

Pathria & Beale, Statistical Mechanics
 Third edition
 Eh, not really. Might want to consider not sticking to a single textbook

CLASS SCHEDULE DATE _____

NAME _____ SCHOOL _____

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Ecclesiastes names you Almighty, the Maccabees name you Creator, the Epistle to the Ephesians names you Freedom, Baruch names you Omnipotence, the Psalms name you Wisdom and Truth, John names you Light, the Book of Kings names you Lord, Exodus names you Providence, Leviticus, sanctity, Cadmus, Justice. Creation names you God. Mankind names you Father. But Solomon names you Mercy, and of all your names, this in the most beautiful. - Monsigneur Myriel (Victor Hugo, The Wretched)

Section 1: The Statistical Basis of Thermodynamics

The Macroscopic and the Microscopic States

Statistical mechanics assumes that in a system, the particles are following some sort of mechanics, either classical or quantum. This leads to the formulation of the ideal gas.

The Ideal Gas

Assumptions

- Large number of point particles (generally order 10^{23})
- Particles don't mutually interact
- Particles can interact with walls of the container
- Each particle has velocity and position and follow Newton's Laws
- Interesting quantities
 - Pressure (P)
 - Energy (E)
 - Temperature (T)
 - Number (N)
 - Volume (V)
 - Density (n) = N/V

Thermodynamic limit

- $N \rightarrow \infty, V \rightarrow \infty, n$ staying fixed
- In this limit, we can establish two types of properties
 - Extensive: directly proportional to size of system
 - Intensive: independent of size of system

If the particles are noninteracting, we can define the total energy (E) of the system as the sum of the energies of the individual particles, ϵ_i , or

$$E = \sum_i \epsilon_i$$

N.B. quantum mechanics declares that E & ϵ_i are discrete, but since the different energy values are very small, E can often be regarded as continuous

Macrostate: defined by N, V, E

Microstate: each of the different ways to define a given macrostate. The number of microstates also gives us the entropy of the system.

At any time, the system is equally likely to be in any one of the possible microstates (equal a priori probabilities). In fact, over time, all possible microstates are visited (ergodicity).

Define $\Omega(N, V, E)$ as the number of possible microstates for a given set of N, V , and E .

Section 2 Contact between statistics and thermodynamics: physical significance of the number $\Omega(N, V, E)$

Consider two systems A_1 & A_2 separately in equilibrium.

If they are then brought into contact,

- Adiabatic - walls do not allow energy to pass through
- Diabatic - walls allow energy to pass through

A_1 (N_1, V_1, E_1)	A_2 (N_2, V_2, E_2)	Energy passes through, but no macroscopic motion
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0th law of thermodynamics: If A_1 is in equilibrium with A_2 & A_2 is in equilibrium with A_3 , then A_1 is in equilibrium with A_3 .

In the above picture, the energy of the system is conserved, $E^{(0)} = E_1 + E_2$.

Since the entire system can be in any of the microstates, which we can write as:

$$\Omega_1(E_1)\Omega_2(E_2) = \Omega_1(E_1)\Omega_2(E^{(0)} - E_1) = \Omega^{(0)}(E^{(0)}, E_1)$$

Postulate of maximum entropy: E_1 takes on the value that maximizes the total number of microstates. This is the equilibrium position.

i.e., we want to maximize $\Omega^{(0)}$, $\frac{\partial \Omega^{(0)}}{\partial E_1} = 0$

$$\begin{aligned} \frac{\partial \Omega^{(0)}}{\partial E_1} &= \frac{\partial \Omega_1(E_1)}{\partial E_1} \Omega_2(E_2) + \Omega_1(E_1) \frac{\partial \Omega_2(E_2)}{\partial E_1} \\ &= \frac{\partial \Omega_1(E_1)}{\partial E_1} \Omega_2(E_2) + \Omega_1(E_1) \frac{\partial \Omega_2(E_2)}{\partial E_2} \frac{\partial E_2}{\partial E_1} \\ &= \frac{\partial \Omega_1(E_1)}{\partial E_1} \Omega_2(E_2) + \Omega_1(E_1) \frac{\partial \Omega_2(E_2)}{\partial E_2} \frac{\partial E_2}{\partial E_1} = 0 \end{aligned}$$

