Homework 2: Phys 7230 (Spring 2022)

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***Problem* 1** (Statistical mechanics and thermodynamic relations)**:** (a) Given the basic definitions of the partition function and of the average energy in the canonical ensemble, derive the average energy relation, $E = -\partial(\ln Z)/\partial\beta$.

(b) Given the definition of Helmholtz free energy $F = -k_B T \ln Z$ and above result for the average energy E, derive the relation $F = E - TS$. *Hint*: Note that the above expression for F is equivalent to $\ln Z = -\beta F$ and from thermodynamics $S = -\left.\partial F/\partial T\right|_{N,V}$, a relation that you will derive below.

(c) From the above Legendre transform relation (also discussed in the lectures) between $E(S)$ and $F(T)$, and the 1st law of thermodynamics for e.g., a gas, namely $dE = TdS - PdV + \mu dN$, derive dF and identify from it the thermodynamic expressions for S, P, and μ, as well as the heat capacity C_v.

(d) In lecture, we discussed the equivalence of canonical and microcanonical ensembles, with the key relation expressing the partition function Z as an integration over energies (rather than microstates) weighted by the density of states $g(E) = \sum_{\{q_i\}} \delta(E - H_q)$,

$$\begin{aligned} Z(\beta) = \sum_{\{q_i\}} e^{-\beta H_q} &= \int dE \sum_{\{q_i\}} \delta(E - H_q) e^{-\beta E}, \\ &= \int dE g(E) e^{-\beta E}, \end{aligned} \tag{1.1}$$

related to multiplicity of the microcanonical ensemble, $\Omega(E) = \Delta g(E)$.

Recall our argument that $g(E)$ is generically an extremely fast growing function of E and therefore above integrand is highly peaked function around average energy E_0, set by the peak. This condition is prime for the saddle-point method evaluation of the integral over E.

(i) By applying the lowest order saddle-point approximation and using the definition of S, show that this gives $Z \approx e^{-\beta F}$, where $F = E - TS$ from above and the standard thermodynamic relation.

(ii) By expanding a logarithm of the integrand in Taylor series to quadratic order around its maximum E_0, derive the general expression for the width of this peaked integrand, and use it to argue that indeed in the thermodynamic limit the width is vanishingly small relative to E_0. *Hint*: (i) What happens to the 1st order term? (ii) What is the general expression for heat capacity in the microcanonical ensemble?

Solution.

(a) From the Boltzmann-Gibbs probability distribution, we can calculate the average energy

$$E = \frac{1}{Z}\sum_{\{q_i\}} H_q e^{-\beta H_q} = -\frac{1}{Z}\sum_{\{q_i\}} \frac{\partial(e^{-\beta H_q})}{\partial\beta} = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\frac{\partial(\ln Z)}{\partial\beta} \tag{1.2}$$

(b) First note that we can write $\beta F = -\ln Z$. Plugging this into the previous result yields

$$F + \beta\frac{\partial F}{\partial\beta} = F + T\frac{\partial F}{\partial T} - \frac{\partial(\ln Z)}{\partial\beta} = E \tag{1.3}$$

(d) First, we write $Z(\beta) = \int_0^\infty dE e^{-f(E)}$ where

$$f(E) = \beta E - \ln g(E) \approx \beta E_0 - \ln g(E_0) + \frac{1}{2}f''(E_0)(E - E_0)^2 \tag{1.4}$$

with E_0 satisfying $g'(E_0) = \beta g(E_0)$ and

$$f''(E_0) = \left[\frac{g'(E_0)}{g(E_0)}\right]^2 - \frac{g''(E_0)}{g(E_0)} = \beta^2 - \frac{g''(E_0)}{g(E_0)} \tag{1.5}$$

being a constant. (i) To the lowest order, we can then write

$$\begin{aligned} Z(\beta) &\approx g(E_0)e^{-\beta E_0}\int_0^\infty dE e^{-(1/2)f''(E-E_0)^2} \\ &= \sigma\sqrt{\frac{\pi}{2}}g(E_0)e^{-\beta E_0}\left[\frac{1}{\sigma\sqrt{2\pi}}\int_{-\infty}^{\infty} dE \exp\left[-\frac{1}{2}\left(\frac{E-E_0}{\sigma}\right)^2\right]\right] \\ &= \sqrt{\frac{\pi}{8}}(2\sigma)g(E_0)e^{-\beta E_0} \end{aligned} \tag{1.6}$$

where we have set $f''(E_0) = 1/\sqrt{\sigma}$ and the integration of the Gaussian distribution in the square bracket equates to unity. Now, note that the full width of the (approximately) Gaussian distribution around $E = E_0$ is $\Delta = 2\sigma$. Letting $E = \langle E\rangle = E_0$, we can write

$$Z(\beta) = \sqrt{\frac{\pi}{8}}\Omega(E)e^{-\beta E} = \sqrt{\frac{\pi}{8}}e^{S/k_B - \beta E} = \sqrt{\frac{\pi}{8}}e^{\beta(TS-E)} = 0.6e^{-\beta F} \approx e^{-\beta F} \tag{1.7}$$

(ii) The entropy is $S(E) = k_B\ln\Omega = k_B\ln[\Delta g(E)]$. So by calculating the temperature,

$$\beta = \frac{\partial(S/k_B)}{\partial E} = \frac{g'(E)}{g(E)} \tag{1.8}$$

Differentiating once more, we get

$$g''(E) = \beta g'(E) + g(E)\frac{\partial}{\partial E}\left(\frac{1}{k_B T}\right) = \beta g'(E) - \beta^2 k_B g(E)\frac{\partial T}{\partial E} = \beta g'(E) - g(E)\frac{\beta^2 k_B}{C_v} \tag{1.9}$$

Then, from (1.5),

$$\frac{1}{\sqrt{\sigma}} = f''(E) = \beta^2 \frac{k_B}{C_v} \tag{1.10}$$

But from equipartition theorem, $C_v = Nk_B$ and $E = (N/2)k_BT$. Thus, the width of the peak is

$$\sigma = \frac{1}{\beta}\sqrt{\frac{C_v}{k_B}} = \frac{2E}{\sqrt{N}} \Rightarrow \frac{\Delta}{E} = \sqrt{\frac{2}{N}} \to 0 \tag{1.11}$$

in the thermodynamic limit ($N \gg 1$). $\square$

***Problem* 2:** *Solution.*

$\square$