PHYSICS 140A : STATISTICAL PHYSICS
HW SOLUTIONS #4

(1) Consider a noninteracting classical gas with Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \varepsilon(\boldsymbol{p}_i) ,$$

where $\varepsilon(\boldsymbol{p})$ is the dispersion relation. Define

$$\xi(T) = h^{-d} \int d^d p \, e^{-\varepsilon(\boldsymbol{p})/k_B T} .$$

(a) Find $F(T, V, N)$.

(b) Find $G(T, p, N)$.

(c) Find $\Omega(T, V, \mu)$.

(d) Show that

$$\beta p \int_0^\infty dV \, e^{-\beta p V} \, Z(T, V, N) = e^{-G(T,p,N)/k_B T} .$$

Solution :

(a) We have $Z(T, V, N) = (V\xi)^N/N!$, so

$$F(T, V, N) = -k_B T \ln Z(T, V, N) = -N k_B T \ln\left(\frac{V}{N}\right) - N k_B T \ln \xi(T) - N k_B T .$$

(b) G is obtained from F by Legendre transform: $G = F + pV$, *i.e.*

$$G(T, p, N) = -N k_B T \ln\left(\frac{k_B T}{p}\right) - N k_B T \ln \xi(T) .$$

Note that we have used the ideal gas law $pV = N k_B T$ here.

(c) Ω is obtained from F by Legendre transform: $\Omega = F - \mu N$. Another way to obtain Ω is to use the grand potential $\Xi = \exp(V\xi(T)\, e^{\mu/k_B T})$, whence

$$\Omega(T, V, \mu) = -V k_B T \, \xi(T) \, e^{\mu/k_B T} .$$

(d) We have

$$Y(T, p, N) = \beta p \int_0^\infty dV \, e^{-\beta p V} \, Z(T, V, N) = \frac{\xi^N(T)}{N!} \, \beta p \int_0^\infty dV \, V^N \, e^{-\beta p V} = \left(\frac{k_B T \, \xi(T)}{p}\right)^N$$

Thus, $G(T,p,N) = -Nk_{\rm B}T\ln\big(k_{\rm B}T\,\xi/p\big)$. Note that if we normalize the volume integral differently and define

$$Y(T,p,N) = \int\limits_0^\infty \frac{dV}{V_0}\, e^{-\beta pV}\, Z(T,V,N) = \left(\frac{k_{\rm B}T}{pV_0}\right)\cdot\left(\frac{k_{\rm B}T\,\xi(T)}{p}\right)^N ,$$

we obtain $G(T,p,N) = -Nk_{\rm B}T\ln\big(k_{\rm B}T\,\xi/p\big) - k_{\rm B}T\ln(k_{\rm B}T/pV_0)$, which differs from the previous result only by an $\mathcal{O}(N^0)$ term, which is subextensive and hence negligible in the thermodynamic limit.

(2) A three-dimensional gas of magnetic particles in an external magnetic field H is described by the Hamiltonian

$$\mathcal{H} = \sum_i \left[\frac{\boldsymbol{p}_i^2}{2m} - \mu_0 H\sigma_i\right] ,$$

where $\sigma_i = \pm 1$ is the spin polarization of particle i and μ_0 is the magnetic moment per particle.

(a) Working in the ordinary canonical ensemble, derive an expression for the magnetization of system.

(b) Repeat the calculation for the grand canonical ensemble. Also, find an expression for the Landau free energy $\Omega(T,V,\mu)$.

(c) Calculate how much heat will be given off by the system when the magnetic field is reduced from H to zero at constant volume, constant temperature, and particle number.

Solution :

(a)The partition function trace is now an integral over all coordinates and momenta with measure $d\mu$ as before, plus a sum over all individual spin polarizations. Thus,

$$\begin{aligned} Z = \mathrm{Tr}\, e^{-\mathcal{H}/k_{\rm B}T} &= \frac{1}{N!}\prod_{i=1}^N \sum_{\sigma_i}\int \frac{d^3\!x_i\, d^3\!p_i}{h^3}\, e^{-\boldsymbol{p}_i^2/2mk_{\rm B}T}\, e^{\mu_0 H\sigma_i/k_{\rm B}T} \\ &= \frac{1}{N!}\, V^N\, \lambda_T^{-3N}\left[2\cosh(\mu_0 H/k_{\rm B}T)\right]^N , \end{aligned}$$

where $\lambda_T = (2\pi\hbar^2/mk_{\rm B}T)^{1/2}$ is the thermal wavelength. The Helmholtz free energy is

$$\begin{aligned} F(T,V,H,N) &= -k_{\rm B}T\ln Z(T,V,H,N) \\ &= -Nk_{\rm B}T\ln\!\left(\frac{V}{N\lambda_T^3}\right) - Nk_{\rm B}T\ln\cosh(\mu_0 H/k_{\rm B}T) - Nk_{\rm B}T(1+\ln 2) . \end{aligned}$$

