PHYSICS 140A : STATISTICAL PHYSICS
HW SOLUTIONS #5

(1) Compute the density of states $D(E,V,N)$ for a three-dimensional gas of particles with Hamiltonian $\hat{H} = \sum_{i=1}^{N} A\,|\boldsymbol{p}_i|^4$, where A is a constant. Find the entropy $S(E,V,N)$, the Helmholtz free energy $F(T,V,N)$, and the chemical potential $\mu(T,p)$.

Solution :

Let's solve the problem for a general dispersion $\varepsilon(\boldsymbol{p}) = A|\boldsymbol{p}|^\alpha$. We can afterwards restrict to the case $d=3$, $\alpha=4$. The density of states is

$$D(E,V,N) = \frac{V^N}{N!}\int\!\frac{d^d\!p_1}{h^d}\cdots\int\!\frac{d^d\!p_N}{h^d}\,\delta\big(E - Ap_1^\alpha - \ldots - Ap_N^\alpha\big)\,.$$

The Laplace transform is

$$\begin{aligned}\widehat{D}(\beta,V,N) &= \frac{V^N}{N!}\bigg(\int\!\frac{d^d\!p}{h^d}\,e^{-\beta A p^\alpha}\bigg)^{\!N} \\ &= \frac{V^N}{N!}\bigg(\frac{\Omega_d}{h^d}\int\limits_0^\infty\!dp\,p^{d-1}\,e^{-\beta A p^\alpha}\bigg)^{\!N} \\ &= \frac{V^N}{N!}\bigg(\frac{\Omega_d\,\Gamma(d/\alpha)}{\alpha h^d A^{d/\alpha}}\bigg)^{\!N}\beta^{-Nd/\alpha}\,.\end{aligned}$$

Now we inverse transform, recalling

$$K(E) = \frac{E^{t-1}}{\Gamma(t)} \qquad \Longleftrightarrow \qquad \widehat{K}(\beta) = \beta^{-t}\,.$$

We then conclude

$$D(E,V,N) = \frac{V^N}{N!}\bigg(\frac{\Omega_d\,\Gamma(d/\alpha)}{\alpha h^d A^{d/\alpha}}\bigg)^{\!N}\frac{E^{\frac{Nd}{\alpha}-1}}{\Gamma(Nd/\alpha)}$$

and

$$\begin{aligned}S(E,V,N) &= k_\mathrm{B}\ln D(E,V,N) \\ &= Nk_\mathrm{B}\ln\!\bigg(\frac{V}{N}\bigg) + \frac{d}{\alpha}\,Nk_\mathrm{B}\,\ln\!\bigg(\frac{E}{N}\bigg) + Nk_\mathrm{B}a_0\,,\end{aligned}$$

where a_0 is a constant, and we take the thermodynamic limit $N\to\infty$ with V/N and E/N fixed. From this we obtain the differential relation

$$\begin{aligned}dS &= \frac{Nk_\mathrm{B}}{V}\,dV + \frac{d}{\alpha}\,\frac{Nk_\mathrm{B}}{E}\,dE + s_0\,dN \\ &= \frac{p}{T}\,dV + \frac{1}{T}\,dE - \frac{\mu}{T}\,dN\,,\end{aligned}$$

where s_0 is a constant. From the coefficients of dV and dE, we conclude

$$pV = Nk_{\rm B}T$$
$$E = \frac{d}{\alpha}\, Nk_{\rm B}T\ .$$

Note that we have replaced $E = \frac{d}{\alpha}\, Nk_{\rm B}T$ in order to express F in terms of its 'natural variables' T, V, and N.

