^{-\beta p_\phi/\sin^2\theta} \mathrm{d}p_\phi \mathrm{d}\theta.$$

Note that the first argument of the integral is another error function so we can further simplify to,

$$q_{rot} = 2\pi \cdot \sqrt{2\pi IkT} \int_{-\infty}^{\infty} \int_0^{\pi} e^{-\beta p_\phi/\sin^2\theta} \mathrm{d}p_\phi \mathrm{d}\theta.$$

From here the last two integrals must be carried out. I am not currently sure how to do them though. The answer becomes,

$$q_{rot} = 8\pi^2 IkT,$$

however. Again notice that a factor of $h^{-2}$ is missing from the partition function.

**Vibrational Partition Function**

For a harmonic oscillator the Hamiltonian is,

$$\mathcal{H} = \frac{p^2}{2\mu} + \frac{k}{2}x^2,$$

where the first term captures the kinetic energy and the second potential. Then, $q_{vib}$ is,

$$
\begin{aligned}
q_{vib} &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\left(-\beta \frac{p^2}{2\mu} + \frac{k}{2}x^2\right) \mathrm{d}x \mathrm{d}p \\
&= \int_{-\infty}^{\infty} e^{-\beta p^2/2\mu} \mathrm{d}p \int_{-\infty}^{\infty} e^{-\beta k x^2/2} \mathrm{d}x \\
&= (2\mu\pi k_b T)^{1/2} \left(\frac{2\pi k_b T}{k}\right)^{1/2} \\
&= \frac{k_b T}{\nu}, \text{ where } \nu = \left(\frac{k}{4\pi^2\mu}\right)^{1/2}.
\end{aligned}
$$

Note once again this integral was done using the error function and that this is off by a factor of $h$.

**Adding Planck's Constant**

For each of the molecular partition functions we have examined thus far, the final result is off by a factor of $h^s$ where $s$ is the dimension of $\vec{p}$ or $\vec{q}$. From this we hypothesis,

$$q = \sum_{j \in J} e^{-\beta\mathcal{H}} \rightarrow \frac{1}{h^s} \int \cdots \int e^{-\beta\mathcal{H}} \prod_{j=1}^{s} \mathrm{d}p_j \mathrm{d}q_j.$$

### 6.1.2   Ensemble Partition Function

Taking the high temperature limit of the ensemble partition function for noniteracting molecules,

$$\mathcal{Q} = \frac{q^N}{N!},$$

we apply the classical molecular partition function to arrive at,

$$
\begin{aligned}
\mathcal{Q} &= \frac{1}{N!} \prod_{j=1}^{N} \left(\frac{1}{h^s} \int \cdots \int e^{-\beta\mathcal{H}_j} \prod_{i=1}^{s} \mathrm{d}p_{ji} \mathrm{d}q_{ji}\right). \\
&= \frac{1}{h^{sN} N!} \prod_{j=1}^{N} \left(\int \cdots \int e^{-\beta\mathcal{H}_j} \prod_{i=1}^{s} \mathrm{d}p_{ji} \mathrm{d}q_{ji}\right).
\end{aligned}
$$

To produce the standard formulation of the classical partition function, we re-label the indices $ji \to k$ so that $k = (j-1)s + i$. That is $k \in [0, s]$ represents the former indices $1i$ or the position and momenta of the first particle. Doing this allows us to simplify the equation as,

$$Q = \frac{1}{h^{sN}N!} \int \cdots \int e^{-\beta \sum_j \mathcal{H}_j} \prod_{k=1}^{sN} \mathrm{d}p_k \mathrm{d}q_k$$

$$= \frac{1}{h^{sN}N!} \int \cdots \int e^{-\beta \mathcal{H}} \prod_{k=1}^{sN} \mathrm{d}p_k \mathrm{d}q_k.$$

The Hamiltonian in the last line is the many body Hamiltonian not to be confused with a molecular or sub-molecular Hamiltonian. This is the correct form of the classical limit even though we assumed noninteracting molecules and merely postulated the form from an observation of the quantum derivation.

Examining a monatomic gas with a Hamiltonian of,

$$\mathcal{H} = \frac{1}{2m} \sum_{j=1}^{N} (p_x^2 + p_y^2 + p_z^2) + U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N),$$

where $\vec{r}_i$ is the position vector of particle $i$. Then taking the momentum integrals (using the error function), we get

$$Q_{class} = \frac{1}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{3N/2} Z_N,$$

where $Z_N$ is

$$Z_N = \int_V e^{-\beta U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)} \mathrm{d}\vec{r}_1 \mathrm{d}\vec{r}_2 \cdots \mathrm{d}\vec{r}_N.$$

$Z_N$ has a special name, *the classical configuration integral*. This integral encompasses all the intermolecular interactions present in a system.

### 6.1.3  Hybrid Partition Functions

When some degrees of freedom can be treated classically and others must be treated quantumly, if the Hamiltonian is separable in those degrees of freedom, so is the partition function into a classical and quantum part.

$$\mathcal{H} = \mathcal{H}_{class} + \mathcal{H}_{quant}$$
$$Q = Q_{class} Q_{quant}$$
$$= \frac{Q_{quant}}{h^{sN}N!} \int e^{-\beta \mathcal{H}_{class}} \mathrm{d}\vec{p}_{class} \mathrm{d}\vec{q}_{class}.$$

Similarly, if the molecular Hamiltonian is separable we have,

$$\mathcal{H} = \mathcal{H}_{class} + \mathcal{H}_{quant}$$
$$q = q_{class} q_{quant}$$
$$= \frac{q_{quant}}{h^s} \int e^{-\beta \mathcal{H}_{class}} \mathrm{d}\vec{p}_{class} \mathrm{d}\vec{q}_{class}.$$

## 6.2   Phase Space and the Liouville Equation

### 6.2.1   Defining of Phase Space and Density of States

We take a system of $N$ particles, where each particle has $s$ degrees of freedom, that is $s$ coordinates can uniquely define the particle. To complete the description of the classical system we also need to define $s$ conjugate momenta that correspond to the $s$ coordinates. The system is then uniquely defined by $l = sN$ coordinates and conjugate momenta. The total system then consists of $2l$ values.

Having an uniquely defined classical system, we now have motivation to define a phase space that projects the classical system into a new dynamical space which we will call the phase space. We project the classical system to a subset of $\mathbb{R}^{2l}$ which works to a prism of $2l$ dimensional Euclidean space where the extent of each dimension is the physical limits of the system. Each system at a specified time is then a point in this space. This space is the *phase space* and those points are *phase points*.

For a given phase point, its past and future is uniquely defined by the laws of motion and the current position in phase space. We postulate that trajectories are continuous which for a Hamiltonian system is true since

$$\dot{q}_j = \frac{\partial \mathcal{H}}{\partial p_j} \text{ and } \dot{p}_j = -\frac{\partial \mathcal{H}}{\partial q_j} \text{ for } j \in 2l.$$

Thus, trajectories in this frame work are uniquely defined just like phase points. This means that the evolution of $q$ and $p$ can be defined as some function of $t$.

We now show the preservation of density on a particular subset of the phase space. Using the microcanonical ensemble conservation of $N, V, E$, we define a mapping $M : P \to \Omega$, where $P$ is the phase space and $\Omega$ is the subset defined by $\{(x_i)_1^{2l} : (x_i)_1^{2l} \sim N, V, E\}$ that is the set of points that correspond to a particular $N, V, E$. This is an energy "surface" of a specified number and volume. We let all $X \in \Omega$ be occupied. That is all states are equally likely, this is the classical meaning of the *postulate of equal a priori probabilities*. This also suggests that each subdomain of $\Omega$ is equally dense since if this was not the case then particular regions of the microcanonical ensemble would be favored. However, it is important to note, that this **does not imply uniform density in** $P$.

### 6.2.2   Deriving the Louiville Equation

To begin with deriving the Louivile equation, we first create a function $f$ that gives the infinitesimal density around a phase point. We then have

$$\rho = f(p(t), q(t))\mathrm{d}p\mathrm{d}q.$$

If we integrate $f$ over the entire domain we retrieve $\mathcal{A}$,

$$\mathcal{A} = \int \cdots \int f(p(t), q(t))\mathrm{d}p\mathrm{d}q.$$

Any property averaged over all systems is

$$\overline{\phi} = \frac{\int \cdots \int \phi(p(t), q(t)) f(p(t), q(t)) \mathrm{d}p \mathrm{d}q}{\int \cdots \int f(p(t), q(t)) \mathrm{d}p \mathrm{d}q}$$

$$\overline{\phi} = \frac{\int \cdots \int \phi(p(t), q(t)) f(p(t), q(t)) \mathrm{d}p \mathrm{d}q}{\mathcal{A}}.$$

Gibb's postulate was originally formulated by saying this average corresponds to thermodynamical observed variables.