$$\begin{aligned} \frac{\partial \Omega_1(E_1)}{\partial E_1} \Omega_2(E_2) &= -\Omega_1(E_1) \frac{\partial \Omega_2(E_2)}{\partial E_2} \frac{\partial E_2}{\partial E_1} \\ \frac{1}{\Omega_1(E_1)} \frac{\partial \Omega_1(E_1)}{\partial E_1} &= -\frac{1}{\Omega_2(E_2)} \frac{\partial \Omega_2(E_2)}{\partial E_2} \end{aligned}$$

$$\frac{\partial \ln \Omega_1(E_1)}{\partial E_1} = \frac{\partial \ln \Omega_2(E_2)}{\partial E_2}$$

We can then define this quantity as $\frac{1}{k_B T} = \beta = \left(\frac{\partial \ln \Omega(N, V, E)}{\partial E} \right)_{N, V, E}$ where k_B is the Boltzmann constant.

T is the thermodynamic temperature

$$S = k_B \ln \Omega$$

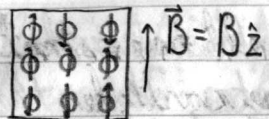
$$\left(\frac{\partial S}{\partial E} \right)_{N, V} = \frac{1}{T}$$

$$\frac{\partial S}{\partial \ln \Omega} = \frac{1}{\beta T}$$

entropy
Thermodynamic formula

If $S=0 \Rightarrow$ lowest energy state (groundstate), this corresponds to a single microstate. This also goes to show that as the number of microstates increases, the entropy (or disorder) of the system also increases.

As an example, let's look at the entropy of the Pauli Paramagnet.



N particles in either up or down spin ($s_i = \pm 1/2$) with an energy $\epsilon(\vec{s}_i) = \Delta\epsilon(\frac{1}{2} - s_i)$

$N_\downarrow = \# \text{ down}$

$$\ln N! \approx N \ln N - N$$

$$\Omega(N, V, E) = \binom{N}{N_\downarrow} = \frac{N!}{(N-N_\downarrow)! N_\downarrow!}$$

Stirling's approximation for large N

$$S = k_B \{ \ln N! - \ln(N-N_\downarrow)! - \ln N_\downarrow! \}$$

large N

$$= k_B \{ N \ln N - (N-N_\downarrow) \ln(N-N_\downarrow) - N_\downarrow \ln N_\downarrow + N - (N-N_\downarrow) - N_\downarrow \}$$

$$= k_B \{ N \ln \frac{N}{N-N_\downarrow} + N_\downarrow \ln \frac{N-N_\downarrow}{N_\downarrow} \}$$

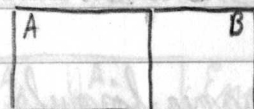
$$= k_B N \{ \ln \frac{1}{1 - \frac{N_\downarrow}{N}} + \frac{N_\downarrow}{N} \ln \left(\frac{N_\downarrow}{N} - 1 \right) \}$$

If we write $\langle \epsilon \rangle = \sum_i \frac{\epsilon(s_i)}{N} = \frac{N_\downarrow}{N} \Delta\epsilon$ Average energy of a site

$$S = k_B N \left\{ \ln \left(\frac{1}{1 - \frac{\langle \epsilon \rangle}{\Delta\epsilon}} \right) + \frac{\langle \epsilon \rangle}{\Delta\epsilon} \ln \left(\frac{\langle \epsilon \rangle}{\Delta\epsilon} - 1 \right) \right\}$$

Section 3 Further contact between statistics and thermodynamics

If you then introduce an identical copy and place it in diabatic contact with the first,



$$\frac{E_{tot}}{N} = \langle \epsilon \rangle_A + \langle \epsilon \rangle_B = \epsilon_A + \epsilon_B$$

$$\frac{S_{tot}}{k_B N} = \frac{\epsilon_A - \Delta\epsilon}{\Delta\epsilon} \ln \left(\frac{\Delta\epsilon - \epsilon_A}{\Delta\epsilon} \right) + \frac{\epsilon_A + \epsilon_A - \Delta\epsilon}{\Delta\epsilon} \ln \left(\frac{\Delta\epsilon - \epsilon_A + \epsilon_A}{\Delta\epsilon} \right) - \frac{\epsilon_A}{\Delta\epsilon} \ln \left(\frac{\epsilon_A}{\Delta\epsilon} \right) - \frac{(\epsilon_A - \epsilon_A)}{\Delta\epsilon} \ln \left(\frac{\epsilon_A - \epsilon_A}{\Delta\epsilon} \right)$$