The Helmholtz free energy is

$$\begin{aligned} F = E - TS &= E - Nk_{\rm B}T\ln\bigg(\frac{V}{N}\bigg) - \frac{d}{\alpha}Nk_{\rm B}T\ln\bigg(\frac{E}{N}\bigg) - Nk_{\rm B}Ta_0 \\ &= \frac{d}{\alpha}\,Nk_{\rm B}T - \frac{d}{\alpha}Nk_{\rm B}T\ln\bigg(\frac{d}{\alpha}\,k_{\rm B}T\bigg) - Nk_{\rm B}T\ln\bigg(\frac{V}{N}\bigg) - Nk_{\rm B}Ta_0\ . \end{aligned}$$

The chemical potential is

$$\begin{aligned} \mu = T\left(\frac{\partial F}{\partial N}\right)_{T,V} &= -\frac{d}{\alpha}\,k_{\rm B}T\ln\bigg(\frac{d}{\alpha}\,k_{\rm B}T\bigg) + \frac{d}{\alpha}\,k_{\rm B}T - k_{\rm B}T\ln\bigg(\frac{V}{N}\bigg) + (1-a_0)\,k_{\rm B}T \\ &= -\frac{d}{\alpha}\,k_{\rm B}T\ln\bigg(\frac{d}{\alpha}\,k_{\rm B}T\bigg) + \frac{d}{\alpha}\,k_{\rm B}T - k_{\rm B}T\ln\bigg(\frac{k_{\rm B}T}{p}\bigg) + (1-a_0)\,k_{\rm B}T\ . \end{aligned}$$

Suppose we wanted the heat capacities C_V and C_p. Setting $dN = 0$, we have

$$\begin{aligned} đQ &= dE + p\,dV \\ &= \frac{d}{\alpha}\,Nk_{\rm B}\,dT + p\,dV \\ &= \frac{d}{\alpha}\,Nk_{\rm B}\,dT + p\,d\bigg(\frac{Nk_{\rm B}T}{p}\bigg)\ . \end{aligned}$$

Thus,

$$C_V = \frac{đQ}{dT}\bigg|_V = \frac{d}{\alpha}\,Nk_{\rm B} \quad , \quad C_p = \frac{đQ}{dT}\bigg|_p = \bigg(1 + \frac{d}{\alpha}\bigg)Nk_{\rm B}\ .$$

(2) For the system described in problem (1), compute the distribution of speeds $\bar{f}(v)$. Find the most probable speed, the mean speed, and the RMS speed.

Solution :

Again, we solve for the general case $\varepsilon(\boldsymbol{p}) = Ap^\alpha$. The momentum distribution is

$$g(\boldsymbol{p}) = C\,e^{-\beta A p^\alpha}\ ,$$

where C is a normalization constant, defined so that $\int d^d p\, g(\boldsymbol{p}) = 1$. Changing variables to $t \equiv \beta A p^\alpha$, we find

$$C = \frac{\alpha\,(\beta A)^{\frac{d}{\alpha}}}{\Omega_d\,\Gamma\big(\frac{d}{\alpha}\big)} \,.$$

The velocity $\boldsymbol{v}$ is given by

$$\boldsymbol{v} = \frac{\partial \varepsilon}{\partial \boldsymbol{p}} = \alpha A p^{\alpha-1}\,\hat{\boldsymbol{p}} \,.$$

Thus, the speed distribution is given by

$$\bar{f}(v) = C \int \! d^d p \; e^{-\beta A p^\alpha}\, \delta\big(v - \alpha A p^{\alpha-1}\big) \,.$$

Now

$$\delta\big(v - \alpha A p^{\alpha-1}\big) = \frac{\delta\big(p - (v/\alpha A)^{1/(\alpha-1)}\big)}{\alpha(\alpha-1)A p^{\alpha-2}} \,.$$

We therefore have

$$\bar{f}(v) = \frac{C}{\alpha(\alpha-1)A}\; p^{d-\alpha+1}\; e^{-\beta A p^\alpha} \bigg|_{p=(v/\alpha A)^{1/(\alpha-1)}} \,.$$

We can now calculate

$$\langle v^r \rangle = C \int \! d^d p \; e^{-\beta A p^\alpha} \big(\alpha A p^{\alpha-1}\big)^r \,,$$

and so

$$\|v\|_r = \langle v^r \rangle^{1/r} = \alpha A^{\alpha^{-1}}\,(k_{\rm B}T)^{1-\alpha^{-1}} \left(\frac{\Gamma\big(\frac{d-r}{\alpha} + r\big)}{\Gamma\big(\frac{d}{\alpha}\big)}\right)^{1/\alpha} \,.$$

