

## Pathria + Beale, Chapter 3

### Problem 3.5

The statement that the Helmholtz free energy is extensive can be expressed as

$$A(\lambda N, \lambda V, T) = \lambda A(N, V, T)$$

Differentiating with respect to  $\lambda$  and then setting  $\lambda = 1$  gives

$$\left(\frac{\partial A}{\partial N}\right)_{VT} N + \left(\frac{\partial A}{\partial V}\right)_{NT} V = A$$

The thermodynamic relation for  $A$  is

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

We can use this to identify the partial derivatives:

$$\left(\frac{\partial A}{\partial N}\right)_{VT} = \mu \quad \left(\frac{\partial A}{\partial V}\right)_{NT} = -P$$

Our identity then becomes

$$\mu N - PV = A$$

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Problem 3.6

(a) If the total number of accessible microstates is  $\Omega$ , they can be labeled  $i=1, 2, \dots, \Omega$ . If the probability of microstate  $i$  is  $P_i$ , the entropy is

$$S = - \sum_{i=1}^{\Omega} P_i \log P_i$$

The sum of the probabilities is  $\sum_{i=1}^{\Omega} P_i = 1$ .

We can regard  $S$  as a function of all the numbers  $P_i$  subject to the constraint  $\sum_{i=1}^{\Omega} P_i = 1$ . To find the probabilities that maximize  $S$ , we can introduce a Lagrange multiplier  $\alpha$  and look for a stationary point of the variational function  $S(P) + \alpha \left( \sum_{i=1}^{\Omega} P_i - 1 \right)$ . If we vary all the  $P_i$ 's, the variation of  $S$  is

$$\begin{aligned} \delta S &= \sum_{i=1}^{\Omega} \left( \delta P_i \log P_i + P_i \cdot \frac{1}{P_i} \delta P_i \right) \\ &= \sum_{i=1}^{\Omega} (\log P_i + 1) \delta P_i \end{aligned}$$

If we vary all the  $P_i$ 's and  $\alpha$ , the variation of the variational function is

$$\begin{aligned} \delta \left( S + \alpha \left( \sum_{i=1}^{\Omega} P_i - 1 \right) \right) &= \delta S + \alpha \left( \sum_{i=1}^{\Omega} \delta P_i \right) + \delta \alpha \left( \sum_{i=1}^{\Omega} P_i - 1 \right) \\ &= \sum_{i=1}^{\Omega} (\log P_i + 1 + \alpha) \delta P_i + \delta \alpha \left( \sum_{i=1}^{\Omega} P_i - 1 \right) \end{aligned}$$

If  $S$  is a stationary point, the coefficient of each  $\delta P_i$  and the coefficient of  $\delta \alpha$  must all be 0:

$$\log P_i + 1 + \alpha = 0 \quad i=1, \dots, \Omega$$

$$\sum_{i=1}^{\Omega} P_i = 1$$

The first equation implies that all the probabilities have the same value:

$$P_i = e^{-1-\alpha}$$

The second equation provides a more useful expression for the probabilities:

$$P_i = \frac{1}{\Omega}$$

(b) If we have an ensemble of systems for which the mean value of the energy is  $\bar{E}$ , we have an additional constraint on the probabilities:

$$\sum_{i=1}^{\Omega} P_i E_i = \bar{E}$$

To maximize the entropy subject to both constraints, we introduce a second Lagrange multiplier  $\beta$ . The variational function is



$$S(P) + \alpha \left( \sum_{i=1}^{\Omega} P_i - 1 \right) + \beta \left( \sum_{i=1}^{\Omega} P_i E_i - \bar{E} \right)$$

Its variation is

$$\begin{aligned} \delta S + \alpha \left( \sum_{i=1}^{\Omega} \delta P_i \right) + \delta \alpha \left( \sum_{i=1}^{\Omega} P_i - 1 \right) \\ + \beta \left( \sum_{i=1}^{\Omega} \delta P_i E_i \right) + \delta \beta \left( \sum_{i=1}^{\Omega} P_i E_i - \bar{E} \right) \\ = \sum_{i=1}^{\Omega} (\log P_i + 1 + \alpha + \beta E_i) \delta P_i + \delta \alpha \left( \sum_{i=1}^{\Omega} P_i - 1 \right) + \delta \beta \left( \sum_{i=1}^{\Omega} P_i E_i - \bar{E} \right) \end{aligned}$$

For  $S$  to be a stationary point, the coefficient of each  $\delta P_i$  and the coefficients of  $\delta \alpha$  and  $\delta \beta$  must all be 0:

$$\log P_i + 1 + \alpha + \beta E_i = 0 \quad i=1, \dots, \Omega$$

$$\sum_{i=1}^{\Omega} P_i = 1$$

$$\sum_{i=1}^{\Omega} P_i E_i = \bar{E}$$

The solution to the first equation is  $P_i = e^{-1-\alpha-\beta E_i}$ .