To find the equilibrium state, we must maximize entropy, $\frac{\partial S}{\partial \epsilon_A} = 0$

$\epsilon_A = \epsilon_{tot}/2$ is the maximum entropy

$dE = TdS - PdV + \mu dN$ basic formula of thermodynamics

This is a statement of energy conservation

$$dE = TdS - PdV$$

$$= dQ - dW$$

where dQ is the energy introduced through the walls,

dW is the work done on the external environment

environment

μdN term comes from imagining the wall has a small hole that allows the system to exchange particles slowly. μ is the chemical potential, the energy needed to remove a particle keeping the other parameters fixed

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

$$\mu = - \left(\frac{\partial S}{\partial N} \right)_{V, E} = \left(\frac{\partial E}{\partial N} \right)_{V, S}$$

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

$$A = E - TS \quad \text{Helmholtz free energy}$$

$$G = A + PV \quad \text{Gibbs free energy}$$

$$H = E + PV \quad \text{Enthalpy}$$

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_{N, V} = \left(\frac{\partial E}{\partial T} \right)_{N, V} \quad \text{Specific heat at a constant volume}$$

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_{N, P} = \left(\frac{\partial(E+PV)}{\partial T} \right)_{N, P} = \left(\frac{\partial H}{\partial T} \right)_{N, P} \quad \text{Specific heat at constant pressure}$$

Section 4 The classical ideal gas

A quick divergence on Second Law of Thermodynamics

Entropy is always increasing (Postulate of max entropy)

Heat flows from hot to cold

$$dE_H + dE_C = 0 \quad \text{Max entropy}$$

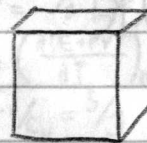
$$T_H dS_H + T_C dS_C = 0 \quad dS_H + dS_C \geq 0$$

$$dS_C = -T_H/T_C dS_H \quad \text{or} \quad (T_H - T_C) dS_H \leq 0$$

$$dS_H \leq 0 \Rightarrow T_H dS_H \leq 0$$

$$dQ_H \leq 0$$

Imagine



$\Omega(E, V, N)$ can be found by breaking the full system into a collection of boxes with side length Δr

$$\Omega(N, EV) = \left(\frac{V}{\Delta r^3} \right)^N$$

$$S = k \ln \Omega$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{N, E} = \frac{\partial}{\partial V} \left(k \ln \left(\frac{V}{\Delta r^3} \right)^N \right) = \frac{\partial}{\partial V} \left(Nk \ln \left(\frac{V}{\Delta r^3} \right) \right)$$

$$S_C - S_A = Nk \ln \frac{\Delta r^3}{V} = k N \frac{\Delta r^3}{V} = k \frac{N}{V}$$

$$PV = NkT = nRT \quad \text{Ideal gas law}$$

Determine the number of ways to satisfy

$$\sum_{r=1}^{3N} \epsilon_r = E$$

where ϵ_r are the energies associated with the various N particles.

$$\text{More specifically, } \epsilon = \sum_i \frac{p_i^2}{2m} \leq E$$

First, we must break the space up into boxes of volume $[\Delta p^3 \Delta x^3]^N$

$$\Delta p \Delta x = h$$

$$[\Delta p \Delta x]^3 = h^3$$

$$G(E) = \frac{1}{h^{3N}} \int_{\Theta} [E - \sum_i \frac{p_i^2}{2m}] d^3 x_1 \dots d^3 x_N d^3 p_1 \dots d^3 p_N$$

$$\Theta = \begin{cases} 1 & \text{if } x < 0 \\ 0 & \text{if } x > 0 \end{cases}$$

$$= \frac{V^N}{h^{3N}} \int_{\Theta} [E - \sum_i \frac{p_i^2}{2m}] d^3 p_1 \dots d^3 p_N$$