We now turn our attention to the flux of phase points into and out of an arbitrary volume about a point $X \in P$. We will prefix quantities in this volume with $\delta$. The instantaneous number of phase points in $\delta V$ is given by,

$$\delta N = f(p(t), q(t)) \delta p_1 \delta q_1 \delta p_2 \cdots \delta q_l \delta p_l.$$

This is just taking $f$ at $X$ and smearing it over the volume $\delta V$. To find the total flux we have to consider $2l$ dimensions. However, each dimension is equivalent in phase space, i.e. momenta and position are not treated differently. Therefore, we look at the dimension $q_1$ and generalize the results. The net flux in the $q_1$ dimension is given by the difference of the individual fluxes through the orthogonal hyper-surfaces defined by $q_1$ and $q_1 + \delta q_1$. The flux through first face is given by,

$$f(q_1, \ldots, q_l, p_1, \ldots, p_l) \dot{q}_1 \delta p_1 \cdots \delta p_l \delta q_1 \cdots \delta q_l.$$

Mathematically, this is taking the number of particles per $\delta q_1$ or a linear density as can be seen by,

$$\frac{\delta N}{\delta q_1} = f(q_1, \ldots, q_l, p_1, \ldots, p_l) \delta p_1 \cdots \delta p_l \delta q_2 \cdots \delta q_l,$$

and multiplying it by the "velocity" in the normal direction to the face $\partial q_1 / \partial t$. This is analogous to a flux taken in real space. Likewise, the flux at the face defined by $q_1 + \delta q_1$ is given by,

$$f(q_1 + \delta q_1, \ldots, q_l, p_1, \ldots, p_l) \dot{q}_1 (q_1 + \delta q_1, q_2, \ldots, q_l, p_1, \ldots, p_l) \delta p_1 \cdots \delta p_l \delta q_2 \cdots \delta q_l.$$

Taking a Taylor expansion around $q_1$ we find the flux at $\delta q_1$ is approximately,

$$\left( f_{q_1} + \left( \frac{\partial f}{\partial q_1} \right)_{q_1} \delta q_1 \right) \left( (\dot{q}_1)_{q_1} + \left( \frac{\partial \dot{q}_1}{\partial q_1} \right)_{q_1} \right) \delta p_1 \cdots \delta p_l \delta q_2 \cdots \delta q_l$$

where we have discarded all higher order terms. If we expand out the terms in the parenthesis we have,

$$f_{q_1} (\dot{q}_1)_{q_1} + \left( \frac{\partial f}{\partial q_1} \right)_{q_1} (\dot{q}_1)_{q_1} + f_{q_1} \left( \frac{\partial \dot{q}_1}{\partial q_1} \right)_{q_1} \delta q_1 + \left( \frac{\partial f}{\partial q_1} \right)_{q_1} \left( \frac{\partial \dot{q}_1}{\partial q_1} \right)_{q_1} \delta q_1^2.$$

Noting again that we will ignore all high order terms, $\delta q_1^2$ is sufficiently small to ignore it. Then if we take the difference between the fluxes at the two faces we have,

$$-\left( f_{q_1} \left( \frac{\partial \dot{q}_1}{\partial q_1} \right)_{q_1} + (\dot{q}_1)_{q_1} \left( \frac{\partial f}{\partial q_1} \right)_{q_1} \right) \delta p_1 \cdots \delta p_l \delta q_1 \cdots \delta q_l.$$

Likewise, for $p_1$

$$-\left( f_{p_1} \left( \frac{\partial \dot{p}_1}{\partial p_1} \right)_{p_1} + (\dot{p}_1)_{p_1} \left( \frac{\partial f}{\partial p_1} \right)_{p_1} \right) \delta p_1 \cdots \delta p_l \delta p_1 \cdots \delta p_l.$$

Here, we recall that there are a total of $2l$ dimensions to analyze the flux over $l$ for momentum and $l$ for position. The total change in number in a instance of time is,

$$-\sum_{i=1}^{l} \left( f_{p_1} \left( \frac{\partial \dot{p}_1}{\partial p_1} \right)_{p_1} + (\dot{p}_1)_{p_1} \left( \frac{\partial f}{\partial p_1} \right)_{p_1} + f_{q_1} \left( \frac{\partial \dot{q}_1}{\partial q_1} \right)_{q_1} + (\dot{q}_1)_{q_1} \left( \frac{\partial f}{\partial q_1} \right)_{q_1} \right) \delta p_1 \cdots \delta p_l \delta p_1 \cdots \delta p_l.$$

The expression is equivalent to,

$$\frac{\partial \delta N}{\partial t}.$$

If we divide by the volume element we get the partial derivative of the density $f$ w.r.t. time. We can further simplify this by noting that

$$\dot{q}_j = \frac{\partial \mathcal{H}}{\partial p_j} \text{ and } \dot{p}_j = -\frac{\partial \mathcal{H}}{\partial q_j}.$$

This means that the derivatives of $\dot{q}_i$ and $\dot{p}_i$ are mixed partials of the Hamiltonian. Since mixed partials are equivalent and the two differ in signs, they cancel leaving,

$$\frac{\partial f}{\partial t} = -\sum_{i=1}^{l} \left( (\dot{p}_1)_{p_1} \left( \frac{\partial f}{\partial p_1} \right)_{p_1} + (\dot{q}_1)_{q_1} \left( \frac{\partial f}{\partial q_1} \right)_{q_1} \right).$$

This is the Louville equation which looks very much like a statement of the conservation of mass because it is the equivalent in phase space. Another common form of the Louville equation given in terms of the Hamiltonian is,

$$\frac{\partial f}{\partial t} = -\sum_{i=1}^{l} \left( \frac{\partial \mathcal{H}}{\partial p_j} \frac{\partial f}{\partial q_j} - \frac{\partial \mathcal{H}}{\partial q_j} \frac{\partial f}{\partial p_j} \right).$$

The last form just follows from the definition of the partials of the Hamiltonian.

### 6.2.3 The Conservation of Extension and Incompressibility

By moving the previous equation to one side we get an expression equal to 0,

$$\frac{\partial f}{\partial t} + \sum_{i=1}^{l} \left( (\dot{p}_1)_{p_1} \left( \frac{\partial f}{\partial p_1} \right)_{p_1} + (\dot{q}_1)_{q_1} \left( \frac{\partial f}{\partial q_1} \right)_{q_1} \right) = 0.$$

We should note though as $f = f(\vec{p}, \vec{q}, t)$ the left hand size is the total derivative, that is,

$$\frac{\mathrm{d}f}{\mathrm{d}t} = 0.$$

To put this into words, the local environment of a phase point at any time $t$ compared to an earlier or later time $t_0$ is equally dense. Another way to phrase this is that the phase space behaves as an incompressible fluid.

Furthermore, if we take the volume element around a phase point $X$ at time $t_0$, for time $t_0 + t$ the density of the volume element must be the same. However, no point can cross the boundary of this volume because to do so two trajectories with different intial conditions would have to converge at the time $t_0 + t$. Since each trajectory is unique in phase space, this cannot happen. Since both number and density of the volume element are conserved, then, volume must be conserved as well. This property is called *conservation of extension in phase space*, or,

$$\delta\vec{p}\,\delta\vec{q} = \delta\vec{p}_0\,\delta\vec{q}_0.$$

Mathematically this can be shown by taking the Jacobian from $(\vec{p}, \vec{q})$ to $(\vec{p}_0, \vec{q}_0)$ and proving that is is unity. From this theorem, an important corollary can be drawn, namely the equivalence of different coordinate systems. Any two sets of coordinates and conjugate momenta that describe a system in phase space equally well, have equivalent volume elements.

if these are two coordiante systems in phase space,

$q_1, q_2, \ldots, q_{3n}, p_1, p_2, \ldots, p_{3n}$
$Q_1, Q_2, \ldots, Q_{3n}, P_1, P_2, \ldots, P_{3n}$
then,
$\mathrm{d}q_1, \mathrm{d}q_2, \ldots, \mathrm{d}q_{3n}, \mathrm{d}p_1, \mathrm{d}p_2, \ldots, \mathrm{d}p_{3n} = \mathrm{d}Q_1, \mathrm{d}Q_2, \ldots, \mathrm{d}Q_{3n}, \mathrm{d}P_1, \mathrm{d}P_2, \ldots, \mathrm{d}P_{3n}.$

## 6.3 Equipartition of Energy

In our previous classical analysis of the average energy contributions by different molecular modes of energy, the energy contribution of classical modes was always $kT/2$. We now show for all Hamiltonian's that can be written as

$$\mathcal{H} = \sum_{j=1}^{m} a_j p_j^2 + \sum_{j=1}^{n} b_j q_j^2 + \mathcal{H}(p_{m+1}, \ldots, p_s, q_{n+1}, \ldots, q_s),$$

where $a_j$ and $b_j$ all quadratic contributions contribute $kT/2$ to the energy.

