PHYS704: Assignment 4

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Rotating gas

1.a

$$
\begin{aligned}
\{\vec{L}_i, \mathcal{H}\} &= \sum_k \{\vec{L}_i, T_k + U_k\} \\
&= \sum_k \{\vec{L}_i, \frac{p_k^2}{2m}\} + \{\vec{L}_i, K\frac{r_k^2}{2}\}
\end{aligned}
$$

since there is no interaction, if $i \neq k$, $\{L_i, T_k\}, \{L_i, U_k\} = 0$, when $i = k$, we will show $\{L, \frac{p^2}{2m}\}$ and $\{L, K\frac{r^2}{2}\}$ are zero, by definition we have

$$
\begin{aligned}
\mathbf{L} &= \sum q_j p_k \epsilon_{ijk} \mathbf{e}_i \\
\vec{r} &= \{q_1, q_2, q_3\}
\end{aligned}
$$

because $q_j p_k$ is symmetric, swapping i, j does not effect the summation, but it change the sign of ϵ , thus

$$
\begin{aligned}
\{L, \frac{p^2}{2m}\} &= \sum \{q_j p_k, \frac{p^2}{2m}\} \epsilon_{ijk} \mathbf{e}_i \\
&= \frac{1}{2}(\sum \{q_j p_k, \frac{p^2}{2m}\} \epsilon_{ijk} \mathbf{e}_i + \sum \{q_k p_j, \frac{p^2}{2m}\} \epsilon_{ikj} \mathbf{e}_i) \\
&= \frac{1}{2} \sum (\{q_j p_k, \frac{p^2}{2m}\} \epsilon_{ijk} - \{q_j p_k, \frac{p^2}{2m}\} \epsilon_{ijk}) \mathbf{e}_i \\
&= 0
\end{aligned}
$$

similarly, since $r^2 = q^2 = \sum_i q_i^2$, we can do the exactly same thing, and get $\{L, K\frac{q^2}{2}\} = 0$, thus $\{\mathbf{L}_i, \mathcal{H}\} = 0$, it is also pretty straight forward to prove interacting terms in the same way, since interacting term $M_{ij} = -M_{ji}$, we have $\{\mathbf{L}, \mathcal{H}\} = \sum_i \{L_i, \mathcal{H}\} = \sum_i \{L_i, M_{jk}\}$ become zero.

1.b

since $\vec{\Omega} = \Omega \hat{z}$, $\vec{\Omega} \cdot \vec{L} = \Omega L_z = \Omega(x p_y - y p_z)$, thus

$$Z = \frac{1}{N!}(\int \frac{dq^3dp^3}{h^3}\exp[-\beta\frac{p_x^2+p_y^2+p_z^2}{2m} - \frac{K\beta}{2}(x^2+y^2+z^2) - \beta\Omega(xp_y - yp_z)])^N$$
$$= \frac{1}{N!h^{3N}}(\frac{2\pi}{\beta}\sqrt{\frac{m}{K}}\int dxdydp_zdp_y\exp[-\frac{\beta}{2m}(p_y^2+p_z^2) - \frac{K\beta}{2}(x^2+y^2) - \beta\Omega(xp_y - yp_z)])^N$$