To find the most probable speed, we extremize $\bar{f}(v)$. We obtain

$$\beta A p^\alpha = \frac{d - \alpha + 1}{\alpha} \,,$$

which means

$$v = \alpha A \bigg(\frac{d-\alpha+1}{\alpha\beta A}\bigg)^{1-\alpha^{-1}} = (\alpha A)^{\alpha^{-1}}\,(d-\alpha+1)^{1-\alpha^{-1}}\,(k_{\rm B}T)^{1-\alpha^{-1}} \,.$$

(3) Consider a gas of classical spin-$\frac{3}{2}$ particles, with Hamiltonian

$$\hat{H} = \sum_{i=1}^N \frac{\boldsymbol{p}_i^2}{2m} - \mu_0 H \sum_i S_i^z \,,$$

where $S_i^z \in \{ -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2} \}$ and H is the external magnetic field. Find the Helmholtz free energy $F(T,V,H,N)$, the entropy $S(T,V,H,N)$, and the magnetic susceptibility $\chi(T,H,n)$, where $n = N/V$ is the number density.

Solution :

The partition function is

$$Z = \mathsf{Tr}\, e^{-\hat{H}/k_B T} = \frac{1}{N!} \frac{V^N}{\lambda_T^{dN}} \Big(2\cosh(\mu_0 H/2k_B T) + 2\cosh(3\mu_0 H/2k_B T) \Big)^N ,$$

so

$$F = -Nk_B T \ln\left(\frac{V}{N\lambda_T^d}\right) - Nk_B T - Nk_B T \ln\Big(2\cosh(\mu_0 H/2k_B T) + 2\cosh(3\mu_0 H/2k_B T)\Big) ,$$

where $\lambda_T = \sqrt{2\pi\hbar^2/mk_B T}$ is the thermal wavelength. The entropy is

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N,H} = Nk_B \ln\left(\frac{V}{N\lambda_T^d}\right) + (\tfrac{1}{2}d + 1)Nk_B + N\ln\Big(2\cosh(\mu_0 H/2k_B T) + 2\cosh(3\mu_0 H/2k_B T)\Big)$$
$$- \frac{\mu_0 H}{2T} \cdot \frac{\sinh(\mu_0 H/2k_B T) + 3\sinh(3\mu_0 H/2k_B T)}{\cosh(\mu_0 H/2k_B T) + \cosh(3\mu_0 H/2k_B T)} .$$

The magnetization is

$$M = -\left(\frac{\partial F}{\partial H}\right)_{T,V,N} = \tfrac{1}{2}N\mu_0 \cdot \frac{\sinh(\mu_0 H/2k_B T) + 3\sinh(3\mu_0 H/2k_B T)}{\cosh(\mu_0 H/2k_B T) + \cosh(3\mu_0 H/2k_B T)} .$$

The magnetic susceptibility is

$$\chi(T,H,n) = \frac{1}{V}\left(\frac{\partial M}{\partial H}\right)_{T,V,N} = \frac{n\mu_0^2}{4k_B T}\, f(\mu_0 H/2k_B T)$$

where

$$f(x) = \frac{d}{dx}\left(\frac{\sinh x + 3\sinh(3x)}{\cosh x + \cosh(3x)}\right) .$$

In the limit $H \to 0$, we have $f(0) = 5$, so $\chi = 4n\mu_0^2/4k_B T$ at high temperatures. This is a version of Curie's law.

(4) Consider a system of identical but distinguishable particles, each of which has a non-degenerate ground state with $\varepsilon_0 = 0$, and a $g-$fold degenerate excited state with energy $\varepsilon > 0$. Study carefully problems #1 and #2 in the example problems for chapter 4 of the lecture notes, where this system is treated in the microcanonical and ordinary canonical ensembles. Here you are invited to work out the results for the grand canonical ensemble.