Say $W_R = \int_{\Theta} [E - \sum_i \frac{p_i^2}{2m}] d^3 p_1 \dots d^3 p_N$ is the volume of a hypersphere of dimension $D = 3N$ and radius $R = \sqrt{2mE}$

$$\vec{q}_i = \vec{p}_i / R$$

$$W_R = \int_{\Theta} [E - \sum_i \frac{R^2}{2m} |\vec{q}_i|^2] R^D d^3 q_1 \dots d^3 q_N$$

$$= \int_{\Theta} [R^2 - \sum_i \frac{R^2}{2m} |\vec{q}_i|^2] R^D d^3 q_1 \dots d^3 q_N$$

$$= R^D \int_{\Theta} [1 - \sum_i |\vec{q}_i|^2] d^3 q_1 \dots d^3 q_N = R^D W_1$$

$$\frac{dW_R}{dR} = DR^{D-1} W_1$$

$$\int_0^{\infty} \frac{dW_R}{dR} \exp(-R^2/R_0^2) dR = \int_0^{\infty} DR^{D-1} W_1 \exp(-R^2/R_0^2) dR$$

$$x = R^2/R_0^2 \quad R = R_0 x^{1/2}$$

$$dx = \frac{2R dR}{R_0^2}$$

$$= DW_1 \int_0^{\infty} R^{D-1} \cdot \frac{R_0^2}{2R} \exp(-x) dx$$

$$= \frac{1}{2} DW_1 \int_0^{\infty} R_0^2 R^{D-2} \exp(-x) dx$$

$$= \frac{1}{2} DW_1 \int_0^{\infty} R_0^2 \cdot R_0^{D-2} x^{D/2-1} \exp(-x) dx$$

$$= \frac{1}{2} DW_1 R_0^D \int_0^{\infty} x^{D/2-1} \exp(-x) dx$$

$$= \frac{1}{2} DW_1 R_0^D \Gamma(D/2)$$

$$\frac{dW_R}{dR} = \int_{\Theta} [R - \sqrt{\sum_i p_i^2}] d^3 p_1 \dots d^3 p_N$$

$$\int_0^{\infty} \frac{dW_R}{dR} \exp(-R^2/R_0^2) dR = \int_{\Theta} d^3 p_1 \dots d^3 p_N \int_0^{\infty} [R - \sqrt{\sum_i p_i^2}] \exp(-R^2/R_0^2) dR$$

$$= \int_{\Theta} \exp(-\sum_i p_i^2/R_0^2) d^3 p_1 \dots d^3 p_N$$

$$= [\int_{\Theta} \exp(-p_x^2/R_0^2) d^3 p_x]^{3N} = R_0^D (\sqrt{\pi})^D \quad \text{Gaussian integral}$$

$$R_0^D \pi^{D/2} = \frac{1}{2} DW_1 \Gamma(D/2) R_0^D$$

$$W_1 = \frac{2\pi^{D/2}}{D\Gamma(D/2)}$$

$$G(E) = \frac{V^N [2\pi m E]^{3N/2}}{h^{3N} (3N/2)!} = \frac{V^N [2\pi m E]^{3N/2}}{h^{3N} (3N/2)!} \quad \text{for } N \text{ even}$$

$$\Omega = \frac{dG}{dE} \Delta E$$

$$\text{N.B. } \Omega < G(E) < \frac{E}{\Delta E} \Omega$$

$$S = k_B \ln \Omega = k_B \ln G = k_B N \ln \left(\frac{V [2\pi m E]^{3/2}}{h^3} \right) - k_B \ln \left(\frac{3N!}{2} \right)$$

$$= k_B N \ln \left(\frac{V [2\pi m E]^{3/2}}{h^3} \right) - k_B \left(\frac{3N}{2} \right) \ln \left(\frac{3N}{2} \right) + \frac{3k_B N}{2}$$

$$= k_B N \ln \left(\frac{V}{R^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right) + \frac{3}{2} k_B N \quad \text{Entropy of ideal gas of distinguishable particles}$$

$$\left(\frac{\partial S}{\partial E} \right)_{N,V} = k_B N \cdot \frac{h^3}{V} \left(\frac{3N}{4\pi m E} \right)^{3/2} \cdot \frac{V}{R^3} \left(\frac{4\pi m}{3N} \right) \cdot \frac{3}{2} E^{-1/2}$$

$$= \frac{3}{2} k_B N \cdot \frac{1}{E} = \frac{1}{T}$$

$$E = \frac{3}{2} N k_B T$$

Example of equipartition theory

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} = \frac{3}{2} N k_B$$

Heat capacity

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

$$S - \frac{3}{2} k_B N = k_B N \ln \left(\frac{V}{R^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right)$$

$$\left(\frac{4\pi m E}{3N} \right)^{3/2} = \frac{h^3}{V} \exp \left(\frac{S}{k_B N} - \frac{3}{2} \right)$$