The magnetization is then

$$M(T,V,H,N) = -\frac{\partial F}{\partial H} = N\mu_0\tanh(\mu_0 H/k_{\rm B}T) .$$

(b) The grand partition function is

$$\Xi(T,V,H,\mu) = \sum_{N=0}^{\infty} e^{\mu N/k_B T}\, Z(T,V,N) = \exp\Big(V\lambda_T^{-3}\cdot 2\cosh(\mu_0 H/k_B T)\cdot e^{\mu/k_B T}\Big)\ .$$

Thus,

$$\Omega(T,V,H,\mu) = -k_B T \ln \Xi(T,V,\mu) = -V k_B T\,\lambda_T^{-3}\cdot 2\cosh(\mu_0 H/k_B T)\cdot e^{\mu/k_B T}\ .$$

Then

$$M(T,V,H,\mu) = -\frac{\partial\Omega}{\partial H} = 2\mu_0\cdot V\lambda_T^{-3}\cdot \sinh(\mu_0 H/k_B T)\cdot e^{\mu/k_B T}\ .$$

Note that

$$N(T,V,H,\mu) = -\frac{\partial\Omega}{\partial \mu} = V\lambda_T^{-3}\cdot \cosh(\mu_0 H/k_B T)\cdot e^{\mu/k_B T}\ ,$$

so $M = N\mu_0 \tanh(\mu_0 H/k_B T)$, which agrees with the result from part (a).

(c) Starting with our expression for $F(T,V,N)$ in part (a), we differentiate to find the entropy:

$$S(T,V,H,N) = -\frac{\partial F}{\partial T} = N k_B \ln\cosh(\mu_0 H/k_B T) - \frac{N\mu_0 H}{T}\tanh(\mu_0 H/k_B T) + S(T,V,0,N)\ ,$$

where $S(T,V,0,N)$ is the entropy at $H = 0$, which we don't need to compute for this problem. The heat absorbed *by* the system is

$$\begin{aligned} Q = \int \text{đ}Q = TS(0) - TS(H) &= N k_B T \ln\cosh(\mu_0 H/k_B T) + N\mu_0 H \tanh(\mu_0 H/k_B T) \\ &= N k_B T \Big(x\tanh x - \ln\cosh x\Big)\ , \end{aligned}$$

where $x = \mu_0 H/k_B T$. Defining $f(x) = x\tanh x - \ln\cosh x$, one has $f'(x) = x\,\mathrm{sech}^2 x$ which is positive for all $x > 0$. Since $f(x)$ is an even function with $f(0) = 0$, we conclude $f(x) > 0$ for $x \neq 0$. Thus, $Q > 0$, which means that the system absorbs heat under this process. *I.e.* the heat released by the system is $(-Q)$.

(3) A classical three-dimensional gas of noninteracting particles has the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \Big[A\,|\boldsymbol{p}_i|^s + B\,|\boldsymbol{q}_i|^t\Big]\ ,$$

where s and t are nonnegative real numbers.

(a) Find the free energy $F(T,V,N)$.

(b) Find the average energy $E(T,V,N)$.

(c) Find the grand potential $\Omega(T,V,\mu)$.

Remember the definition of the Gamma function, $\Gamma(z) = \int\limits_{-\infty}^{\infty} du\, u^{z-1}\, e^{-u}$.