and we have

$$\int dxdydp_zdp_y\exp[-\frac{\beta}{2m}(p_y^2+p_z^2) - \frac{K\beta}{2}(x^2+y^2) - \beta\Omega(xp_y - yp_z)]$$
$$= \int dydp_zdp_y\exp[-\frac{\beta}{2m}(p_y^2+p_z^2) - \frac{K\beta}{2}y^2 + \beta\Omega yp_z]\int dx\exp[-\frac{K\beta}{2}x^2 - \beta\Omega xp_y]$$
$$= \sqrt{\frac{2\pi}{K\beta}}\int dydp_zdp_y\exp[-\frac{\beta}{2m}(p_y^2+p_z^2) - \frac{K\beta}{2}y^2 + \beta\Omega yp_z + \frac{\beta\Omega^2p_y^2}{2K}]$$
$$= \sqrt{\frac{2\pi}{K\beta}}\int dp_zdp_y\exp[-\frac{\beta}{2m}(p_y^2+p_z^2) + \frac{\beta\Omega^2p_y^2}{2K}]\int dy\exp[-\frac{K\beta}{2}y^2 + \beta\Omega yp_z]$$
$$= \frac{2\pi}{K\beta}\int dp_zdp_y\exp[-(\frac{\beta}{2m} - \frac{\beta\Omega^2}{2K})(p_y^2+p_z^2)]$$
$$= \frac{2\pi}{K\beta}\frac{2\pi mK}{K\beta - m\beta\Omega^2} = \frac{4\pi^2m}{\beta(K\beta - m\beta\Omega^2)}$$

the last integral uses the assumption that $\Omega < \sqrt{K/m}$, so the partition function Z is

$$Z = \frac{1}{N!h^{3N}}(\sqrt{\frac{m}{K}}\frac{8\pi^3m}{\beta^3(K-m\Omega^2)})^N = \frac{1}{N!}[(\frac{2\pi}{\beta h})^3\sqrt{\frac{m}{K}}\frac{m}{K-m\Omega^2}]^N$$

1.c

$$\langle L_z\rangle = \frac{1}{N!Z}\int(\prod_{i=1}^N\frac{d^3q_id^3p_i}{h^3})L_z\exp[-\beta\mathcal{H}(\mu) - \beta\Omega L_z]$$
$$= -\frac{1}{N!Z}\int(\prod_{i=1}^N\frac{d^3q_id^3p_i}{h^3})\frac{1}{\beta}\frac{\partial}{\partial\Omega}\exp[-\beta\mathcal{H}(\mu) - \beta\Omega L_z]$$
$$= -\frac{1}{\beta Z}\frac{\partial}{\partial\Omega}\frac{1}{N!}\int(\prod_{i=1}^N\frac{d^3q_id^3p_i}{h^3})\exp[-\beta\mathcal{H}(\mu) - \beta\Omega L_z]$$
$$= -\frac{1}{\beta Z}\frac{\partial Z}{\partial\Omega}$$

and the derivative is

$$\frac{\partial Z}{\partial \Omega} = \frac{1}{(N-1)!}[(\frac{2\pi}{\beta h})^3\sqrt{\frac{m}{K}}\frac{m}{K-m\Omega^2}]^{N-1}(\frac{2\pi}{\beta h})^3\sqrt{\frac{m}{K}}\frac{\partial}{\partial \Omega}\frac{m}{K-m\Omega^2}$$
$$= \frac{1}{(N-1)!}[(\frac{2\pi}{\beta h})^3\sqrt{\frac{m}{K}}\frac{m}{K-m\Omega^2}]^{N-1}(\frac{2\pi}{\beta h})^3\sqrt{\frac{m}{K}}\frac{m}{(K-m\Omega^2)^2}2m\Omega$$
$$= NZ\frac{2m\Omega}{K-m\Omega^2}$$

thus

$$\langle L_z \rangle = -\frac{N}{\beta}\frac{2m\Omega}{K-m\Omega^2}$$

1.d

$$\rho(x,y,z,p_x,p_y,p_z) = \frac{1}{N}\frac{1}{(N-1)!}\int\prod_{i=2}^{N}\frac{d^3q_i d^3p_i}{h^3}\rho(\mu)$$
$$= \frac{1}{N!h^{3(N-1)}}\frac{1}{Z}[(\frac{2\pi}{\beta})^3\sqrt{\frac{m}{K}}\frac{m}{K-m\Omega^2}]^{N-1}\exp[-\beta(T_i+U_i)]$$
$$= \frac{N!h^{3N}}{N!h^{3(N-1)}}[(\frac{2\pi}{\beta})^3\sqrt{\frac{m}{K}}\frac{m}{K-m\Omega^2}]^{-1}\exp[-\beta(T_i+U_i)]$$
$$= h^3[(\frac{2\pi}{\beta})^3\sqrt{\frac{m}{K}}\frac{m}{K-m\Omega^2}]^{-1}\exp[-\beta(T_i+U_i)]$$

