PHYSICS 210A : STATISTICAL PHYSICS
HW ASSIGNMENT #2 SOLUTIONS

(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 $\varepsilon(\boldsymbol{p}) = A|\boldsymbol{p}|^\alpha$. 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

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

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

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

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

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

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

The Helmholtz free energy is

$$\begin{aligned} F = E - TS &= E - N k_B T \ln\left(\frac{V}{N}\right) - \frac{d}{\alpha} N k_B T \ln\left(\frac{E}{N}\right) - N k_B T a_0 \\ &= \frac{d}{\alpha} N k_B T - \frac{d}{\alpha} N k_B T \ln\left(\frac{d}{\alpha}\, k_B T\right) - N k_B T \ln\left(\frac{V}{N}\right) - N k_B T a_0 \,. \end{aligned}$$

The chemical potential is

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

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

$$\begin{aligned} đQ &= dE + p\, dV \\ &= \frac{d}{\alpha}\, N k_B\, dT + p\, dV \\ &= \frac{d}{\alpha}\, N k_B\, dT + p\, d\left(\frac{N k_B T}{p}\right) . \end{aligned}$$

Thus,

$$C_V = \frac{đQ}{dT}\bigg|_V = \frac{d}{\alpha}\, N k_B \quad , \quad C_p = \frac{đQ}{dT}\bigg|_p = \left(1 + \frac{d}{\alpha}\right) N k_B \,.$$

(2) 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 $S_i^z \in \big\{ -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2} \big\}$ 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

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

so

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

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

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

The magnetization is

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

The magnetic susceptibility is

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

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 $\chi = 4n\mu_0^2/4k_BT$ at high temperatures. This is a version of Curie's law.

(3) Compute the RMS volume fluctuations in the $T-p-N$ ensemble.

Solution :

Averages within the $T-p-N$ ensemble are computed by

$$\langle A\rangle = \frac{\mathsf{Tr}\ A\, e^{-\beta(\hat{H}+pV)}}{\mathsf{Tr}\ e^{-\beta(\hat{H}+pV)}} \ .$$

Let $Y = \mathsf{Tr}\ ^{-\beta(\hat{H}+pV)} = e^{-\beta G}$. Then

$$\langle V^2\rangle = \frac{1}{\beta^2 Y}\frac{\partial^2 Y}{\partial p^2} = \beta^{-2}\, e^{\beta G}\,\frac{\partial^2}{\partial p^2}\, e^{-\beta G}$$
$$= -\frac{1}{\beta}\frac{\partial^2 G}{\partial p^2} + \left(\frac{\partial G}{\partial p}\right)^2 ,$$

and since $\frac{\partial G}{\partial p} = V$, we have

$$\langle V^2\rangle - \langle V\rangle^2 = -k_BT\,\frac{\partial^2 G}{\partial p^2} \ .$$

For the case of a nonrelativistic ideal gas, we have

$$\begin{aligned}\langle V^k\rangle &= \int_0^\infty dV\, e^{-\beta pV}\, Z(T,V,N)\, V^k \bigg/ \int_0^\infty dV\, e^{-\beta pV}\, Z(T,V,N) \\ &= \int_0^\infty dV\, e^{-\beta pV}\, V^{N+k} \bigg/ \int_0^\infty dV\, e^{-\beta pV}\, V^N = \frac{(N+k)!}{N!}\left(\frac{k_B T}{p}\right)^k ,\end{aligned}$$

since $Z(T,V,N) = \frac{1}{N!}(V/\lambda_T)^N$. Thus,

$$\langle V\rangle = (N+1)\,\frac{k_B T}{p} \qquad , \qquad \langle V^2\rangle = (N+1)(N+2)\left(\frac{k_B T}{p}\right)^2$$

and therefore

$$V_{\rm rms}^2 = \langle V^2\rangle - \langle V\rangle^2 = (N+1)\left(\frac{k_B T}{p}\right)^2 \quad \Rightarrow \quad V_{\rm rms} = N^{1/2}\,\frac{k_B T}{p} .$$

Thus $V_{\rm rms}/\langle V\rangle = N^{-1/2} \ll 1$. This is, once again, the Central Limit Theorem in action.

(4) 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

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

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

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