First we note that for the separable Hamiltonian, the partition function is also separable,

$$q = \frac{1}{h^s} \int \cdots \int e^{-\beta(\sum_{j=1}^m \mathcal{H}_{p_j} + \sum_{j=1}^n \mathcal{H}_{q_j} + \mathcal{H}_{else})}$$

$$= \frac{1}{h^s} \prod_{j=1}^m \int p_j e^{-\beta \mathcal{H}_{p_j}} dp_j \prod_{j=1}^n \int_{q_j} e^{-\beta H_{q_j}} dq_j \int \cdots \int e^{-\beta \mathcal{H}_{else}} dq_{n+1} \ldots dq_s dp_{m+1} \ldots dp_s$$

$$= \prod_{j=1}^n q_{q_j} \prod_{j=1}^m q_{p_j} \cdot q_{else}.$$

Thus, for a particular energy mode in the conjugate momenta $p_i \quad 0 < i \le m$, the average energy in that mode is

$$\langle \mathcal{H}_i \rangle = \frac{\int \cdots \int \mathcal{H}_i e^{-\beta \mathcal{H}}}{q}$$

$$= \frac{\prod_{j=1}^n q_{q_j} \prod_{j=1, \; j \neq i}^m q_{p_j} \cdot q_{else} \int \mathcal{H}_i e^{-\beta \mathcal{H}_i} dp_i}{\prod_{j=1}^n q_{q_j} \prod_{j=1}^m q_{p_j} \cdot q_{else}}$$

$$= \frac{\int \mathcal{H}_i e^{-\beta \mathcal{H}_i} dp_i}{q_{p_i}}.$$

From here we can use integration by parts to determine $\langle \mathcal{H}_i \rangle$,

$$\langle \mathcal{H}_i \rangle = \frac{1}{q_{p_i}} \int a_j p_j^2 e^{-\beta \mathcal{H}_i}$$

$$\text{Let,} \; u = -\frac{p_i kT}{2} \qquad du = \frac{kT}{2} dp_i$$

$$dv = -\frac{a_j p_j}{kT} e^{-\beta p_j^2/kT} dp_j \qquad v = e^{-a_j p_j^2/kT}$$

$$= \frac{1}{q_{p_i}} \left( \left[ -\frac{p_i kT}{2} e^{-a_j p_j^2/kT} \right]_\alpha^\delta + \frac{kT}{2} \int_\alpha^\delta e^{-a_j p_j^2/kT} dp_i \right).$$

An important aside for momentum $[\alpha, \delta)$ represent $[0, \infty)$, but for coordinates can vary but some notable examples are $[0, L]$ or $[-L/2, L/2]$ where $L$ is the length of that dimension. In other words, either $q_j = 0$ or $\mathcal{H}_j \to \infty$ at the two limits of integration. The second is due to the potential at the wall being infinite. Therefore, in both cases of momentum and position, the limits of integration make the first term above zero. Then it is easy to see,

$$\langle \mathcal{H}_i \rangle = \frac{1}{q_{p_i}} \left( \frac{kT}{2} \int_\alpha^\delta e^{-a_j p_j^2/kT} dp_i \right)$$

$$= \frac{kT q_{p_i}}{2 q_{p_i}}$$

$$= \frac{kT}{2}.$$

This result also holds when $a_j$ or $b_j$ is a function of a different variable.

# Chapter 7

# Polyatomic Partition Function

## 7.1 Form of Polyatomic Partition Function

With the knowledge of appropriateness to treat particular degrees of freedom classically, we can approach the topic of polyatomic molecule using an suitable combination of classical and quantum mechanics. Of course the full quantum mechanical solution will be strictly more accurate, but not necessarily usefully more accurate.

### 7.1.1 Approximations

In order to derive the vibrational and electronic modes, the Born-Oppenheimer approximation is necessary. In doing so we wish to arrive at a description of the electronic potential in as a function of a currently unknown number of variables. To fully describe a polyatomic molecule's position $3n$ coordinates are needed, where $n$ is the number of atoms in the molecule. 3 coordinates can describe the center of mass of the particle. 2 ($\theta$ and $\phi$) or 3 ($\theta$, $\phi$, and $\psi$) coordinates uniquely specify the rotation of a rigid linear and non-linear body respectively. This leaves $3n - 5$ or $3n - 6$ degrees of freedom internal to the molecule. Thus, the internal motion of the molecule occurs in a potential energy landscape of $3n - 5$ or $3n - 6$ dimensions.

Furthermore, in order to deal with vibrational and rotational energy modes separately, we will make the rigid-rotor harmonic oscillator approximation again.

### 7.1.2 Translational, Electric, and Nuclear Partition Functions

The translational partition function is identical to the previous cases except that we must be careful to define translation as the movement of the center of mass of the particle. Therefore, the translational partition function is

$$q_{trans} = \left( \frac{2\pi mkT}{h^3} \right) V. \tag{7.1}$$

The electronic partition function is also identical. We set the energy zero to the energy where all atoms are separated in their ground state, in other words the ground state is at an energy, $-D_e$. The partition function is then,

$$q_{elect} = \omega_{e1} e^{D_e/kT}.$$

We ignore any state other than the ground state for nuclei and set the nuclear partition function, $q_{nucl} = 1$.

## 7.2 Vibrational Partition Function

Given the previous analysis of the potential energy field of the nuclei of the molecule, the nuclei vibrate in $(3n - 5)$ or $(3n - 6)$ dimensions. These relative

dimensions will involve combinations of the nuclei's positions such that in the squaring of terms leave cross terms. An example would be the combination,

$$(x_2 - x_1)^2 = x_2^2 - 2x_1 x_2 + x_1^2.$$

The square comes from the assumption that force is roughly linear with small deviations from the equilibrium positions this is the harmonic oscillator assumption. Luckily using a method called *normal coordinate analysis* can determine a set of coordinates $\{Q_i\}$ such that each harmonic oscillator is devoid of cross terms. The Hamiltonian is thus

$$\mathcal{H} = K + U$$

$$= -\sum_{j=1}^{\alpha} \frac{\hbar^2}{2\mu_j} \frac{\partial^2}{\partial Q_j^2} + \sum_{j=1}^{\alpha} \frac{k_j}{2} Q_{j^2} \quad \alpha = 3n - 5 \text{ or } 3n - 6$$

where $\mu_j$ and $k_j$ are effective masses and force constants for these normal coordinates respectively. In solving the above Hamiltonian, the total energy becomes,

$$\varepsilon = \sum_{j=1}^{\alpha} \sum_{i=0}^{\infty} (n_{j,i} + \frac{1}{2})h\nu_j \quad \text{for} \quad n_{j,i} = 0, 1, 2, \ldots$$

where,

$$\nu_j = \frac{1}{2\pi} \left( \frac{k_j}{\mu_j} \right)^{1/2}.$$

The normal coordinates come from analyzing the potential modes of vibration in a molecular system. Each independent mode $M$ has a corresponding coordinate $Q$ that denotes deviation from the equilibrium position inherent to the mode. For $CO_2$, an example of normal coordinate analysis can be found, see Fig 7.1. With the normal coordinates then, the partition function is
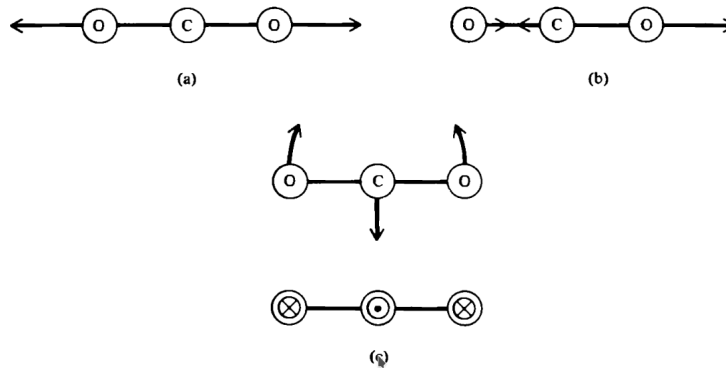