(a) Find the grand partition function $\Xi(T,z)$ and the grand potential $\Omega(T,z)$. Express your answers in terms of the temperature T and the fugacity $z = e^{\mu/k_B T}$.

(b) Find the entropy $S(T, \mu)$.

(c) Find the number of particles, $N(T, \mu)$.

(d) Show how, in the thermodynamic limit, the entropy agrees with the results from the microcanonical and ordinary canonical ensembles.

Solution :

(a) The ordinary canonical partition function is

$$Z(T, N) = \left(1 + g\, e^{-\varepsilon/k_{\rm B}T}\right)^N \quad ,$$

hence the grand partition function is

$$\Xi(T, z) = \sum_{N=0}^{\infty} z^N\, Z(T, N) = \frac{1}{1 - z(1 + g\, e^{-\varepsilon/k_{\rm B}T})} \quad ,$$

with $z = \exp(\mu/k_{\rm B}T)$ the fugacity. The grand potential is

$$\Omega(T, z) = -k_{\rm B}T \ln \Xi = k_{\rm B}T \ln\Big[1 - z\big(1 + g\, e^{-\varepsilon/k_{\rm B}T}\big)\Big] \quad .$$

(b) The entropy is $S = -(\partial\Omega/\partial T)_\mu$ so we must allow z to vary with T. Differentiating, we obtain

$$\begin{aligned} S(T, \mu) &= -\left(\frac{\partial\Omega}{\partial T}\right)_z - \left(\frac{\partial\Omega}{\partial z}\right)_T \left(\frac{\partial z}{\partial T}\right)_\mu \\ &= -k_{\rm B} \ln\Big(1 - z\big(1 + g\, e^{-\varepsilon/k_{\rm B}T}\big)\Big) - \frac{\mu}{T} \cdot \frac{z\,(1 + g\, e^{-\varepsilon/k_{\rm B}T})}{1 - z(1 + g\, e^{-\varepsilon/k_{\rm B}T})} + \frac{\varepsilon}{T} \cdot \frac{gz\, e^{-\varepsilon/k_{\rm B}T}}{1 - z(1 + g\, e^{-\varepsilon/k_{\rm B}T})} \\ &= -k_{\rm B} \ln\Big(1 - \big(1 + g\, e^{-\varepsilon/k_{\rm B}T}\big)\, e^{\mu/k_{\rm B}T}\Big) + \frac{1}{T} \cdot \frac{g\,\varepsilon\, e^{-\varepsilon/k_{\rm B}T} - \mu\,(1 + g\, e^{-\varepsilon/k_{\rm B}T})}{e^{-\mu/k_{\rm B}T} - 1 - g\, e^{-\varepsilon/k_{\rm B}T}} \quad . \end{aligned}$$

(c) The particle number is

$$N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_T = -\frac{z}{k_{\rm B}T}\left(\frac{\partial\Omega}{\partial z}\right)_T = \frac{1 + g\, e^{-\varepsilon/k_{\rm B}T}}{e^{-\mu/k_{\rm B}T} - 1 - g\, e^{-\varepsilon/k_{\rm B}T}} \quad .$$

Solving for $z = \exp(\mu/k_{\rm B}T)$, we obtain

$$z = \frac{1}{1 + N^{-1}} \cdot \frac{1}{1 + g\, e^{-\varepsilon/k_{\rm B}T}} \quad .$$

(d) Expresssing the entropy $S(T, \mu)$ in terms of T and N, we obtain

$$S(T, N) = Nk_{\rm B} \ln\big(1 + g\, e^{-\varepsilon/k_{\rm B}T}\big) + \frac{N\varepsilon}{T}\, \frac{1}{g^{-1}\, e^{\varepsilon/k_{\rm B}T} + 1} + k_{\rm B} \ln(N + 1) + Nk_{\rm B} \ln(1 + N^{-1}) \quad .$$

In the thermodynamic limit $N \to \infty$, the first two terms are extensive. The penultimate term is $\mathcal{O}(\ln N)$ and the last term is $\mathcal{O}(N^0)$. The results agree in this limit with the OCE results in problem 4.2c from the examples.