$$\rho(x,y,z) = h^3[(\frac{2\pi}{\beta})^3\sqrt{\frac{m}{K}}\frac{m}{K-m\Omega^2}]^{-1}\exp[-\frac{K\beta}{2}(x^2+y^2+z^2)]$$
$$\int\frac{d^3p}{h^3}\exp[-\beta\frac{p_x^2+p_y^2+p_z^2}{2m}-\beta\Omega(xp_y-yp_z)]$$

for the integral, we have

$$\int d^3p\exp[-\beta\frac{p_x^2+p_y^2+p_z^2}{2m}-\beta\Omega(xp_y-yp_z)]$$
$$= \sqrt{\frac{2\pi m}{\beta}}\int dp_y dp_z\exp[-\frac{\beta}{2m}(p_y^2+p_z^2)-\beta\Omega xp_y+\beta\Omega yp_z]$$
$$= (\frac{2\pi m}{\beta})^{3/2}exp[\frac{1}{2}\beta m\Omega^2(x^2+y^2)]$$

thus

$$\rho(x,y,z) = [(\frac{2\pi}{\beta})^3\sqrt{\frac{m}{K}}\frac{m}{K-m\Omega^2}]^{-1}(\frac{2\pi m}{\beta})^{3/2}$$
$$\exp[-\frac{K\beta}{2}(x^2+y^2+z^2)+\frac{1}{2}\beta m\Omega^2(x^2+y^2)]$$
$$= ((\frac{2\pi}{\beta})^{3/2}\sqrt{\frac{1}{K}}\frac{1}{K-m\Omega^2})^{-1}\exp[-\frac{K\beta}{2}(x^2+y^2+z^2)+\frac{1}{2}\beta m\Omega^2(x^2+y^2)]$$

we first calculate $\langle z^2\rangle$, since

$$\int dxdydz z^2\exp[-\frac{K\beta}{2}(x^2+y^2+z^2)+\frac{1}{2}\beta m\Omega^2(x^2+y^2)]$$
$$= \frac{2\pi}{\beta(K-m\Omega^2)}\int z^2\exp[-\frac{K\beta}{2}z^2]dz$$
$$= \frac{2\pi}{\beta(K-m\Omega^2)}\sqrt{\frac{2\pi}{K\beta}}\frac{1}{K\beta}$$
$$\langle z^2\rangle = ((\frac{2\pi}{\beta})^{3/2}\sqrt{\frac{1}{K}}\frac{1}{K-m\Omega^2})^{-1}\frac{2\pi}{\beta(K-m\Omega^2)}\sqrt{\frac{2\pi}{K\beta}}\frac{1}{K\beta}$$
$$= \frac{1}{\beta K}$$

$\langle x^2\rangle$ is equal to $\langle y^2\rangle$, and since

$$\int dxdydz x^2\exp[-\frac{K\beta}{2}(x^2+y^2+z^2)+\frac{1}{2}\beta m\Omega^2(x^2+y^2)]$$
$$= \sqrt{\frac{2\pi}{K\beta}}\sqrt{\frac{2\pi}{\beta(K-m\Omega^2)}}\int dx x^2\exp[-\frac{K\beta}{2}x^2+\frac{1}{2}\beta m\Omega^2x^2]$$
$$= \sqrt{\frac{2\pi}{K\beta}}\frac{2\pi}{\beta(K-m\Omega^2)}\frac{1}{\beta(K-m\Omega^2)}$$

we have their expectation

$$\langle x^2\rangle = \langle y^2\rangle = \sqrt{\frac{2\pi}{K\beta}}\frac{2\pi}{\beta(K-m\Omega^2)}\frac{1}{\beta(K-m\Omega^2)}((\frac{2\pi}{\beta})^{3/2}\sqrt{\frac{1}{K}}\frac{1}{K-m\Omega^2})^{-1}$$
$$= \frac{1}{\beta(K-m\Omega^2)}$$