Figure 7.1: $CO_2$ normal coordinate analysis

$$q_{vib} = \prod_{j=1}^{\alpha} \frac{e^{-\theta_{\nu_j}/2T}}{(1 - e^{-\theta_{\nu_j}/T})}.$$

The energy and heat capacity are,

$$E_{vib} = Nk \sum_{j=1}^{\alpha} \left( \frac{\theta_{\nu_j}}{2} + \frac{\theta_{\nu_j} e^{-\theta_{\nu_j}/2T}}{1 - e^{-\theta_{\nu_j}/T}} \right)$$

$$C_{v,vib} = Nk \sum_{j=1}^{\alpha} \left[ \left( \frac{\theta_{\nu_j}}{T} \right)^2 \frac{e^{-\theta_{\nu_j}/2T}}{1 - e^{-\theta_{\nu_j}/T}} \cdot \right]$$

## 7.3 Rotational Partition Function

The rotational partition function depends a lot on the molecules inherent symmetries. A theorem of rigid body motion which is the mode of energy in consideration here, is always definable on 3 orthogonal principle axis where the inertia tensor becomes diagonal. Each entry in the tensor is defined by

$$I_{ij} = \sum_{l=1}^{n} m_l (x_{l,i} - x_{i,cm})(x_{l,j} - x_{j,cm}).$$

So the theorem states there are orthogonal coordinate axes that make $I_{ij} = 0$ for $i \neq j$.

$$\begin{bmatrix} I_{xx} & 0 & 0 \\ 0 & I_{yy} & 0 \\ 0 & 0 & I_{zz} \end{bmatrix}.$$

From the diagaonalization of the tensor $\bar{I}$ 4 cases exist: 3 identical $I$'s, 2 equal $I$'s, 3 unique $I$'s, and 2 identical nonzero $I$'s and 1 zero $I$. These different cases are known as spherical top, symmetric top, asymmetric top, and linear.

As a brief aside, a nomenclature for these 3 values have the subscripts as $I_a, I_b, I_c$ and a convenient rescaling of the moments is given by,

$$(\overline{A}, \overline{B}, \overline{C}) = \frac{h}{8\pi I_{a,b,c} c}.$$

### 7.3.1 Linear Molecules

For linear molecules, the problem is the same as the diatomic case. The moment of inertia is given by $I = \sum_{i=1}^{n} m_i r_i^2$, where $r_i^2$ is the distance from the center of mass. The final partition function is the same as before

$$q_{rot} = \frac{8\pi^2 I k T}{\sigma h^2} = \frac{T}{\sigma \Theta_r}.$$

Once again $\sigma$ is the symmetry number which represents the number of indistinguishable configurations a molecule has. The purpose of $\sigma$ is important to mention here. Its meaning classically comes from the number of different equivalent arrangements of the molecule that are identical over specific rotations. In

other words, The number of configurations of the atoms that make the same structure will have rotations which show them to be identical. This prevents their over-counting. In terms of quantum mechanics, the particles are indistinguishable so the symmetry number is immediately required.

## 7.3.2 Non-Linear Molecules

Non-linear rigid bodies have at least two different diagonal moments of inertia. The principle axis are usually located on the axis of symmetry and highly symmetric molecules usually have more of their moment of inertia components the same.

### Spherical Tops

The case of the spherical top applies to molecules like $CH_4$ and $CCl_4$ and other highly symmetric molecules. The energy levels of this system are

$$\varepsilon_j = \frac{J(J+1)\hbar^2}{2I} \qquad J = 0, 1, 2, \ldots$$

with degeneracy

$$\omega_j = (2J+1)^2.$$

The taking the classical approximation $q_{rot}$ is given by

$$q_{rot} = \frac{1}{\sigma} \int_0^\infty (2J+1)^2 e^{-J(J+1)\hbar^2/2kT} \mathrm{d}J.$$

In addition, at large values of $J$ the $(J+1) \approx J$, so

$$q_{rot} = \frac{1}{\sigma} \int_0^\infty 4J^2 e^{-J^2\hbar^2/2IkT} \mathrm{d}J$$

Let,

$$u = 2J \qquad \text{and} \quad \mathrm{d}v = 2Je^{-J^2\hbar^2/2kT}$$

$$\mathrm{d}u = 2\mathrm{d}J \qquad \text{and} \quad v = \frac{4IkT}{\hbar^2}e^{-J^2\hbar^2/2IkT},$$

Here, I note that the integral is directly analogous to that used to prove the law of equipartition derived in Section 6.3. Then, the final solution is

$$q_{rot} = \frac{1}{\sigma}\left(\frac{8\pi^{2/3}IkT}{h^2}\right)^{3/2}.$$

Note that the 3/2 power comes from the constant of $v$ and the evaluation of $\int v \mathrm{d}u$ which provides 1 and 1/2 power respectively.

## Symmetric Tops

The symmetric top also has a analytical quantum mechanical solution. A theorem states that any rigid body with at least $n \geq 3$ fold axis of symmetry is at least a symmetric top. The energy levels are

$$\varepsilon_{JK} = \frac{\hbar^2}{2} \left( \frac{J(J+1)}{I_A} + K^2 \left[ \frac{1}{I_c} - \frac{1}{I_a} \right] \right)$$

$$J = 0, 1, 2, \ldots \text{ and } K = J, J-1, \ldots, -J$$

with degeneracy

$$\omega_{JK} = (2J+1).$$

$K$ represents the distribution of energy in the non symmetric axis. By definition then,

$$q_{rot} = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1) e^{-\alpha_A J(J+1)} \sum_{K=-J}^{J} e^{-(\alpha_C - \alpha_A)K^2},$$

with

$$\alpha_j = \frac{\hbar^2}{2I_j kT}.$$

The classical limit (integral) of this equation evaluates much the same as previously using the results of the error function as has been repeatedly done,

$$q_{rot} = \frac{\pi^{1/2}}{\sigma} \left( \frac{8\pi^2 I_A kT}{h^2} \right) \left( \frac{8\pi^2 I_C kT}{h^2} \right)^{1/2}.$$

## Asymmetric Tops

The case of asymmetric tops is only numerically solvable in quantum mechanics; thus, a fully classical approach is necessary to get a closed form partition function. The classical solution is of the same ilk as the other as one might expect,

$$q_{rot} = \frac{\pi^{1/2}}{\sigma} \left( \frac{8\pi^2 I_A kT}{h^2} \right)^{1/2} \left( \frac{8\pi^2 I_B kT}{h^2} \right)^{1/2} \left( \frac{8\pi^2 I_C kT}{h^2} \right)^{1/2}.$$

With rotational temperatures,

$$q_{rot} = \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3}{\Theta_A \Theta_B \Theta_C} \right).$$

## Hindered Rotation

If rotation around a particular bond — such as the carbon-carbon bond in ethane — causes a meaningful change in potential the rotation is hindered. Previously in this chapter, we have only considered molecules whose internal rotation occurs in a equa-potential field or internal rotation is unhindered (free).

When internal rotation is free, such motion does not contribute to the partition function. Taking the ethane example, such internal rotation must be taken into consideration when deriving the partition function. Let's use the potential energy of the rotation of the hydrogen in ethane as shown in Figure 7.2.
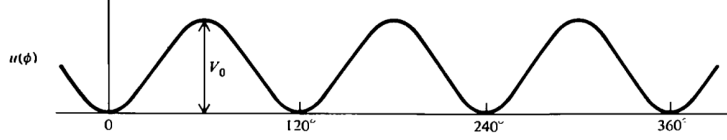


Figure 7.2: Generic hindered rotation potential field

At low temperatures where $kT \ll V_0$ the energy mode can be treated as a harmonic oscillator around a energy minimum. If $kT \gg V_0$ the problem rotation is free and a rigid rotor approximation is valid. However, when $kT \approx V_0$ a different approach must be taken. In this case, we need an analytical form of the potential, in this case $\frac{1}{2}V_0(1 - \cos 3\phi)$. The Schrödinger equation is difficult or impossible to solve analytically, but the eigenvalues of the function are known.

