

Physics 210A — Spring 2024
Problem Set #2 Solutions

1. Classical ideal gas

(a) The partition function is

$$\begin{aligned}
 Z(\beta, V, N) &= \frac{V^N}{h^{3N} N!} \prod_{i=1}^N \int d^3 p_i \exp \left[-\beta \sum_{i=1}^N \frac{p_i^2}{2m} \right] \\
 &= \frac{V^N}{h^{3N} N!} \left[\int d^3 p \exp \left(-\beta \frac{p^2}{2m} \right) \right]^N \\
 &= \frac{V^N}{N!} \left(\frac{2\pi m}{h^2 \beta} \right)^{3N/2} = \frac{1}{N!} \frac{V^N}{\lambda_T^{3N}},
 \end{aligned} \tag{1}$$

where $\lambda_T = h/\sqrt{2\pi m k_B T}$ is the thermal deBroglie wavelength.

(b) The density of states is given by

$$\Omega(E, V, N) = \int_{-i\infty}^{i\infty} e^{\beta E} Z(\beta, V, N). \tag{2}$$

This integral may be evaluated using the integration contours shown in Fig. 1. For N even, $Z(\beta)$ has a pole at the origin, whereas for N odd it has a branch cut along the negative real axis. In either case, we obtain

$$\Omega(E, V, N) = \frac{V^N}{N!} \left(\frac{2\pi m}{h^2} \right)^{3N/2} \frac{E^{3N/2-1}}{\Gamma(3N/2)}, \tag{3}$$

which is the correct result.

(c) In the thermodynamic limit,

$$\ln Z(\beta, V, N) = N \left[\ln V + \frac{3}{2} \ln \left(\frac{2\pi m}{h^2 \beta} \right) - \ln N + 1 \right]. \tag{4}$$

The energy is

$$E = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2} N k_B T, \tag{5}$$

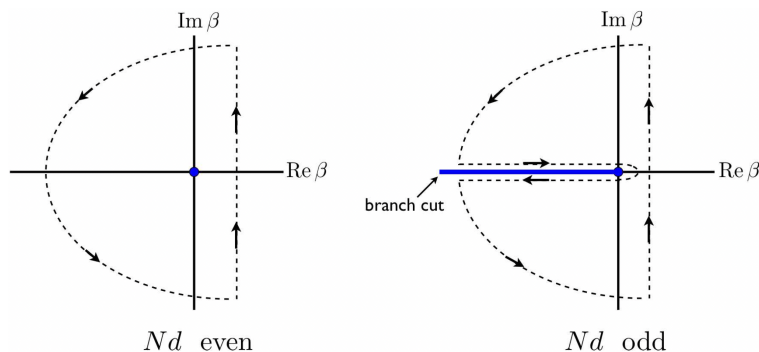


Figure 1: Complex integration contours for inverse Laplace transform.

as expected. So $\beta = \frac{3}{2}N/E$ and

$$S(E, V, N)/k_B = \ln Z[\beta(E), V, N] + \beta(E)E = N \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi m E}{3h^2 N} \right)^{3/2} \right] + \frac{5}{2} \right\}. \quad (6)$$

(d) We have

$$S(T, V, N)/k_B = \ln Z + \beta E = N \left\{ \ln \left[\frac{V}{N} \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} \right] + \frac{5}{2} \right\}, \quad (7)$$

and

$$P(T, V, N) = -\frac{\partial F}{\partial V} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{k_B T N}{V}. \quad (8)$$

Also, $E = \frac{3}{2}Nk_B T$, so the specific heat is $C_V = \frac{3}{2}Nk_B$. From the lecture,

$$\langle (\mathcal{H} - E)^2 \rangle = k_B T^2 C_V = \frac{3}{2}Nk_B^2 T^2. \quad (9)$$

2. Isobaric ensemble

(a) Let the height of the piston be z and its momentum p_z . Thermodynamic averages take the form

$$\langle \mathcal{O} \rangle = \frac{\int dz \int dp_z e^{-\beta(p_z^2/2m + Mgz)} \int d\Gamma \mathcal{O} e^{-\beta H_N(\Gamma)}}{\int dz \int dp_z e^{-\beta(p_z^2/2m + Mgz)} \int d\Gamma e^{-\beta H_N(\Gamma)}}. \quad (10)$$

The kinetic energy terms for the piston cancel out. The potential energy term may be rewritten as $Mgz = PV$ where $V = Az$ is the of fluid volume enclosed by the piston and $P = Mg/A$ is the pressure it exerts on the fluid. We then obtain

$$\langle \mathcal{O} \rangle = \frac{\int dV e^{-\beta PV} \int d\Gamma \mathcal{O} e^{-\beta H_N(\Gamma)}}{Q(\beta, P, N)}, \quad (11)$$

where

$$Q(\beta, P, N) = \int dV e^{-\beta PV} \int d\Gamma e^{-\beta H_N(\Gamma)} = \int dV e^{-\beta PV} Z(\beta, V, N) \quad (12)$$

is the isobaric partition function.

