Statistical Mechanics

4. The **grand free energy** or **grand potential**, Ξ, can be obtained from the Helmholtz, $F(T, V, N)$ free energy or the internal energy $U(S, V, N)$ via:

$$\Xi = F - \mu N = U - TS - \mu N$$

   (a) What are the normal or proper variables for Ξ? (When Ξ is written in terms of its normal or proper variables, it constitutes a complete thermodynamic description, without loss of information). (1 point)

   (b) Derive expressions for the conjugate variables in this description. (1 point)

   (c) What are the Maxwell relations governing derivatives of Ξ (2 points)

   (d) Consider a small system connected to a large thermodynamic reservoir. State under what conditions (e.g. specify what quantities are exchanged between the system and reservoir) Ξ is minimized in equilibrium. Prove that this is the case by showing that Ξ is minimized when the system is in equilibrium. (3 points)

   (e) Given the Helmholtz free energy for an ideal gas:

$$F(T, V, N) = -NkT\left(1 + \log\left(\frac{VT^{3/2}}{N\Phi}\right)\right)$$

   where Φ is an unspecified fixed constant, calculate the grand free energy for an ideal gas. (3 points)

a) V, T, & μ are the "proper" variables.

b) $d\mathcal{G} = -PdV - SdT - Nd\mu$ so $P = -\frac{\partial \mathcal{G}}{\partial V}$, $S = -\frac{\partial \mathcal{G}}{\partial T}$, $N = -\frac{\partial \mathcal{G}}{\partial \mu}$

c) Take double partials & switch places: (holding appropriate stuff const)

$$\frac{\partial}{\partial V}\frac{\partial}{\partial T}\mathcal{G} = \frac{\partial}{\partial T}\frac{\partial}{\partial V}\mathcal{G} \qquad \& \qquad \frac{\partial}{\partial V}\frac{\partial}{\partial \mu}\mathcal{G} = \frac{\partial}{\partial \mu}\frac{\partial}{\partial V}\mathcal{G} \qquad \& \qquad \frac{\partial}{\partial V}\frac{\partial}{\partial T}\mathcal{G} = \frac{\partial}{\partial T}\frac{\partial}{\partial V}\mathcal{G}$$

$$-\frac{\partial S}{\partial V} = \frac{\partial P}{\partial T} \qquad -\frac{\partial N}{\partial V} = \frac{\partial P}{\partial \mu} \qquad -\frac{\partial S}{\partial V} = \frac{\partial P}{\partial T}$$

d) $d\mathcal{G} = -PdV - SdT - Nd\mu$ so for system of two, reservoir + small system:

$d(\mathcal{G}_1 + \mathcal{G}_2) = -(P_1 - P_2)dV - (S_1 - S_2)dT - (N_1 - N_2)d\mu$ minuses bc $dV_1 = -dV_2$ etc.

For equil, $T_1 = T_2$, $\mu_1 = \mu_2$, $P_1 = P_2$ so Ξ must be minimized at equil.

e) $\mathcal{G} = F - \mu N$

use $\mu = \frac{\partial F}{\partial N}$ from C.E.:

$$\mu = \frac{\partial}{\partial N}\left[-NkT + \overset{NkT}{\wedge}\ln N + NkT\ln\left(\frac{\Phi}{VT^{3/2}}\right)\right]$$

$$= \cancel{-kT} + kT\ln N + \frac{\cancel{NkT}}{N} + kT\ln\left(\frac{\Phi}{VT^{3/2}}\right)$$

$$= kT\ln\left(\frac{\Phi N}{VT^{3/2}}\right) \to N = \frac{VT^{3/2}}{\Phi}e^{\mu/kT}$$

$$\boxed{\mathcal{G} = -NkT + NkT\ln\left(\frac{N\Phi}{VT^{3/2}}\right) - \frac{\mu V T^{3/2}}{\Phi}e^{\mu/kT}}$$

plug in for N everywhere

then $\mathcal{G}$ simplifies to

$$\mathcal{G} = -\frac{kVT^{5/2}}{\Phi}e^{\mu/kT}$$

Statistical Mechanics

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4. It can be shown that the Helmholtz free energy for a photon gas is given by:

$$F(T, V, N) = -\frac{1}{3}\sigma V T^4$$

where σ is the Stefan-Boltzmann constant. Using this relation, answer the following:

(a) What are the equations of state (that is, P, S, and μ as functions of T, V and N)? (3pts.)

(b) Consider a Carnot cycle using a photon gas as its working fluid. The cycle is driven by one hot and one cold temperature reservoir, with temperatures T_h and T_c respectively. Draw the cycle in the P-V plane. **Caution:** This is **not** an ideal gas! Think carefully about the steps in a Carnot cycle and use your results from above to determine what the cycle will look like. (2pts.)

(c) Solve for the heat exchanged in each leg of your Carnot cycle. Your answer may depend upon T_h, T_c, and any other variables you might choose in defining your cycle. (2pts.)

(d) Using these values for the heat exchanged, calculate the efficiency of a Carnot cycle that uses a photon gas as its working fluid. If you cannot calculate it, devise a careful argument for its value. (3pts.)

a) $F = E - TS \quad dE = TdS - PdV + \mu dN$

$dF = dE - TdS - SdT = \cancel{TdS} - PdV + \mu dN - \cancel{TdS} - SdT$

$-\frac{dF}{dV} = P = \frac{1}{3}\sigma T^4$ $\qquad -\frac{dF}{dT} = S = \frac{4}{3}\sigma V T^3$

$\frac{dF}{dN} = \mu = 0$

b) Carnot has 2 isotherms, 2 adiabats.