Looking ahead, we want E as some function of V

$$E = \text{constant} \cdot V^{-2/3}$$

$$P = \frac{2}{3} \text{constant} \cdot V^{-5/3} = \frac{2}{3} E/V$$

$$PV = \frac{2}{3} E = \frac{2}{3} \cdot \frac{3}{2} N k_B T = N k_B T$$

$$C_P = \left(\frac{\partial (E+PV)}{\partial T} \right)_{N,P} = \left(\frac{\partial}{\partial T} \left(\frac{5}{2} N k_B T \right) \right)_{N,P} = \frac{5}{2} N k_B$$

$$\gamma = C_P/C_V = 5/3$$

adiabatic ($T = \text{constant} + N = \text{constant}$)

Total energy of the gas remains constant

Pressure varies inversely with volume

$$S_f - S_i = Nk \ln (V_f/V_i)$$

Reversible adiabatic ($S = \text{constant} + N = \text{constant}$)

$E + T$ vary as $V^{-2/3}$

P varies as $V^{-5/3}$

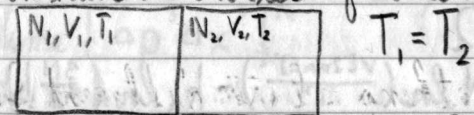
$PV^\gamma = \text{constant}$

$TV^{\gamma-1} = \text{constant}$

$(dE)_{\text{adiabatic}} = -PdV = -\frac{2E}{3V} dV$

Section 5. The entropy of mixing and the Gibbs paradox

Say you have two boxes of ideal gas



Before mixing: $S_i = N_i k_B \ln V_i + \frac{3}{2} N_i k_B \left\{ 1 + \ln \left(\frac{2\pi m_i k_B T}{h^2} \right) \right\}, i = 1, 2$

After mixing: $S_T = \sum_i [N_i k_B \ln V + \frac{3}{2} N_i k_B \left\{ 1 + \ln \left(\frac{2\pi m_i k_B T}{h^2} \right) \right\}]$

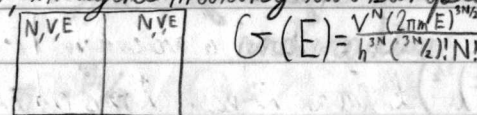
where $V = V_1 + V_2$

Entropy of mixing

$(\Delta S) = S_T - \sum_i S_i = k_B [N_1 \ln \left(\frac{V_1 + V_2}{V_1} \right) + N_2 \ln \left(\frac{V_1 + V_2}{V_2} \right)] > 0$

$\Delta S > 0$ which is true for an irreversible process

Now, imagine mixing two samples of the same gas



Before mixing: $S_i = N k_B \ln V + \frac{3}{2} N k_B \left\{ 1 + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right\}$

After mixing: $S_T = N k_B \ln V + \frac{3}{2} N k_B \left\{ 1 + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right\}$

$\Rightarrow (\Delta S) = 0 \Rightarrow$ this is a reversible system, which is not true. Which means we must add some additional terms

$S = k_B \ln \left[\frac{V}{N} \cdot \frac{1}{h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{5}{2} k_B N$

Sackur-Tetrode equation: entropy of an ideal gas of indistinguishable particles

From this, we can derive the following quantities:

$E(N, V, S) = \frac{3h^2 N^{5/3}}{4\pi m V^{2/3}} \exp \left(\frac{2S}{3Nk} - \frac{5N}{3} \right)$

$\mu = E \left[\frac{5}{3N} - \frac{2S}{3N^2 k} \right] = \frac{G}{N} = kT \ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \right\}$

$A = NkT \left[\ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \right\} - 1 \right]$

Section 6. The "correct" enumeration of the microstates

This section goes over how the way we've been enumerating microstates is not entirely correct. We will see the correct enumeration later.