Atomic/molecular hydrogen

2.a

since interaction and quantum degeneracies can be ignored, this is an ideal gas, we can use the equation from textbook,

$$Z_a(N_1,T,V) = \int \frac{1}{N_1!}\prod_{i=1}^{N_1}\frac{d^3q_i d^3p_i}{h^3}\exp[-\beta\sum_{i=1}^{N_1}\frac{p_i^2}{2m}]$$
$$= \frac{V^{N_1}}{N_1!}(\frac{2\pi m k_B T}{h^2})^{3N_1/2}$$

2.b

since transition and rotation is independent, we have

$$Z_m(N_2,T,V) = Z_{trans}Z_{rot}\exp[N_2\beta\epsilon]$$

for transition we have

$$Z_{trans} = \frac{1}{N_2!}\int\prod_{i=1}^{N_2}\frac{d^3q_i d^3p_i}{h^3}\exp[-\beta\sum_{i=1}^{N_1}\frac{p_i^2}{4m}]$$
$$= \frac{V^{N_2}}{N_2!}(\frac{4\pi m k_B T}{h^2})^{3N_2/2}$$

for rotation, by definition of L, the Hamiltonian can be written as

$$H_{rot} = \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2\theta}$$

thus the partition function of rotation is

$$Z_{rot} = (\int\frac{d\theta d\phi dp_\theta dp_\phi}{h^2}\exp[-\beta(\frac{p_\theta^2}{2I}+\frac{p_\phi^2}{2I\sin^2\theta})])^{N_2}$$
$$= (\frac{1}{h^2}\sqrt{\frac{2\pi I}{\beta}}\int_0^\pi d\theta\sqrt{\frac{2\pi I\sin^2\theta}{\beta}}\int_0^{2\pi}d\phi)^{N_2}$$
$$= (\frac{8\pi^2 I}{\beta h^2})^{N_2}$$
$$= (\frac{8\pi^2 I k_B T}{h^2})^{N_2}$$

thus the partition function is

$$Z = \frac{1}{N_2!}(V(\frac{4\pi m k_B T}{h^2})^{3/2}(\frac{8\pi^2 I k_B T}{h^2})\exp[\beta\epsilon])^{N_2}$$
$$= \frac{1}{N_2!}(\frac{16\sqrt{2}\pi^2 I k_B T V}{\lambda^3 h^2}\exp[\beta\epsilon])^{N_2}$$

where $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$

2.c

$$F_1 = -k_B T \ln(Z) = -N_1 k_B T[\ln(\frac{Ve}{N_1}) + \frac{3}{2}\ln(\frac{2\pi m k_B T}{h^2})]$$

$$\begin{aligned} F_2 &= -k_B T \ln(Z) = -k_B T \ln(Z) \\ &= -k_B T \ln(\frac{1}{N_2!}(\frac{16\sqrt{2}\pi^2 I k_B T V}{\lambda^3 h^2}\exp[\beta\epsilon])^{N_2}) \\ &= -k_B T N_2(-\ln(N_2) + 1 + \ln(\frac{16\sqrt{2}\pi^2 I k_B T V}{\lambda^3 h^2}\exp[\beta\epsilon])) \end{aligned}$$

when equilibrium, the Gibbs free energy is a constant, indicates

$$dG = \mu_a dN_a + \mu_m dN_m = 0, 2dN_m = -dN_a$$

thus $2\mu_a = \mu_m$,

$$\mu_a = \frac{\partial F_1}{\partial N_1}\bigg|_{T,V} = -k_B T \ln(\frac{V}{N_1\lambda^3})$$