(b) We have

$$Q(\beta, P, N) = \int_0^\infty dV e^{-\beta PV + \ln Z(\beta, V, N)}. \quad (13)$$

The saddle point \bar{V} is determined by

$$\frac{\partial}{\partial \bar{V}} [-\beta P \bar{V} + \ln Z(\beta, \bar{V}, N)] = 0 \rightarrow P = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \bar{V}}. \quad (14)$$

Hence,

$$Q(\beta, P, N) \sim e^{-\beta P \bar{V} + \ln Z(\beta, \bar{V}, N)}, \quad (15)$$

or

$$G(\beta, P, N) = F(\beta, \bar{V}, N) + P \bar{V}, \quad (16)$$

with $P = -\frac{\partial F}{\partial \bar{V}}$. As expected, G and F are related by a Legendre transform.

(c) We have

$$dG = dF + d(PV) = -SdT - PdV + PdV + VdP = -SdT + VdP, \quad (17)$$

which implies

$$S = - \left(\frac{\partial G}{\partial T} \right)_{P,N}, V = \left(\frac{\partial G}{\partial P} \right)_{T,N}. \quad (18)$$

(d) In analogy to calculating energy fluctuations, we have

$$\langle (V - \bar{V})^2 \rangle = \frac{1}{\beta^2} \frac{\partial^2 \ln Q}{\partial P^2}. \quad (19)$$

Noting that $V = -\frac{1}{\beta} \frac{\partial \ln Q}{\partial P}$, the thermal compressibility is

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,N} = \frac{1}{\beta V} \frac{\partial^2 \ln Q}{\partial P^2} = \frac{\beta}{V} \langle (V - \bar{V})^2 \rangle, \quad (20)$$

which is the desired relation.

(e) The probability distribution of volumes is

$$p(V) = \frac{e^{-\beta PV} Z(\beta, V, N)}{Q(\beta, P, N)} = \frac{e^{-\beta PV + \ln Z(\beta, V, N)}}{Q(\beta, P, N)}. \quad (21)$$

We expand the numerator to quadratic order in $V - \bar{V}$:

$$p(V) = p(\bar{V}) \exp \left[\frac{1}{2} \frac{\partial^2 \ln Z(\beta, \bar{V}, N)}{\partial \bar{V}^2} (V - \bar{V})^2 \right]. \quad (22)$$

The linear term vanishes since $P = -\frac{\partial F}{\partial V}$, and

$$\frac{\partial^2 \ln Z(\beta, \bar{V}, N)}{\partial \bar{V}^2} = \beta \frac{\partial P}{\partial \bar{V}} = -\frac{\beta}{\bar{V} \kappa_T}. \quad (23)$$

Therefore,

$$p(V) = p(\bar{V}) \exp \left[-\frac{\beta}{2\bar{V} \kappa_T} (V - \bar{V})^2 \right]. \quad (24)$$

3. Anharmonic oscillator

The partition function is

$$\begin{aligned} Z(\beta, N) &= \frac{1}{h^N N!} \prod_{i=1}^N \int dp_i \int dx_i \exp \left[-\beta \sum_{i=1}^N \left(\frac{p_i^2}{2m} + \frac{\epsilon_0 |x_i|^n}{a^n} \right) \right] \\ &= \frac{1}{h^N N!} \left[\int dp \exp \left(-\beta \frac{p^2}{2m} \right) \int dx \exp \left(-\beta \frac{\epsilon_0 |x|^n}{a^n} \right) \right]^N \\ &= \frac{1}{h^N N!} \left[\left(\frac{2\pi m}{\beta} \right)^{1/2} \frac{2a}{n(\beta \epsilon_0)^{1/n}} \int_0^\infty du u^{1/n-1} e^{-u} \right]^N \\ &= \frac{1}{h^N N!} \left[\frac{2a \Gamma(1/n) (2\pi m)^{1/2}}{\epsilon_0^{1/n} \beta^{1/2+1/n}} \right]^N. \end{aligned} \quad (25)$$

The average thermal energy is

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \left(\frac{1}{2} + \frac{1}{n}\right)Nk_B T. \quad (26)$$

Note that for $n = 2$ the kinetic and potential energies each contribute $\frac{1}{2}k_B T$ per oscillator, in accordance with the equipartition theorem.