This can be expressed as

$$P_i = \frac{1}{Z} e^{-\beta E_i}$$

The other two equations determine  $Z$  and  $\beta$ :

$$Z = \sum_{i=1}^{\Omega} e^{-\beta E_i} \quad \frac{1}{Z} \sum_{i=1}^{\Omega} E_i e^{-\beta E_i} = \bar{E}$$

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Problem 3.15

The Hamiltonian for an ultrarelativistic of  $N$  particles confined to a volume  $V$  is

$$H = \sum_{i=1}^N |\vec{p}_i| c$$

Since there are no interactions between the particles, the partition function for inverse temperature  $\beta = \frac{1}{kT}$  can be expressed as

$$Z_N = \frac{1}{N!} Z_1^N$$

where  $Z_1$  is the partition function for 1 particle:

$$\begin{aligned} Z_1 &= \frac{1}{(2\pi\hbar)^3} \int d^3x \int d^3p e^{-\beta |\vec{p}| c} \\ &= \frac{1}{(2\pi\hbar)^3} V \int_0^\infty 4\pi p^2 dp e^{-\beta p c} \\ &= \frac{1}{(2\pi\hbar)^3} V 4\pi \cdot \frac{2}{(\beta c)^3} \end{aligned}$$

The partition function for the  $N$  particles is then

$$Z_N = \frac{1}{N!} \left( \frac{8\pi V}{(2\pi\hbar\beta c)^3} \right)^N$$

Sterling's approximation for  $\log N!$  can be expressed in the form  $N! \approx (N/e)^N$ . The logarithm of the partition function can then be expressed as

$$\log Z_N = N \log \left( \frac{8\pi e V/N}{(2\pi k\beta)^3} \right)$$

The average energy is

$$\begin{aligned} U &= -\frac{\partial}{\partial \beta} \log Z_N \\ &= -N \frac{\partial}{\partial \beta} (-3 \log \beta) \\ &= 3N \frac{1}{\beta} = 3NkT \end{aligned}$$

The Helmholtz free energy is

$$F = -\frac{1}{\beta} N \log \left( \frac{8\pi e V/N}{(2\pi k\beta)^3} \right)$$

The thermodynamic relation for  $F$  is

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

The pressure is therefore

$$\begin{aligned} P &= -\left( \frac{\partial F}{\partial V} \right)_{T,N} \\ &= \frac{1}{\beta} N \frac{\partial}{\partial V} (\log V) \end{aligned}$$

$$= NkT \frac{1}{V}$$

This is the ideal gas law. It implies  $PV = \frac{1}{3}U$

The specific heat at constant volume is

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

$$= 3Nk$$

The enthalpy is

$$H = U + PV = \frac{4}{3}U = 4NkT$$

The specific heat at constant pressure is

$$C_P = T \left( \frac{\partial S}{\partial T} \right)_{P,N} = \left( \frac{\partial H}{\partial T} \right)_{P,N}$$

$$= 4Nk$$

The adiabatic ratio is

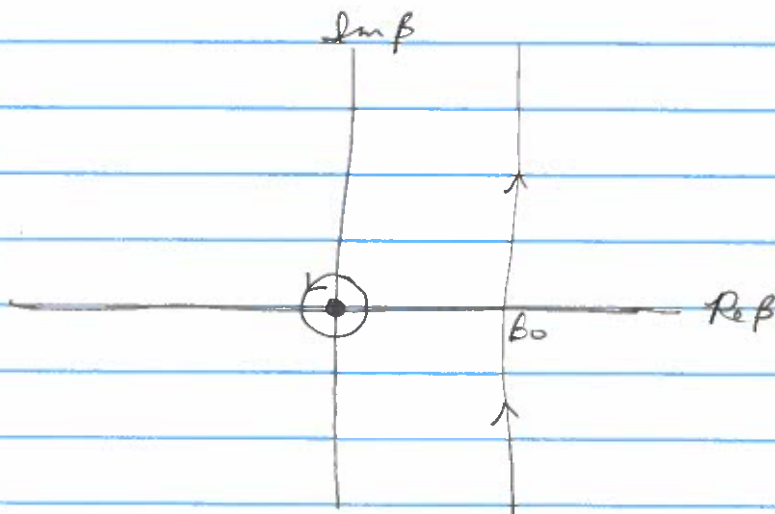
$$\gamma = \frac{C_P}{C_V} = \frac{4}{3}$$