$$\begin{aligned} \mu_m &= \frac{\partial F_2}{\partial N_2}\bigg|_{T,V} \\ &= -k_B T(-\ln(N_2) + \ln(\frac{16\sqrt{2}\pi^2 I k_B T V}{\lambda^3 h^2}\exp[\beta\epsilon])) \\ &= -k_B T \ln(\frac{16\sqrt{2}\pi^2 I k_B T V}{\lambda^3 h^2 N_2}\exp[\beta\epsilon]) \end{aligned}$$

so we have

$$\begin{aligned} (\frac{V}{N_1\lambda^3})^2 &= (\frac{16\sqrt{2}\pi^2 I k_B T V}{\lambda^3 h^2 N_2}\exp[\beta\epsilon]) \\ (\frac{1}{n_a\lambda^3})^2 &= (\frac{16\sqrt{2}\pi^2 I k_B T}{\lambda^3 h^2 n_m}\exp[\beta\epsilon]) \\ \frac{n_m}{n_a^2} &= (\frac{16\sqrt{2}\pi^2 \lambda^3 I k_B T}{h^2}\exp[\beta\epsilon]) \end{aligned}$$

Molecular adsorption

3.a

the smallest energy is zero, and since it has to be aligned in x or y directions, thus we have

$$\Omega(0, N) = \frac{N!}{(N-2)!N!} = N(N-1)$$

the largest energy is when they all stand up, which is $N\epsilon$

3.b

at energy E, the number of zero energy molecules are $N - N_1$, they can be x or y direction, the number of macrostates is

$$\Omega(E, N) = \frac{N!}{N_1!(N-N_1)!}(N-N_1)(N-N_1-1) = \frac{N!}{N_1!(N-N_1-2)!}$$

where $N_1 = \frac{E}{\epsilon}$, assume $N_1, N >> 1$, the entropy is

$$\begin{aligned} S(E, N) &\approx -Nk_B[\frac{N_1}{N}\ln\frac{N_1}{N} + \frac{N-N1-2}{N}\ln\frac{N-N_1-2}{N}] \\ &= -Nk_B[\frac{E}{N\epsilon}\ln(\frac{E}{N\epsilon}) + (1-\frac{E}{N\epsilon}-\frac{2}{N})\ln(1-\frac{E}{N\epsilon}-\frac{2}{N})] \end{aligned}$$

3.c

The energy can be calculated using

$$\frac{1}{T} = \frac{\partial S}{\partial E}\bigg|_N = -\frac{k_B}{\epsilon}\ln(\frac{E}{N\epsilon - E - 2\epsilon})$$

thus we have the internal energy

$$E(T) = \frac{(N-2)\epsilon}{\exp(\frac{\epsilon}{k_B T}) + 1}$$

the heat capacity is

$$C(T) = \frac{dE}{dT} = (N-2)k_B(\frac{\epsilon}{k_B T})^2\exp(\frac{\epsilon}{k_B T})[\exp(\frac{\epsilon}{k_B T}) + 1]^{-2}$$

3.d

$$\begin{aligned} p(n = 0_x) = p(n = 0_y) &= \frac{\Omega(E, N-1)}{\Omega(E, N)} \\ &= \frac{(N-1)!}{N_1!(N-N_1-3)!}\frac{N_1!(N-N_1-2)!}{N!} \\ &= (1 - \frac{N_1}{N} - \frac{2}{N}) \end{aligned}$$

thus the probability of standing up is

$$
\begin{aligned}
p(n=1) &= 1-2p(n=0_x)\\
&= 1-2(1-\frac{N_1}{N}-\frac{2}{N})\\
&= \frac{2N_1}{N}+\frac{4}{N}-1\\
&= \frac{2E}{N\epsilon}+\frac{4}{N}-1\\
&= \frac{2(1-2/N)}{\exp(\frac{\epsilon}{k_BT})+1}+\frac{4}{N}-1
\end{aligned}
$$