4. Polymer elasticity

- (a) The Hamiltonian is simply the potential energy of the end monomer due to the applied force. Up to an arbitrary constant, it is (noting that $\mathbf{r}_0 = 0$)

$$\mathcal{H} = -\mathbf{f} \cdot \mathbf{r}_N = -\sum_{i=1}^N \mathbf{f} \cdot \mathbf{a}_i. \quad (27)$$

- (b) Since the links have fixed length a , we may write the Hamiltonian as

$$\mathcal{H} = -fa \sum_{i=1}^N \cos \theta_i, \quad (28)$$

where θ_i is the angle between \mathbf{f} and \mathbf{a}_i . The partition function is given by averaging $\exp(-\beta\mathcal{H})$ over the solid angle of each link:

$$\begin{aligned} Z(\beta, f) &= \prod_{i=1}^N \frac{1}{4\pi} \int_{-1}^1 d \cos \theta_i \int_0^{2\pi} d\phi_i \exp\left(\beta fa \sum_{i=1}^N \cos \theta_i\right) \\ &= \left[\frac{1}{2} \int_{-1}^1 d \cos \theta e^{\beta fa \cos \theta}\right]^N = \left[\frac{\sinh(\beta fa)}{\beta fa}\right]^N \end{aligned} \quad (29)$$

The free energy is

$$F(\beta, f) = -\frac{1}{\beta} \ln Z = -\frac{N}{\beta} \ln \left[\frac{\sinh(\beta fa)}{\beta fa}\right] = -\frac{N}{\beta} \ln \left[1 + \frac{(\beta fa)^2}{6} + \dots\right] = -\frac{N\beta a^2}{6} f^2 + \dots \quad (30)$$

- (c) The average displacement of the end of the polymer is

$$\langle \mathbf{R} \rangle = \left\langle \sum_{i=1}^N \mathbf{a}_i \right\rangle = \frac{1}{\beta} \nabla_{\mathbf{f}} \ln Z = -\nabla_{\mathbf{f}} F = \frac{Na^2}{3k_B T} \mathbf{f}. \quad (31)$$

This is elastic behavior because the displacement is proportional to the force. It is entirely an entropic effect: as the two ends of the polymer get further apart the number of available microstates and hence the entropy of the polymer decrease. This results in an effective restoring force as the system tries to maximize its entropy.

5. DNA denaturation bubble

- (a) The probability $p_L(n)$ is simply the binomial distribution with probability $p = 1/2$, so

$$p_L(n) = \binom{L}{n} \frac{1}{2^L}. \quad (32)$$

There are $N - L + 1 \approx N$ locations to place the bubble in the strand. The energy of a bubble with n broken G/C pairs is $E = n\Delta\epsilon$. In the annealed approximation, each starting position is treated independently, so the expected number of states with energy E is given by multiplying N by the probability that a segment of length L has $n = E/\Delta\epsilon$ G/C pairs, which is $p_L(E/\Delta\epsilon)$. Therefore,

$$\Omega(E, L, N) = Np_L(E/\Delta\epsilon). \quad (33)$$

In the limit $L, n \gg 1$,

$$\ln \binom{L}{n} \simeq L \ln L - n \ln n - (L - n) \ln(L - n) = -n \ln(n/L) - (L - n) \ln(1 - n/L). \quad (34)$$

The entropy is

$$S(E, L, N)/k_B = \ln \Omega(E, L, N) = \ln N - Lf(E/E_0), \quad (35)$$

with

$$f(x) = \ln 2 + x \ln x + (1 - x) \ln(1 - x). \quad (36)$$

- (b) The entropy for different values of L is plotted versus energy in Fig. 2(a). The entropy has a maximum at $E = E_0/2$ and is symmetric about this point. For large enough L , it can become negative below a critical energy E_c . The energy E_c is given by solving $S(E_c, L, N) = 0$ and depends on the ratio $\ln N/L$. Since the maximum value of $f(x)$ is $\ln 2$, a solution E_c will exist provided $\ln N/L < \ln 2$, or $N < 2^L$. We plot the numerical solution for E_c versus $\ln N/L$ in Fig. 2(b).
- (c) The average energy \bar{E} is the point at which a line of slope β is tangent to the curve defined by $S(E)$, and the free energy is the x-intercept of this line. This is shown in Fig. 3. As $T \rightarrow \infty$, the entropy approaches its maximum value $S/k_B = \ln N$. Physically, this means that the bubble is equally likely to be in any of the N positions along the strand.
- (d) Using the same approximation as in part a, the partition function is

$$Z = N \sum_{n=0}^L e^{-\beta n \Delta\epsilon} p_L(n) = \frac{N}{2^L} \sum_{n=0}^L \binom{L}{n} e^{-\beta n \Delta\epsilon} = \frac{N}{2^L} (1 + e^{-\beta \Delta\epsilon})^L. \quad (37)$$