The density of states  $g(E)$  for the system can be obtained from the partition function  $Z(\beta)$  by an inverse Laplace transform:

$$g(E) = \frac{1}{2\pi i} \int_{\beta_0 - i\infty}^{\beta_0 + i\infty} d\beta e^{\beta E} Z(\beta)$$

The integration contour runs along a vertical line in the complex  $\beta$  plane with real part  $\beta_0 > 0$ .



If  $E > 0$ , the factor  $e^{\beta E}$  decreases as  $\text{Re } \beta$  increases.

The contour can therefore be moved to the right to  $\text{Re } \beta \rightarrow +\infty$ , where the integral is 0.

If  $E < 0$ , the factor  $e^{\beta E}$  decreases as  $\text{Re } \beta$  decreases. The contour can therefore be moved to the left. It gives a contour wrapped around  $\beta = 0$ , plus a contour at  $\text{Re } \beta \rightarrow -\infty$ , where the integral is 0. The integral along the contour around  $\beta = 0$  is



$$\begin{aligned}
 g(E) &= \frac{1}{N!} \left( \frac{8\pi V}{(2\pi\hbar c)^3} \right)^N \underbrace{\frac{1}{2\pi i} \oint d\beta e^{\beta E} \frac{1}{\beta^{3N}}}_{\frac{1}{2\pi i} \oint d\beta \frac{(\beta E)^{3N-1}}{(3N-1)!} \frac{1}{\beta^{3N}}} \\
 &= \frac{E^{3N-1}}{(3N-1)!} \frac{1}{2\pi i} \oint d\beta \frac{1}{\beta} = \frac{E^{3N-1}}{(3N-1)!}
 \end{aligned}$$

The density of states for large  $N$  is therefore

$$g(E)dE = \frac{1}{N!(3N)!} \left( \frac{8\pi V E^3}{(2\pi\hbar c)^3} \right)^N \frac{dE}{E}$$

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### Problem 3.17

We represent the Boltzmann-weighted average of a function  $F(p, q)$  of the phase-space variables by

$$\langle F(p, q) \rangle = \frac{\int F(p, q) e^{-\beta H(p, q)} d\omega}{\int e^{-\beta H(p, q)} d\omega}$$

The equation  $\langle H \rangle = U$  implies

$$\int (U - H(p, q)) e^{-\beta H(p, q)} d\omega = 0$$

Differentiating with respect to  $\beta$  gives

$$\int \left[ \frac{\partial U}{\partial \beta} e^{-\beta H} + (U - H)(-H e^{-\beta H}) \right] d\omega = 0$$

Dividing by  $\int d\omega e^{-\beta H}$ , we get

$$\frac{\partial U}{\partial \beta} - U \langle H \rangle + \langle H^2 \rangle = 0$$

$$\frac{\partial U}{\partial \beta} - U^2 + \langle H \rangle^2 = 0$$

The mean-square fluctuation in the energy is

$$\begin{aligned} \langle (H - U)^2 \rangle &= \langle H^2 \rangle - 2U \langle H \rangle + U^2 \\ &= \langle H^2 \rangle - U^2 \end{aligned}$$

This can be expressed in terms of a derivative of  $U$  with respect to  $\beta = 1/kT$ :

$$\begin{aligned}\langle (H-U)^2 \rangle &= -\frac{\partial U}{\partial \beta} \\ &= -\left(-kT^2 \frac{\partial U}{\partial T}\right) \\ &= kT^2 \frac{\partial U}{\partial T} \\ &= kT^2 C_V\end{aligned}$$