## 7.4   Thermodynamic Relations

Here I copy some general thermodynamic relations,

$$q = q_{trans}q_{rot}q_{vib}q_{elec}$$

$$= \left(\frac{2\pi mkT}{h^3}\right)^{3/2} V \cdot \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2}\left(\prod_{j=1}^{3n-6}\frac{e^{-\theta_{\nu_j}/2T}}{(1 - e^{-\theta_{\nu_j}/T})}\right)\omega_{e1}e^{D_o/kT}$$

$$\frac{-A}{NkT} = \ln\left(\frac{2\pi MkT}{h^2}\right)\frac{Ve}{N} + \ln\left[\frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2}\right]\sum_{j=1}^{3n-6}\left(\frac{\Theta_{\nu_j}}{2T} + \ln\left(1 - e^{-\Theta_{\nu_j}/T}\right)\right) + \frac{D_e}{kT} + \ln\omega_{e1}$$

$$\frac{E}{NkT} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{3n-6}\left(\frac{\Theta_{\nu_j}}{2T} + \frac{\Theta_{\nu_j}/T}{e^{\Theta_{\nu_j}/T} - 1}\right) - \frac{D_e}{kT}$$

$$\frac{C_v}{Nk} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{3n-6}\left(\left(\frac{\Theta_{\nu_j}}{T}\right) + \frac{e^{\Theta_{\nu_j}/T}}{e^{\Theta_{\nu_j}/T} - 1}\right)$$

$$\frac{S}{Nk} = \ln\left[\frac{2\pi MkT}{h^2}\right]^{3/2}\frac{Ve^{5/2}}{N} + \ln\left[\frac{\pi^{1/2}e^{3/2}}{\sigma}\left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2}\right]$$

$$+ \sum_{j=1}^{3n-6}\left(\left(\frac{\Theta_{\nu_j}/T}{e^{\Theta_{\nu_j}/T} - 1}\right) - \ln\left(1 - e^{-\Theta_{\nu_j}/T}\right)\right) + \ln\omega_{e1}$$

$$pV = kNT.$$

Notice that despite the more complicated molecular nature of polyatomic molecules, the ideal gas law still "pops" out. This is because the ideal gas law is a consequence of non interacting molecules or equivalently low density systems not the features of the particles themselves. The other properties are easily found from thermodynamic relationship that have been used previously.

Using these equations, entropy can be calculated more accurately than some experiments. However, discrepancies can exist. For instance, carbon monoxide has too weak a dipole moment to enforce the most energetically favorable arrangement at low temperatures, so the molecules lack the kinetic energy to rearrange but also are in a non-optimal arrangement. This kind of behavior is termed *residual* entropy.

# Chapter 8

# Chemical Equilibrium

Like other properties such as pressure, temperature, and free energy can be calculated from the partition function of a system, chemical equilibrium can be derived from them as well.

*Note:* that examples present in the book will not be reproduced because they are straight forward and just involve using the equations from Section 8.1 and those of the partition functions of different molecule types as previously derived.

## 8.1 Chemical Equilibrium in Terms of Partition Functions

We first note that chemical equilibrium in a reaction or phase change occurs when,

$$\mu_I = \mu_{II},$$

or when chemical potentials are equal between the products and reactants or between the two phases. This holds for multiple reactions and multiphase behavior as well. One can also derive the necessary relations from a free energy argument. Take an arbitrary homogeneous gas reaction,

$$\nu_A A + \nu_B B \leftrightarrow \nu_C C + \nu_D D.$$

We assume that the reaction is at equilibrium in a rigid thermostatted container. By definition of the canonical ensemble this means that the Helmholtz free energy is at a minimum. By the conservation of mass and the definition of equilibrium we know

$$\nu_C C + \nu_D D - \nu_A A - \nu_B B = 0.$$

Taking the definition of the Helmholtz free energy as,

$$dA = -SdT - pdV + \sum_j \mu_j dN_j,$$

and using the fact that we are at constant $T$ and $V$, we get

$$dA = \sum_j \mu_j dN_j = \left( \sum_j \nu_j \sigma_j \mu_j \right) d\lambda,$$

where $\sigma_j \nu_j d\lambda = dN_j$ with $\sigma_j$ being 1 for products and $-1$ for reactants. Since at equilibrium we are at a minimum with respect to $A$, we know that $\partial A / \partial \lambda$ must be zero, and

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

Now to put statistical mechanics back into it we need an expression for the partition function for the multicomponent system. If the systems is an ideal gas, the partition function of the system is just the multiplication of the

$$\mathcal{Q}_{tot} = \mathcal{Q}_{N_A} \mathcal{Q}_{N_B} \mathcal{Q}_{N_C} \mathcal{Q}_{N_D}$$
$$= \frac{q_A^{N_A}}{N_A!} \frac{q_B^{N_B}}{N_B!} \frac{q_C^{N_C}}{N_C!} \frac{q_D^{N_D}}{N_D!}.$$

Using the previously derived relation,

$$\mu_A = -kT \left( \frac{\partial \ln \mathcal{Q}}{\partial N_A} \right)_{N_j, V, T} = -kT \left( \partial \sum_i^{A,B,C,D} \ln \left[ \frac{q_i}{N_i!} \right] / \partial N_A \right) = -kT \left( \partial \ln \left( \frac{q_A}{N_A!} \right) / \partial N_A \right)$$

$$= -kT \partial (N_A \ln q_A - N_A \ln N_A + N_A) / \partial N_A = -kT \left( N_A \ln \left[ \frac{q_A}{N_A} \right] + N_A \right) / \partial N_A$$

$$= -kT \left( \ln \left[ \frac{q_A}{N_A} \right] - 1 + 1 \right)$$

$$= -kT \ln \left[ \frac{q_A}{N_A} \right].$$

The second to last line uses the product rule. This results states that the chemical potential of species A is only dependent on species A which is what one expects for an ideal gas. We know that

$$\sigma_j \nu_j \mu_j = -kT \sigma_j \nu_j \ln \left[ \frac{q_j}{N_j} \right] = \ln \left[ \frac{q_j}{N_j} \right]^{\sigma_j \nu_j}$$

$$\sum_j \sigma_j \nu_j \mu_j = \nu_D \mu_D + \nu_C \mu_C - \nu_A \mu_A - \nu_B \mu_B = 0$$

$$= \sum_j \sigma_j \nu_j \ln \left[ \frac{q_j}{N_j} \right] = \sum_j \ln \left[ \frac{q_j}{N_j} \right]^{\sigma_j \nu_j}$$

$$= \ln \left[ \left( \frac{q_D}{N_D} \right)^{\nu_D} \left( \frac{q_C}{N_C} \right)^{\nu_C} \left( \frac{N_B}{q_B} \right)^{\nu_B} \left( \frac{N_A}{q_A} \right)^{\nu_A} \right] = 0$$

$$= \ln \left[ \frac{q_D^{\nu_D} q_C^{\nu_C}}{q_B^{\nu_B} q_A^{\nu_A}} \right] + \ln \left[ \frac{N_B^{\nu_B} N_A^{\nu_A}}{N_D^{\nu_D} N_C^{\nu_C}} \right] = \ln \left[ \frac{q_D^{\nu_D} q_C^{\nu_C}}{q_B^{\nu_B} q_A^{\nu_A}} \right] - \ln \left[ \frac{N_D^{\nu_D} N_C^{\nu_C}}{N_B^{\nu_B} N_A^{\nu_A}} \right] = 0$$

$$\frac{q_D^{\nu_D} q_C^{\nu_C}}{q_B^{\nu_B} q_A^{\nu_A}} = \frac{N_D^{\nu_D} N_C^{\nu_C}}{N_B^{\nu_B} N_A^{\nu_A}}$$

For an ideal gas, the partition function is of the form $f(T)V$. Thus, a purely temperature dependent equilibrium constant $K_c(T)$ can be defined as

$$K_c(T) = \frac{\rho_D^{\nu_D} \rho_C^{\nu_C}}{\rho_B^{\nu_B} \rho_A^{\nu_A}} = \frac{(q_D/V)^{\nu_D} (q_C/V)^{\nu_C}}{(q_B/V)^{\nu_B} (q_A/V)^{\nu_A}}.$$

The ideal gas law $p_j = \rho_j kT$ can be used to derive an expression for a pressure based equilibrium constant $K_p(T)$,

$$K_p(T) = \frac{p_D^{\nu_D} p_C^{\nu_C}}{p_B^{\nu_B} p_A^{\nu_A}} = (kT)^{\sum_j \sigma_j \nu_j} K_c(T).$$

## 8.2 Thermodynamic Tables

Tables of experimentally determined thermodynamic properties exist when can give us the desired equilibrium constants. Taking the ideal gas relation,

$$\mu(T, p) = \mu_0(T) + kT \ln p.$$

Using the fact that $\sum_j \sigma_j \nu_j \mu_j = 0$, we have

$$\sum_j \sigma_j \nu_j kT \ln p_j + \sum_j \sigma_j \nu_j \mu_{0,j}(T) = 0$$

$$kT \ln K_p = -\Delta \mu_0.$$

Looking once more at the expression developed for $\mu$, in terms of $q$, we can put $\mu$ into terms of $(T, p)$.

$$\mu = -kT \ln \left[\frac{q}{N}\right] = -kT \ln \left[\frac{q}{V}\frac{V}{N}\right]$$

$$= -kT \ln \left[\frac{q}{V}\right] + kT \ln [\rho] = -kT \ln \left[\frac{q}{V}\right] + kT \ln \left[\frac{p}{kT}\right]$$

$$= -kT \ln \left[\frac{q}{V}kT\right] + kT \ln [p]$$

$$\mu_0(T) = -kT \ln \left[\frac{q}{V}kT\right].$$

Here one should note that the logarithm in the last line has units of pressure.