Problems

I'm planning to do something a little different for this class. Since I don't really like Pathria problems, I'm going to copy Fertig's questions and work through those questions instead.

1. The Schottky Defect

At zero temperature, atoms of a solid order into perfect lattices. At finite temperatures, various types of defects may appear. Among these are the Schottky defect, a missing atom ("a vacancy") in the lattice. For this problem, we will treat these atoms as if they have vanished, although in reality they migrate to the surface of the crystal. At low temperature, these defects are very dilute, so when n of them are present the energy of the system relative to the zero temperature state may be written as $E = n\epsilon$, where ϵ is the energy to create a single such defect.

a. For a system with N atoms, what is the number of states $\Omega(n)$ with n Schottky defects? What is the associated entropy?

$$\Omega = \binom{N}{n} = \frac{N!}{(N-n)!n!}$$

$$S = k \ln \Omega = k \ln \left(\frac{N!}{(N-n)!n!} \right)$$

- b. Find an expression relating the temperature of the system to n , valid for large N .

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)$$

$$S = k[\ln N! - \ln(N-n)! - \ln n!]$$

$$= k[N \ln N - (N-n) \ln(N-n) - n \ln n]$$

$$= k \left[N \ln \frac{N}{N-n} + n \ln \frac{N-n}{n} \right]$$

$$= k \left[N \ln \left(\frac{N}{N-E/\epsilon} \right) + \frac{E}{\epsilon} \ln \left(\frac{N-E/\epsilon}{E/\epsilon} \right) \right]$$

$$\frac{\partial S}{\partial E} = k \left[N \cdot \left(\frac{N-E/\epsilon}{N} \right) \cdot \left(\frac{N}{(N-E/\epsilon)^2} \right) + \frac{1}{\epsilon} \ln \left(\frac{N-E/\epsilon}{E/\epsilon} \right) + \frac{E/\epsilon}{N-E/\epsilon} \cdot \left(\frac{-N}{E^2} \right) \right]$$

$$= k \left[\frac{N}{N-E/\epsilon} - \frac{N}{N-E/\epsilon} + \frac{1}{\epsilon} \ln \left(\frac{N-E/\epsilon}{E/\epsilon} \right) \right]$$

$$= \frac{k}{\epsilon} \ln \left(\frac{N-E/\epsilon}{E/\epsilon} \right) = \frac{1}{T}$$

$$T = \frac{\epsilon}{k \ln \left(\frac{N-E/\epsilon}{E/\epsilon} \right)}$$

- c. A typical energy scale for a Schottky defect is $\epsilon = 1 \text{ eV}$. Estimate the relative number of defects N/n at room temperature.

As our assumption that the defects are very dilute supported by this estimate?

$$\epsilon = 1 \text{ eV}$$

$$k = 10^{-4} \text{ eV}$$

$$T = 300 \text{ K}$$

$$300 = \frac{1}{10^{-4}} \ln \left(\frac{N-E/\epsilon}{E/\epsilon} \right) = 10^4 \ln \left(\frac{N-n}{n} \right)$$

$$\ln \left(\frac{N-n}{n} \right) = \frac{1}{3} \times 10^{-2}$$

$$\frac{N}{n} + 1 = 3 \times 10^{14}$$

$$\frac{N}{n} = 3 \times 10^{15} \text{ very dilute}$$

- d. Find an expression for the heat capacity of this system, $C = \left(\frac{\partial E}{\partial T} \right)_N$.

Show that C vanishes in both the limits $T \rightarrow 0$ and $T \rightarrow \infty$, so that C must be peaked at a finite T . This is a common behavior for heat capacities of systems with a finite maximum energy, and is known as the Schottky effect.