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Problem 3.20

The Hamiltonian is the sum of the kinetic energy  $K$ , the external potential energy  $V_{\text{ext}}$  that confines particles to a volume  $V$ , and an interaction potential energy  $U_{\text{int}}$ :

$$H = K + V_{\text{ext}} + U_{\text{int}}$$

The interaction potential energy is a homogeneous function of degree  $n$  in the coordinates:

$$\sum_{\alpha} q_{\alpha} \frac{\partial}{\partial q_{\alpha}} U = n U$$

The kinetic energy is a homogeneous function of degree 2 in the momenta:

$$\sum_{\alpha} p_{\alpha} \frac{\partial}{\partial p_{\alpha}} K = 2K$$

If the only coordinates are the  $3N$  Cartesian coordinates for  $N$  particles, the equipartition function applied to the momenta gives

$$\begin{aligned} \sum_{\alpha} \left\langle p_{\alpha} \frac{\partial}{\partial p_{\alpha}} H \right\rangle &= 3N \cdot kT \\ &= \sum_{\alpha} \left\langle p_{\alpha} \frac{\partial}{\partial p_{\alpha}} K \right\rangle = 2 \langle K \rangle \end{aligned}$$

The virial is

$$\begin{aligned} \mathcal{V} &= \left\langle \sum_{\alpha} q_{\alpha} p_{\alpha} \right\rangle \\ &= \sum_{\alpha} \left\langle q_{\alpha} \left( -\frac{\partial H}{\partial q_{\alpha}} \right) \right\rangle \\ &= - \sum_{\alpha} \left\langle q_{\alpha} \frac{\partial}{\partial q_{\alpha}} V_{\text{ext}} + q_{\alpha} \frac{\partial}{\partial q_{\alpha}} U_{\text{int}} \right\rangle \end{aligned}$$

The interaction term is simple:

$$\sum_{\alpha} \left\langle q_{\alpha} \frac{\partial}{\partial q_{\alpha}} U_{\text{int}} \right\rangle = n \langle U_{\text{int}} \rangle$$

The confining term is the sum of  $N$  terms, one for each particle. The term for one particle is

$$\begin{aligned} \langle \vec{r} \cdot \vec{\nabla} V_{\text{ext}} \rangle &= \int d^3r \vec{r} \cdot (\nabla V_{\text{ext}}) e^{-\beta V_{\text{ext}}} / \int d^3r e^{-\beta V_{\text{ext}}} \\ &= -\frac{1}{\beta} \int d^3r \vec{r} \cdot \nabla (e^{-\beta V_{\text{ext}}}) / \int d^3r e^{-\beta V_{\text{ext}}} \end{aligned}$$

If we integrate by parts, the surface term is 0, and we are left with

$$\begin{aligned} \langle \vec{r} \cdot \vec{\nabla} V_{\text{ext}} \rangle &= \frac{1}{\beta} \int d^3r (\nabla \cdot \vec{r}) e^{-\beta V_{\text{ext}}} / \int d^3r e^{-\beta V_{\text{ext}}} \\ &= \frac{1}{\beta} 3 = 3 kT \end{aligned}$$

The complete confining term is

$$\sum_{\alpha} \left\langle q_{\alpha} \frac{\partial}{\partial q_{\alpha}} V_{\text{ext}} \right\rangle = 3NkT$$

The virial is therefore

$$\mathcal{V} = -3NkT - n \langle U_{\text{int}} \rangle$$

Using the ideal gas law  $PV = NkT$ , this can be expressed as

$$\mathcal{V} = -3PV - n \langle U_{\text{int}} \rangle$$

The equipartition theorem applied to the  $3N$  Cartesian coordinates gives an alternative expression for the virial.

$$\begin{aligned} \mathcal{V} &= - \sum_{\alpha} \left\langle q_{\alpha} \frac{\partial H}{\partial q_{\alpha}} \right\rangle \\ &= -3N \cdot kT \end{aligned}$$

The expression for the kinetic energy is  $\langle K \rangle = \frac{3}{2}NkT$   
Thus the virial can also be expressed as

$$\mathcal{V} = -2 \langle K \rangle$$

The total energy is  $\langle H \rangle = \langle K \rangle + \langle U_{\text{int}} \rangle$ . We can easily verify the final expression for  $\mathcal{V}$ :

$$\begin{aligned} \mathcal{V} &= - \frac{2}{n+2} \left[ 3PV + n \left( \langle K \rangle + \langle U_{\text{int}} \rangle \right) \right] \\ &= \frac{2}{n+2} \left[ -3PV - n \langle U_{\text{int}} \rangle \right] + \frac{n}{n+2} \left[ -2 \langle K \rangle \right] \end{aligned}$$