### 8.2.1 Zero of Energy

One important consideration when using thermodynamic tables is the zero of energy. Previously we have set the translational and rotational ground states to 0 energy, the vibrational zero point energy to be the bottom of the potential well, and the electronic zero to be the energy of complete atomic separation. Experimentally, the complete ground state is taken to be zero energy. This requires changing the electronic and vibrational partition functions from what we have previously derived.

We first take the electronic partition function,

$$q_{elec} = \omega_{e1} e^{-\varepsilon_{e1}/kT} + \omega_{e2} e^{-\varepsilon_{e2}/kT} + \cdots$$

Using the same convention that the zero energy is the electrically neutral separated atoms then,

$$\varepsilon_{e_2} = -D_e$$

$$\varepsilon_{e_2} = -D_e + \Delta \varepsilon_{12}$$

$$q_{elec} = \omega_{e1} e^{D_e/kT} + \omega_{e2} e^{D_e/kT} e^{-\Delta \varepsilon_{12}/kT} + \cdots$$

$$= e^{D_e/kT} \left(\omega_{e_1} + \omega_{e_2} e^{-\Delta \varepsilon_{12}/kT} + \cdots\right)$$

$$= e^{D_e/kT} q_{elec}^0.$$

By factoring out the $e^{D_o/kT}$, the partition function becomes a constant times the partition function with zero of energy the ground state as $\omega_{e_1}$ is multiplied by 1 or $e^0$. We can similarly take the vibrational partition function,

$$q_{vib} = \prod_j \frac{e^{-\Theta_{\nu_j}/2T}}{(1 - e^{-\Theta_{\nu_j}/2T})}, where \Theta_{\nu_j} = \frac{h\nu}{k}$$

and remove the part from the non-zero ground state. Here it is important to note from the derivation in Section 5.3 that the numerator comes from the $1/2$ term in the energy levels which is a result of having a nonzero ground state. Thus,

$$q_{vib} = e^{-\Theta_{\nu_j}/2T} \prod_j (1 - e^{-\Theta_{\nu_j}/2T}) = e^{-\Theta_{\nu_j}/2T} q_{vib}^0.$$

From these two equations we can redefine the molecular partition function as,

$$q = q_{trans}^0 q_{rot}^0 q_{vib}^0 q_{elec}^0 e^{(D_e - 1/2 \sum_j h\nu_j)/kT} = q_{trans}^0 q_{rot}^0 q_{vib}^0 q_{elec}^0 e^{D_o/kT}.$$

The substitution to $D_o$ is graphically explained in Figure 5.2. From the graphical argument and the definition of $D_o$, $-D_o$ can been seen to be the total ground state energy from our original convention. Thus, for any zero energy convention the partition function is

$$q = q^0 e^{-\varepsilon_0^0/kT}.$$

Substituting this into the equation for chemical potential we have,

$$\mu = -kT \ln \left[ \frac{q}{V} kT \right] + kT \ln [p]$$

$$= -kT \ln \left[ e^{-\varepsilon_0^0} \frac{q^0}{V} kT \right] + kT \ln [p]$$

$$\mu - \varepsilon_0^0 = -kT \ln \left[ \frac{q^0}{V} kT \right] + kT \ln [p].$$

An important fact here is that $\mu \to \varepsilon$ as $T \to 0$. If we treat $\mu - \varepsilon_0^0$ as the relative chemical potential, then it goes to 0 at $T \to 0$. Multiplying by Avogadro's number, we obtain,

$$G^0 - E_0^0 = -RT \ln \left[ \frac{q^0}{V} kT \right] + kT \ln [p].$$

This means that $E^0$ is the standard free energy at 0 K which means $G^0 - G_0^0$ is an equally appropriate choice. Likewise, since $H = E + pV$ and $p \to 0$ as $T \to 0$, then $H_0^0 = E_0^0$. Thus, these three notations are equivalent and possible. An important comment on convention is required to use the derived quantities above. An elements energy is considered 0 at 0 K if the element is in the same physical state that is stable at 25°C and 1 atm.

# Chapter 9

# Crystals

## 9.1 Degrees of Freedom in a Crystal

The degrees of freedom within a crystal are essentially all vibrations. To show this take a crystal composed of $N$ particles. Then, there are $3N$ coordinates that uniquely specify the crystal's configuration. Like the polyatomic molecule, 3 coordinates can describe the center of mass for translational motion, and 3 can describe the rotation of the crystal. Thus, $3N - 6$ describe the vibration of atoms around their equilibrium positions. Since at large $N$, $3N \approx 3N - 6$, the translational and rotational degrees of freedom can be safely ignored.

## 9.2 Derivation of the Partition Function

In the crystal we assume that the potential well each particle experiences is steep, so that deviations from the lattice sites are small. Because deviations are small, a Taylor's series expansion of the potential, $U$, around a deviation of 0, $\zeta = 0$, can be taken.

$$U(\zeta_1, \zeta_2, \ldots, \zeta_N) = U(0, 0, \ldots, 0) + \sum_{j=1}^{N} \left( \frac{\partial U}{\partial \zeta_j} \right)_0 \zeta_j + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \frac{\partial^2 U}{\partial \zeta_i \partial \zeta_j} \right)_0 \zeta_i \zeta_j + \cdots$$

As the first derivative at a local extrema is 0, this reduces to

$$U(\zeta_1, \zeta_2, \ldots, \zeta_N) \approx U(0, 0, \ldots, 0) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \frac{\partial^2 U}{\partial \zeta_i \partial \zeta_j} \right)_0 \zeta_i \zeta_j$$

$$\approx U(0, 0, \ldots, 0) + \frac{1}{2} \sum_{i,j}^{N} k_{ij} \zeta_i \zeta_j,$$

where $k_{ij}$ is the force constant for all pairs of particles. We can see then that $U(\vec{\zeta})$ is a quadratic function. In addition, $U(\vec{0})$ is not a function of displacement, but is a function of density. This occurs because the interatomic potential changes when the lattice spacing changes. One way to show this is by writing $U(\vec{0})$ as $U(\vec{0}; \rho)$. This system of equations is coupled, meaning the $i$-th and $j$-th terms are inseparable. However, just like the polyatomic case, the vibrational modes can be separated using normal coordinate analysis into $3N - 6$ independent harmonic oscillators. Taking the equation from Chapter 6,

$$\nu_j = \frac{1}{2\pi} \left( \frac{k_j}{\mu_j} \right)^{1/2},$$

we can generate a partition function ignoring the fact we do not know $k$ or $\mu$.

$$\mathcal{Q}(V/N, T) = e^{-U(\vec{0}; \rho)/kT} \prod_{j=1}^{3N-6} q_{vib,j}$$

Q is a function of the inverse of density because $k_j$ is related to $k_{ij}$ from the Taylor expansion, and the potential depends on the lattice spacing as does $U(\vec{0}; \rho)$. We have ignored the translational and rotational contribution since these are nearly meaningless in this case. Since the particles are restricted to a specific lattice site, the particles are in fact distinguishable and no factor of $\frac{1}{N!}$ needs to be introduced. $\mathcal{Q}$ can also be expanded as so,

$$\mathcal{Q} = \prod_{j=1}^{3N} \left( \frac{e^{-h\nu_j/2kT}}{1 - e^{-h\nu_j/kT}} \right) e^{-U(\vec{0};\rho)/kT}.$$

Taking the natural log,

$$\ln \mathcal{Q} = -\frac{-U(\vec{0};\rho)}{kT} + \sum j = 1^{3N} \left( \frac{-h\nu_j}{2kT} - \ln 1 - e^{-h\nu_j/kT} \right).$$

As $3N$ is large, the distribution of frequencies can be taken to be continuous. That means the summation can be substituted for an integral with a density of frequencies term added to ensure a correct weighting of frequencies.

$$\ln \mathcal{Q} = -\frac{-U(\vec{0};\rho)}{kT} + \int_0^\infty \left( \frac{-h\nu}{2kT} - \ln 1 - e^{-h\nu/kT} \right) \cdot g(\nu) \mathrm{d}\nu$$

$$\int_0^\infty g(\nu)\mathrm{d}\nu = 3N.$$

Thus if $g(\nu)$ is known, all thermodynamic properties of the crystal can be calculated. The specific heat formula is given to compare the Einstein, Debye, and phonon methods of looking at crystals,

$$C_v = k \int_0^\infty \frac{(h\nu/kT)^2 e^{-h\nu/kT} g(\nu)\mathrm{d}\nu}{(1 - e^{-h\nu/kT})^2}.$$

## 9.3 Einstein Crystal

The Einstein model of crystals assumes that all particles vibrate independently from each other and have identical local environments. This means they all vibrate at the same frequency $\nu$. Classically this would just lead to a constant heat capacity of $3Nk = 3R = 6cal/deg \cdot mole$. In fact, this relation is known as the law of Dulong and Petit and comes from the law of equipartition which states that each quadratic degree of freedom contributes $kcal/deg \cdot mole$ per atom. However, the D&P law only holds asymptotically at sufficiently high temperatures. At lower temperatures $C_v$ drops as $T^3$. What, Einstein did that was novel and provided an advance was to quantized the vibrational modes first which is of course correct since all energy is quantized.