$$T = \frac{\epsilon}{k \ln \left(\frac{N-E/\epsilon}{E/\epsilon} \right)}$$

$$\ln \left(\frac{N-E/\epsilon}{E/\epsilon} \right) = \frac{\epsilon}{kT}$$

$$\frac{E}{\epsilon} - 1 = \exp \left(\frac{\epsilon}{kT} \right)$$

$$\epsilon N = E \left(1 + \exp \left(\frac{\epsilon}{kT} \right) \right)$$

$$E = \frac{\epsilon N}{1 + \exp \left(\frac{\epsilon}{kT} \right)}$$

$$\frac{\partial E}{\partial T} = \frac{-\epsilon N}{\left(1 + \exp \left(\frac{\epsilon}{kT} \right) \right)^2} \cdot \exp \left(\frac{\epsilon}{kT} \right) \cdot \left(-\frac{\epsilon}{kT^2} \right)$$

$$= \frac{\epsilon^2 N \exp \left(\frac{\epsilon}{kT} \right)}{kT^2 \left(1 + \exp \left(\frac{\epsilon}{kT} \right) \right)^2}$$

$T \rightarrow 0$: $C \rightarrow \frac{1}{\exp(\epsilon/kT)} \rightarrow 0$ since exp. terms decay faster than quadratic terms

$T \rightarrow \infty$: $C \rightarrow \frac{1}{T^2} \rightarrow 0$

2. Pathria 1.4, In a classical gas of hard spheres (of diameter D), the spatial distribution of the particles is no longer uncorrelated. Roughly speaking, the presence of n particles in the system leaves only a volume $(V - nv_0)$ available for the $(n+1)^{\text{th}}$ particle; clearly v_0 would be proportional to D^3 . Assuming that $Nv_0 \ll V$, determine the dependence of $\Omega(N, V, E)$ on V and show that, as a result of this, V in the ideal-gas law gets replaced by $(V - b)$, where b is four times the actual volume occupied by the particles.

$$\Omega = V \cdot (V - v_0) (V - 2v_0) \dots (V - (N-1)v_0)$$

$$= \prod_{i=1}^N [V - (i-1)v_0]$$

For, $Nv_0 \ll V$, $\Omega \approx V^N - V^{N-1} v_0 \frac{(N-1)N}{2}$

$$= S = k \ln \Omega = k \ln [V^N - V^{N-1} v_0 \frac{(N-1)N}{2}]$$

$$P/T = \left(\frac{\partial S}{\partial V} \right)_{N,E} = k \ln \left[\frac{N V^{N-1} - \frac{1}{2} N(N-1) v_0 V^{N-2}}{V^N - V^{N-1} v_0 \frac{N(N-1)}{2}} \right]$$

$$\rho = \frac{N}{V}$$

$$\frac{P}{T} = \frac{Nk}{V} \cdot \frac{1 - \frac{1}{2} \rho N v_0 \frac{(N-1)}{N}}{1 - \frac{1}{2} \rho N v_0 \frac{(N-1)}{N}}$$

$$\approx \frac{Nk}{V} \left\{ 1 - \frac{1}{2} \rho N v_0 \left[\left(\frac{N-1}{N} \right)^2 - \left(\frac{N-1}{N} \right) \right] \right\} \approx \frac{Nk}{V} \left\{ 1 + \frac{1}{2} \rho v_0 \right\}$$

$$\approx PV \left[1 - \frac{1}{2} \rho v_0 \right] = NkT$$

$$b = \frac{1}{2} V \rho v_0 = \frac{1}{2} \left[\frac{4\pi}{3} \sigma_0^3 \right] = 4N \left[\frac{4\pi}{3} \left(\frac{1}{2} \sigma_0 \right)^3 \right]$$

3. Maxwell Relations

The Helmholtz free energy is defined as $A = E - TS$. Show that a differential change dA can be written in terms of the differentials dT , dV , and dN , and use this to establish the thermodynamic Maxwell relations.

$$A = E - TS$$

$$dA = dE - TdS - dT \cdot S$$

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

$$= -PdV + \mu dN - SdT$$

$$(dA)_{N,T} = (dA)_{V,N}$$

$$-PdV = -SdT$$

$$\left(\frac{dP}{dT} \right)_{N,V} = \left(\frac{dS}{dV} \right)_{N,T}$$

$$(dA)_{V,T} = (dA)_{V,N}$$

$$\mu dN = -SdT$$

$$\left(\frac{d\mu}{dT} \right)_{V,N} = - \left(\frac{dS}{dN} \right)_{V,N}$$

$$(dA)_{V,T} = (dA)_{T,N}$$

$$\mu dN = -PdV$$

$$\left(\frac{d\mu}{dV} \right)_{N,T} = - \left(\frac{dP}{dN} \right)_{T,V}$$