Solution :

(a) Working in the OCE, the partition function is $Z = \xi_p^N(T)\,\xi_q^N(T)/N!$, where

$$\xi_p(T) = \frac{1}{h^3}\int d^3\!p\, \exp\!\big(-\,A\,p^s/k_{\rm B}T\big)$$
$$\xi_q(T) = \int d^3\!q\, \exp\!\big(-\,B\,q^t/k_{\rm B}T\big)\,.$$

We focus first on the momentum integral, changing variables to $u = Ap^s/kT$. Then

$$u = \frac{A\,p^s}{k_{\rm B}T} \quad \Rightarrow \quad p = \bigg(\frac{k_{\rm B}T\,u}{A}\bigg)^{1/s} \quad , \quad p^2\,dp = \bigg(\frac{k_{\rm B}T}{A}\bigg)^{3/s}\cdot s^{-1}\,u^{(3/s)-1}\,du\,,$$

and

$$\xi_p(T) = \frac{1}{h^3}\int d^3\!p\, \exp\!\big(-\,A\,p^s/k_{\rm B}T\big) = \frac{4\pi}{h^3}\bigg(\frac{k_{\rm B}T}{A}\bigg)^{3/s}\cdot\frac{1}{s}\int\limits_{-\infty}^{\infty} du\, u^{(3/s)-1}\,e^{-u}$$
$$= \frac{4\pi}{sh^3}\,\Gamma(3/s)\bigg(\frac{k_{\rm B}T}{A}\bigg)^{3/s}\,,$$

where we have used $z\,\Gamma(z) = \Gamma(z+1)$. *Mutatis mutandis*,

$$\xi_q(T) = \int d^3\!q\, \exp\!\big(-\,B\,q^t/k_{\rm B}T\big) = \frac{4\pi}{t}\,\Gamma(3/t)\bigg(\frac{k_{\rm B}T}{B}\bigg)^{3/t}\,.$$

Thus, the free energy is

$$F(T,V,N) = -k_{\rm B}T\ln Z = -Nk_{\rm B}T\ln\!\bigg(\frac{\xi_p(T)\,\xi_q(T)}{N}\bigg) - Nk_{\rm B}T\,.$$

(b) The average energy is

$$E = \frac{\partial}{\partial\beta}\,(\beta F) = \bigg(\frac{3}{s}+\frac{3}{t}\bigg)\,Nk_{\rm B}T\,.$$

(c) The grand potential is $\Omega = -k_{\rm B}T\ln\Xi$, and $\Xi = \exp\!\Big(\xi_p(T)\,\xi_q(T)\,e^{\mu/k_{\rm B}T}\Big)$. Thus,

$$\Omega(T,V,N) = -k_{\rm B}T\,\xi_p(T)\,\xi_q(T)\,e^{\mu/k_{\rm B}T}\,.$$

Note that F and Ω are both independent of V, which means that the pressure p vanishes!

(4) A gas of nonrelativistic particles of mass m is held in a container at constant pressure p and temperature T. It is free to exchange energy with the outside world, but the particle number N remains fixed. Compute the variance in the system volume, $\mathsf{Var}(V)$, and the ratio $(\Delta V)_{\rm rms}/\langle V\rangle$. Use the Gibbs ensemble.

Solution

The Gibbs free energy is

$$G(T,p,N) = -Nk_{\rm B}T \ln\!\left(\frac{k_{\rm B}T}{p\,\lambda_T^3}\right) ,$$

where $\lambda_T = (2\pi\hbar^2/mk_{\rm B}T)^{1/2}$ is the thermal wavelength. Thus, with

$$Y = e^{-G/k_{\rm B}T} = \int \frac{dV}{V_0}\, e^{-\beta p V}\, Z(T,V,N) ,$$

we have

$$\langle V\rangle = -\frac{1}{\beta}\,\frac{1}{Y}\,\frac{\partial Y}{\partial p} = \frac{\partial G}{\partial p} = \frac{Nk_{\rm B}T}{p}$$
$$\mathsf{Var}(V) = \langle V^2\rangle - \langle V\rangle^2 = \frac{1}{\beta^2}\left\{\frac{1}{Y}\,\frac{\partial^2 Y}{\partial p^2} - \left(\frac{1}{Y}\,\frac{\partial Y}{\partial p}\right)^{\!2}\right\} = -k_{\rm B}T\,\frac{\partial^2 G}{\partial p^2} = N\left(\frac{k_{\rm B}T}{p}\right)^{\!2} .$$

Thus, $(\Delta V)_{\mathsf{RMS}} = \sqrt{\mathsf{Var}(V)}/\langle V\rangle = N^{-1/2}$.