For an Einstein crystal $g(\nu)$ is given by $3N\delta(\nu - \nu_E)$, where $\nu_E$ is the Einstein frequency of a crystal. The integral of the delta function is just the remainder

of the integrand evaluated at $\nu_E$. Then,

$$\ln \mathcal{Q} = -\frac{U(\vec{0}; \rho)}{kT} + \left(\frac{-h\nu_E}{2kT} - \ln 1 - e^{-h\nu_E/kT}\right),$$

and the specific heat is,

$$C_v = 3Nk\left(\frac{h\nu_E}{kT}\right)^2 \frac{e^{-h\nu_E/kT}}{(1 - e^{-h\nu_E/kT})^2}$$

$$= 3Nk\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{-\Theta_E/T}}{(1 - e^{-\Theta_E/T})^2}.$$

In the last equation, $\Theta_E = h\nu_E/k$ and is known as the Einstein temperature.

While Einstein's theory provided must further understanding about crystal behavior, it incorrectly predicts the low temperature behavior. The low temperature limit is,

$$C_v \to 3Nk\left(\frac{\Theta_E}{T}\right)^2 e^{-\Theta_E/T}.$$

## 9.4 Debye Crystal

The Debye view of a crystal assumes the entire crystal behaves as an elastic continuous body. This assumption allows for accurate treatment of the low frequency, large wavelength regime of a crystal's normal frequencies. In the limit of infinitely long wavelength's this approximation is exact. To analyze the frequencies then we must define the wave travelling through the continuum crystal. A wave function can be written as

$$u(r, t) = Ae^{i(\vec{k}\cdot\vec{r} - \omega t)},$$

with wave vector $\vec{k}$ of magnitude $\frac{2\pi}{\lambda}$ and frequency $\omega = 2\pi\nu$. The wave vector defines a direction and the frequency defines how quickly the phase changes. By adding another wave in direction $-k$, we can form a standing wave,

$$u = A(e^{i(\vec{k}\vec{r} - \omega t)} + e^{i(-\vec{k}\vec{r} - \omega t)})$$

$$= 2Ae^{i\vec{k}\vec{r}} \cos\omega t.$$

We need the imaginary component to vanish at the crstal edges to ensure the wave is standing. This can be accomplished by setting $k_{xi}L_{xi} = n_{xi}\pi$, or,

$$\vec{k} = \frac{\pi}{L}\vec{n}.$$

This just ensures that in every direction the vibration of the endpoints of the crystal go to zero. The magnitude of k is given by

$$|\vec{k}| = \left[\left(\frac{\pi}{L}\right)(n_x^2 + n_y^2 + n_z^2)^2\right]^{1/2}.$$

Frequency is just $\nu = \omega/|\vec{k}|$. The density of wave numbers can be taken in the same manner as the density of translational states of a molecule, so

$$R^2 = \left(\frac{kL}{\pi}\right)^2 = (n_x^2 + n_y^2 + n_z^2)^2$$

$$\phi(k) = \frac{1}{8}\frac{4}{3}\pi R^3 = \frac{\pi}{6}\left(\frac{kL}{\pi}\right)^3 = \frac{k^3 L^3}{6\pi^2}.$$

The method here takes the volume of one octant of a sphere of radius $R$. The density between $k$ and $k + \mathrm{d}k$ is then,

$$\delta(k)\mathrm{d}k = \frac{\mathrm{d}\phi}{\mathrm{d}k}\mathrm{d}k = \frac{L^3 k^2 \mathrm{d}k}{2\pi^2}.$$

Using $\nu = v/\lambda$ where $v$ is the velocity of propagation, and $\nu = vk/2\pi$ we have,

$$g(\nu)\mathrm{d}\nu = \frac{4\pi L^3 \nu^2}{v^3}\mathrm{d}\nu.$$

For every magnitude of $\vec{k}$, we can create two linearly independent transversal waves and one longitudinal wave. The speed of propagation for these two types of waves can be different and must be averaged. The final result is then,

$$g(\nu)\mathrm{d}\nu = 4\pi L^3 \nu^2 \left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\mathrm{d}\nu$$

$$= \frac{12\pi L^3 \nu^2}{v_0^3}.$$

In the last line $v_0$ represents the effective velocity of propagation in the medium. To ensure the proper nomralization of $g(\nu)$ a frequency $\nu_D$ is defined, called the Debye frequency, such that

$$\int_0^{\nu_D} g(\nu)\mathrm{d}\nu = 3N.$$

In terms of other quantities this makes $\nu_D$,

$$\nu_D = \left(\frac{3N}{4\pi L^3}\right)^{1/3} v_0.$$

Specific heat in the theory is then,

$$C_v = 9Nk\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2}\mathrm{d}x$$

$$\Theta_D = \frac{h\nu_D}{k}.$$

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**Correspondence of States**

We should note that in both the case for Einstein's and Debye's theories that heat capacity ends up being a function of temperature ratioed with some material specific constant. This means that if the curves for heat capacity is normalized with respect to $\Theta_D$ or $\Theta_E$ then all the curves are identical. This implies that the behavior of all crystals once normalized is identical. The general name for a result like this is the *theory of corresponding states*. The theory is true for all phases of matter not just crystals that are guided by the same driving forces.

At low temperatures $(\Theta_D/T) \to \infty$, and the integral converges to $4\pi^4/15$. The low temperature limit in Debye theory is then,

$$C_v = \frac{12\pi^4}{5} Nk \left( \frac{T}{\Theta_D} \right)^3.$$

This is the famous $T^3$-law that was experimentally seen for crystals at low temperatures.

It bears saying that though Debye's theory has the correct limits; it is still approximate and $\Theta_D$ which should be constant across $T$ often varies as a function of $T$. Furthermore, since Debye theory is a continuum theory the spectra of diatomic crystals is not readily explained by it. Another interesting point is that the thermodynamic properties of crystals can be estimated from their mechanical, i.e. elastic, properties.

## 9.5   The Phonon Gas Model

Yet another way to derive the properties of a crystal is to treat it as an ideal gas of phonons. To derive what a phonon is we first reconsider the energy of a crystal in terms of its normal coordinates,

$$E_{cryst} = \sum_{j=1}^{3N} h\nu_j \left( n_j + \frac{1}{2} \right)$$

$$= \sum_{j=1}^{3N} h\nu_j n_j + \sum_{j=1}^{3N} \frac{h\nu_j}{2}$$

$$E_{cryst}(\{n_j\}) = \sum_{j=1}^{3N} h\nu_j n_j + E_0.$$

The last line explicitly shows that the energy is a function of the "occupancy number" of the particular mode of energy. We should note that the occupancy number of a particle mode is not restricted, and, equally important, the sum over occupancy numbers is not conserved. In this formulation, each of the $3N$ vibrational modes is a phonon which acts as an ideal gas of bosons. The choice of treating phonons as bosons comes from the fact that phonons do not have occupancy restrictions.