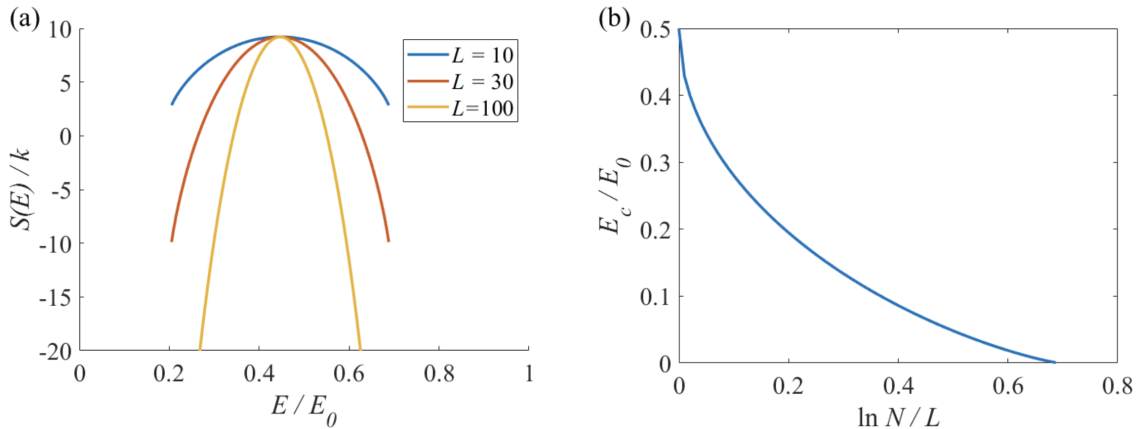


Figure 2: (a) Entropy versus energy for different values of L and $N = 10^4$. (b) Energy E_c versus $\ln N/L$.

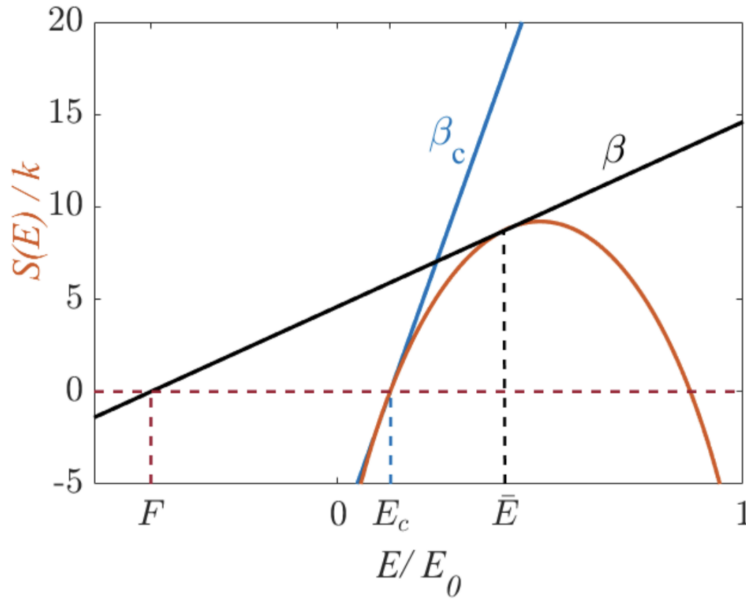


Figure 3: Graphical construction for finding the average energy and free energy from $S(E)$ for $N = 10^4$, $L = 30$.

The average energy is

$$E = -\frac{\partial \ln Z}{\partial \beta} = \frac{E_0}{1 + e^{\beta \Delta \epsilon}}, \quad (38)$$

and the entropy is

$$S = \ln Z + \beta E = \ln N + L \left[\frac{\beta \Delta \epsilon}{1 + e^{\beta \Delta \epsilon}} + \ln(1 + e^{-\beta \Delta \epsilon}) - \ln 2 \right]. \quad (39)$$

Solving Eq. (38) for $\beta(E)$ and substituting into Eq. (39), we obtain the expression of part a.

- (e) The critical length L_c is given by solving $S(T, L_c, N) = 0$:

$$L_c = \frac{\ln N}{\ln 2 - \beta \Delta \epsilon / (1 + e^{\beta \Delta \epsilon}) - \ln(1 + e^{-\beta \Delta \epsilon})}. \quad (40)$$

For the given values, we find $L_c = 36$.

- (f) As shown in Fig. 3, β_c is simply the slope of the tangent line to S at E_c . From part b, a solution exists provided $N < 2^L$.
- (g) Physically, the approximation breaks down because, at sufficiently low temperatures, the bubble becomes localized to a single location on the strand which has the lowest energy. See also Hwa et al., *Proc. Nat. Acad. Sci.* **100**, 4411-4416 (2003).