3.e

this is when $T \to +\infty$, which gives $E = (N-2)\epsilon$

Curie susceptibility

4.a

$$
\begin{aligned}
Z(T,B) &= \sum_{\{m_i\}} \exp[\beta B\mu \sum_{i=1}^{N} m_i]\\
&= \prod_{i=1}^{N}(\sum_{\{m_i\}} \exp[\beta B\mu m_i])\\
&= (\exp[-\beta B\mu s]\sum_{m=1}^{2s+1} \exp[\beta B\mu m])^N\\
&= (\frac{\exp[-\beta B\mu s]-\exp[\beta B\mu(s+1)]}{1-\exp[\beta B\mu]})^N\\
&= (\frac{\exp[-\beta B\mu(s+1/2)]-\exp[\beta B\mu(s+1/2)]}{\exp[-\beta B\mu/2]-\exp[\beta B\mu/2]})^N\\
&= (\frac{\sinh(\beta B\mu[s+1/2])}{\sinh(\beta B\mu/2)})^N
\end{aligned}
$$

4.b

Gibbs free energy

$$
\begin{aligned}
G &= -k_B T \ln Z \\
&= -Nk_B T \ln(\frac{\sinh(\beta B\mu[s+1/2])}{\sinh(\beta B\mu/2)}) \\
&= -Nk_B T[\ln(\sinh(\beta B\mu[s+1/2])) - \ln(\sinh(\beta B\mu/2))] \\
&\approx -Nk_B T[\ln(\beta B\mu[s+1/2] + \frac{(\beta B\mu[s+1/2])^3}{6}) - \ln(\beta B\mu/2 + \frac{(\beta B\mu/2)^3}{6})] \\
&= -Nk_B T[\ln(\beta B\mu(s+1/2)) + \ln(1 + \frac{(\beta B\mu[s+1/2])^2}{6}) - \ln(\beta B\mu/2) - \ln(1 + \frac{(\beta B\mu/2)^2}{6})] \\
&= G(0) - Nk_B T[\ln(1 + \frac{(\beta B\mu[s+1/2])^2}{6}) - \ln(1 + \frac{(\beta B\mu/2)^2}{6})] \\
&= G(0) - Nk_B T[\frac{(\beta B\mu[s+1/2])^2}{6} - \frac{(\beta B\mu/2)^2}{6}] \\
&= G(0) - \frac{N\mu^2 s(s+1)B^2}{6k_B T}
\end{aligned}
$$

since $G(B)$ is even, thus the high order terms start from $O(B^4)$

4.c

$$
M = -\frac{\partial G}{\partial B} = \frac{2N\mu^2 s(s+1)}{3k_B T} B + O(B^3)
$$

thus

$$
\chi = \left.\frac{\partial M}{\partial B}\right|_{B=0} = \frac{2N\mu^2 s(s+1)}{3k_B T} = c/T
$$

4.d

$$
\begin{aligned}
C_B &= \left.\frac{\partial H}{\partial T}\right|_B \\
&= -B \left.\frac{\partial M}{\partial T}\right|_B \\
&= -B\frac{\partial}{\partial T}\frac{2N\mu^2 s(s+1)}{3k_B T}B \\
&= B^2 \frac{2N\mu^2 s(s+1)}{3k_B T^2}
\end{aligned}
$$

$$
C_M = \left.\frac{\partial H}{\partial T}\right|_M = -M \left.\frac{\partial B}{\partial T}\right|_M = 0
$$

thus $C_B - C_M = cB^2/T^2$

Disordered glass

6.a

it is a two level system

$$
\begin{aligned}
Z(T) &= \sum_{m_i \in 0,1} \exp[-\beta \sum_i \epsilon_i + \delta_i m_i] \\
&= \prod_{i=1}^{N} \exp[\beta \epsilon_i] \sum_{m_i \in 0,1} \exp[-\beta \delta_i m_i]
\end{aligned}
$$