We can mathematically write down the expected occupancy of a phonon using Bose-Einstein statistics,

$$\overline{n}_j = \frac{1}{\lambda^{-1}e^{\beta\varepsilon_j} - 1}.$$

However, we do not immediately know $\lambda$. We do know that the number is not conserved. This requires that $\mu = 0$ or $\lambda = 1$ in these cases. Thermodynamically, however, the requirement must be $\mu = 0$. If we treat the transition of occupancy number as a reaction, following from the notes on chemical equilibrium for the "reaction" $nA \leftrightarrow mA$ $n \neq m$, $(m-n)\mu = 0$, and $\mu = 0$ and $\lambda = 1$. Thus,

$$\overline{n}_j = \frac{1}{e^{\beta\varepsilon_j} - 1}.$$

The average energy is then,

$$\overline{E} = \sum_{j=1}^{3N} \frac{h\nu_j n_j}{e^{\beta\varepsilon_j} - 1} + E_0.$$

Using the function $g(\nu)$ as before,

$$\overline{E} = E_0 + \int_0^\infty \frac{g(\nu)h\nu}{e^{\beta h\nu} - 1}\mathrm{d}\nu.$$

This equation is equivalent to the previous treatment in the beginning of this chapter. Thus a fully examination of the statistical mechanics of crystal can be done from the perspective of phonons. Phonons also have useful quirks. Since they are pseudo-particles, phonons can have momentum and the transfer between phonons can be examined. This transfer is also the cause for electrical resistance in metals. In addition, the interaction of phonons with photons can be studied and is the basis of Brillouin scattering and many crystal observed optical effects.

## 9.6   Lattice Dynamics

Lattice dynamics seek to exactly determine the vibrational frequencies of a lattice. To examine this technique two 1 dimensional lattices will be examine the monoatomic and diatomic cases.

### 9.6.1   Monotonic 1D Crystal

The Hamiltonian following from the beginning of this chapter is

$$\mathcal{H} = \sum_{j=1}^{N} \frac{m}{2}\zeta_j^2 + \sum_{j=2}^{N} \frac{f}{2}(\zeta_j - \zeta_{j-1})^2 = K + U,$$

where $f$ are the force constants. The equations of motion for this system is

$$m\ddot{\zeta}_j = f(\zeta_{j+1} + \zeta_{j-1} - 2\zeta_j).$$

This is simple stating that $ma = F$. We can further assume since the oscillation is harmonic that

$$\zeta_j(t) = e^{i\omega t} y_j,$$

where $y_j$ represents the spacial component of the oscillation. This allows for a simplification of the equations of motion to,

$$-m\omega^2 y_j = f(y_{j+1} + y_{j-1} - 2y_j).$$

This difference equation, which mimics differential equations, is of the form $e^{i\phi}$. Then,

$$-m\omega^2 = f(e^{1i\phi} + e^{-1i\phi} - 2e^{0i\phi})$$
$$= f(2\cos\phi - 2).$$

Using the relation $\sin^2\theta + \cos^2\theta = 1$,

$$\omega^2 = \frac{4f}{m}\sin^2\frac{\phi}{2}.$$

Because $\zeta$ is harmonic it repeats every $\Delta = 2\pi/\phi$. This implies that $\lambda = 2\pi a/\phi$ where $a$ is the lattice spacing. Thus, $\phi = 2\pi a/\lambda = ka$. Taking this all together we can get the dispersion function which shows how different waves travel at different velocities in a crystal.

$$\omega^2 = \frac{4f}{m}\sin^2\frac{\phi}{2}$$
$$\omega = \left(\frac{4f}{m}\right)^{1/2}|\sin\frac{\phi}{2}| = \omega_{max}|\sin\frac{\phi}{2}|$$
$$= \omega_{max}|\sin\frac{ka}{2}|$$
$$\lambda\nu = \frac{\omega_{max}}{k}|\sin\frac{ka}{2}| = c(k).$$

Note that $\omega_{max}$ is the maximum frequency in the crystal. As $\lambda\nu$ is usually not constant, different waves travel at different speeds in crystals.

To solve the equations of motion, we must place another constraint on the system. A common constraint is periodic boundary conditions. When solving for the energy of the system, the result is

$$E = \sum_j \frac{\hbar\omega_j}{e^{\beta\hbar\omega_j} - 1} = \frac{Na}{\pi}\int_0^{\pi/a} \frac{\hbar\omega(k)}{e^{\beta\hbar\omega(k)} - 1}dk.$$

The bounds on the integral are from the fact that $\omega(k) = \omega(|k|)$. Using chain rule we can eliminate $k$,

$$
\begin{aligned}
\mathrm{d}k &= \frac{\mathrm{d}k}{\mathrm{d}\omega}\mathrm{d}\omega = \frac{\mathrm{d}}{\mathrm{d}\omega}\left[\frac{2}{a}\sin^{-1}\left(\frac{\omega}{\omega_{max}}\right)\right]\mathrm{d}\omega \\
&= \frac{2\mathrm{d}\omega}{a(\omega_{max}^2 - \omega^2)^{1/2}}.
\end{aligned}
$$

This can be used to rewrite the above integral in terms of $\omega$ with limits $0, \omega_{max}$.

### 9.6.2  Diatomic 1D Crystal

The Hamiltonian for a diatomic alternating crystal is

$$
\mathcal{H} = \sum_{j=1}^{N}\frac{m_1}{2}\zeta_{2j}^2 + \frac{m_2}{2}\zeta_{2j-1}^2 + \frac{f}{2}\sum_{j=1}^{N}[(\zeta_{2j} - \zeta_{2j-1})^2 + (\zeta_{2j+1} - \zeta_{2j})^2].
$$

This system leads to one set of equations of motion for each particle type. The solution is

$$
\omega^2 = \omega_0^2\left[1 \pm \left(1 - \frac{4m_1 m_2 \sin^2\phi}{(m_1 m_2)^2}\right)^{1/2}\right]
$$

$$
\omega_0^2 = \frac{f}{\mu}.
$$

One interesting part of the solution, is that two sets of frequencies exist depending on if $+$ or $-$ is chosen. When atoms move together, the branch is called the acoustic branch. When neighboring atoms and displaced in opposite directions, it is called the optical branch. If the atoms have differing charges, the optical branch can absorb and emit light. This is usually in the infrared spectrum.

## 9.7  Defects

We shall now look at the energetic and entropic effects on defects in solids. Defects in a solid phase are energetically costly, but as we will see, when entropic effects are taken into consideration, they are almost certain.

### 9.7.1  Lattice Vacancy

A missing atom in a lattice site is called an *Schottky defect*. Assume that a *Schottky defect* cost a crystal an energy of $\varepsilon_s$. Then the free energy as a function of defects becomes,

$$
\begin{aligned}
A(n) &= E - TS \\
&= n\varepsilon_s - kT\ln\frac{N!}{n!(N-n)!},
\end{aligned}
$$

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where the argument in the logarithm is the number of unique ways to distribute n *Schottky defect*. If we take the derivative with respect to $n$ we get,

$$\frac{\partial A}{\partial n} = \varepsilon_s - kT\frac{\partial}{\partial n}[\ln N! - \ln n! - \ln(N-n)!]$$

$$\approx \varepsilon_s - kT\frac{\partial}{\partial n}[-\ln n + n - \ln(N-n)! + N - n]$$

$$\approx \varepsilon_s + kT\left(\frac{1}{n} - \frac{1}{N-n}\right).$$

### 9.7.2   Interstitial Defect

When an atom is not placed correctly on a lattice site it is called an *Frenkel defect*. If $N'$ interstitial sites exist then $A(n)$ is

$$A(n) = n\varepsilon_i - kT\ln\left[\frac{N!}{n!(N-n)!} \cdot \frac{N'!}{n!(N'-n)!}\right].$$

The minimization of free energy can similarly be done in this case.

### 9.7.3   Summary

The dominate type of defect can be determined using a careful measure of density. Frenkel defects do not change density while Schottky defect since they move particles to the surface do. The diffusion of atoms through a lattice depends in large measure to the concentration of defect. If moving to a vacant site takes an energy $\varepsilon$ then the probability an atom has an energy to overcome the barrier is $e^{-\varepsilon/kT}$. An atom with a fequency of $\nu$ then has a time probability of jumping $p \approx \nu e^{-\varepsilon/kT}$. The flux of atoms across one lattice constant is then $pa(\mathrm{d}c/\mathrm{d}x)$ where c is the number of impurities. If $n$ represents the linear concentration of impurities then $c = an$ and $j = -pa^2(\partial n/\partial x)$. Comparing this to Fick's law,

$$j = -D\frac{\partial n}{\partial x},$$

we see that $D = pa^2 \approx \nu a^2 e^{-\varepsilon/kT}$.

Colors in alkali halide crystals is completely a result of defects. The defects are appropriately known as *color centers*. One type F centers occur when an alkali metal vapor is introduced to the alkali halide crystal. The alkali metal get incorporated and separated from its electron. The electron becomes effectively attached to its lattice site and can absorb visible light.