Isotherm: $dP = d\left(\frac{1}{3}\sigma T^4\right) = \frac{4}{3}\sigma T^3 dT$

So $dP \propto dT$; $dT = 0 \rightarrow dP = 0$

Straight line for isotherm!

Adiabat: $dS = \frac{dQ}{T}$; $dQ = 0$ for adiabat, $\xrightarrow{\text{so}} dS = 0$

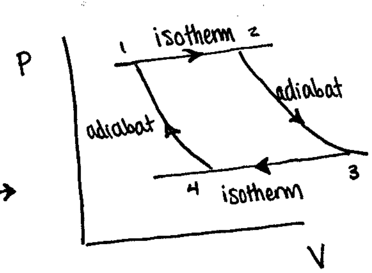
$dS = 0 = \frac{4}{3}\sigma\left(T^3 dV + 3VT^2 dT\right)$

$-T^{\cancel{3}} dV = 3V\cancel{T^2} dT \qquad dP = \frac{4}{3}\sigma T^3 dT$

$-\frac{T}{3V}dV = \frac{3dP}{4\sigma T^3} \qquad dT = \frac{3dP}{4\sigma T^3}$

$-\frac{4}{9V}dV = \frac{dP}{\sigma T^4} = \frac{dP}{\sigma\left(\frac{3P}{\sigma}\right)} \rightarrow \frac{4}{3}\ln V = \ln P$

$P = V^{-4/3}$ steep downwd curve



c) $dQ = 0$ for adiabats

For isotherms, $dU = 0 = \frac{3}{2}Nk\Delta T$

$dU = dQ - dW$

$dW = P(\Delta V) = dQ$

$Q_h = P_h \Delta V_h = \frac{\sigma}{3}T_h^4 (V_2 - V_1)$

$Q_c = \frac{\sigma}{3}T_c^4 (V_4 - V_3)$

d) $\eta = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c^4 (V_4 - V_3)}{T_h^4 (V_2 - V_1)}$

Statistical Mechanics

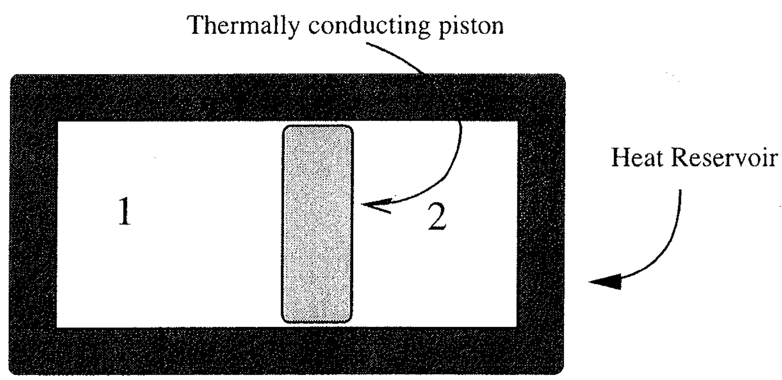
4. **Helmholtz Free Energy**: The Helmholtz free energy of an ideal monoatomic gas can be written as

$$F(T,V,N) = NkT\left\{A - \log\left[T^{3/2}\frac{V}{N}\right]\right\}$$

★ Assume whole system is at const T the whole time ★ - Mason

where N is the total number of gas atoms, V is the volume, T is temperature, k is Boltzmann's constant and A is a dimensionless constant.

Consider a piston separating a system into two parts, with equal numbers of particles on the left and the right hand side. The whole system is in good thermal contact with a reservoir at constant temperature T. Initially, $V_1 = 2V_2$. The total volume, $V_{tot} = V_1 + V_2$, is fixed for this whole problem.



(a) Calculate the equilibrium position of the piston, once it is released. You must prove your answer, and not simply assert it. (3 points)

(b) Calculate the maximum available work the system can perform as it changes from the initial condition to the equilibrium position. (3 points)

(c) Calculate the change in the internal energy, U of gas 1 and gas 2 in the process. (2 points)

(d) Given your answers above, explain the source of energy for the work done during the expansion. (2 points)

a) $P_1 = P_2$ at equil, & $T_1 = T_2$

$P = -\frac{\partial F}{\partial V}\Big|_{\text{const } N,T}$ so $P = -\frac{NkT}{V}$

at equil: $\frac{N_1kT_1}{V_1} = \frac{N_2kT_2}{V_2}$ since $N_1 = N_2$ & $T_1 = T_2$, $V_1 = V_2$ at equil

($V_1 = V_2 = \frac{1}{2}V_{tot}$ at equil)

b) $W = \int PdV = NkT\int\frac{1}{V}dV = NkT\ln\left(\frac{V_f}{V_i}\right) = NkT\ln\left(\frac{\frac{1}{2}V}{\frac{1}{3}V}\right) = NkT\ln\left(\frac{3}{2}\right)$

c) $\Delta U = \Delta F + T\Delta S + \cancel{S\Delta T}^{0}$ or $dE = dF + TdS$

$S = -\frac{\partial F}{\partial T} = -Nk\left\{A - \ln\frac{T^{3/2}V}{N}\right\} + \frac{3}{2}Nk$

$dS = \frac{Nk}{V}dV$ $\quad dF = -\frac{NkT}{V}dV$ $\Big\}$ since only V changes

$dE = dF + TdS$

$= -\frac{NkT}{V}dV + \frac{NkT}{V}dV$

$= 0$ no change in internal energy!

d) Side 2 had to be at a higher pressure initially, since it had same N & T but smaller V. The higher pressure pushed the pistons till pressure equalized, at $V_1 = V_2$.