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.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,

$$A = \sum_j a_j$$

$$E_{tot} = \sum_j a_j E_j \text{ where } a_j \text{ is the occupancy number of state j.}$$

We also know that for each energy $E_j, \Omega(E_j)$ unique quantum states exist. We do not know the occupancy 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 micro-canonical ensemble; that is all combinations of occupancy numbers is equally likely.

The number of distributions 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 then,

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

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 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

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

Then,

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

For each k then,

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

or

$$a_k^* = e^{-\alpha'} e^{-\beta E_k}.$$

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 know show the ensemble energy and some of its derivatives.

1.2.2 Finding β

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

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

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

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.

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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 average energy increase in a system, while the second is the average work done on a system meaning the argument in parenthesis is nothing but the reversible heat. This requires that β 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,

$$\Omega_2 \geq \Omega_1.$$

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 $a_{\bar{N}j}$ is

$$W(a_{\bar{N}j}) = \frac{A!}{\prod_N \prod_j a_{Nj}!}.$$

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 βE_{Nj} and γN. Like the C ensemble this will be called the partition function of the GC ensemble. We label it Ξ.

2.1.1 Finding β and γ

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 Ξ 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, β must be the same as the canonical ensemble.

γ 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 γ must be

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

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

2.1.2 Other Points

Ξ can be written as,

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

Often times we see $e^{\beta\mu}$ as λ 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. Δ 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 Ensembles

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 Ω. 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,

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

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

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

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,

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

Compared to the average energy then the average fluctuations are,

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

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

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

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

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

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

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,

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

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

Here κ 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 -4th. 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,

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

$$= q_a q_b q_c \dots$$

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,

$$E_{tot} = \epsilon_i^a + \epsilon_j^b + \epsilon_j^c + \dots$$

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

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, ϵ_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 Ξ 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 λ into the second summation which just distributes λ^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 ϵ into q_{trans}.

$$q_{trans} = \sum_{j,k,l} e^{-\beta(\epsilon_{n_x} + \epsilon_{n_y} + \epsilon_{n_z})}$$

$$= \sum_{i} e^{-\beta\epsilon_{n_i}} \sum_{j} e^{-\beta\epsilon_{n_j}} \sum_{l} e^{-\beta\epsilon_{n_l}}$$

$$= \left(\sum_{i=0}^{\infty} e^{-\beta\epsilon_{n_l}} \right)^3$$

$$= \left(\sum_{i=0}^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8ma^2} \right) \right)^3$$

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 $a = 10cm$, Δ 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,

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

Λ 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.