MAU34406: Statistical Physics II
Homework 1 due 14/02/2022

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JS Theoretical Physics

Exercise 1

$$\begin{aligned}
\Omega(E,V,N) &= \frac{1}{M!}\,\frac{d^M}{dx^M}(1-x)^{-N}\bigg|_{x=0} \\
&= \frac{(-1)^M}{M!}\,(-N)\,(-N-1)\ldots(-N-M+1)\,(1-0) \\
&= \frac{(N+M-1)!}{M!\,(N-1)!} \\
&\approx \frac{\sqrt{2\,\pi}}{\sqrt{2\,\pi}}\,\frac{\sqrt{N+M-1}}{\sqrt{M}}\left(\frac{N+M-1}{e}\right)^{N+M-1}\left(\frac{e}{M}\right)^M\frac{1}{(N-1)!} \\
&\qquad\qquad\text{(Stirling's approximation: } n!\approx\sqrt{2\,\pi\,n}\left(\tfrac{n}{e}\right)^n\text{)} \\
&= (N+M-1)^{N+M-\frac{1}{2}}\,M^{-M-\frac{1}{2}}\,e^{1-N}\,\frac{1}{(N-1)!} \\
&\approx (N+M)^{N+M-\frac{1}{2}}\,M^{-M-\frac{1}{2}}\,\frac{1}{(N-1)!} && (N\gg 1) \\
&\approx \frac{M^{N+M-\frac{1}{2}}\,M^{-M-\frac{1}{2}}}{(N-1)!} && (M\gg N) \\
&= \frac{M^{N-1}}{(N-1)!}
\end{aligned}$$

$$\begin{aligned}
\mathcal{W}(E) &= \sum_{M=0}^{\infty}\Omega(E)\,\delta\left(E-M\,\hbar\omega-\frac{N\,\hbar\omega}{2}\right) \\
&\approx \sum_{M=0}^{\infty}\frac{M^{N-1}}{(N-1)!}\,\delta(E-M\,\hbar\omega) && (M\gg N) \\
&\approx \int_0^{\infty}dM\,\frac{M^{N-1}}{(N-1)!}\,\delta(E-M\,\hbar\omega)
\end{aligned}$$

$$\mathcal{W}(E) = \frac{1}{(N-1)!}\left(\frac{E}{\hbar\,\omega}\right)^{N-1}$$

Exercise 2

$$
\begin{aligned}
\langle \epsilon \rangle &= -\frac{\partial(\ln \xi)}{\partial \beta} \\
&= \frac{\partial}{\partial \beta}\left(\ln\left(1 - e^{-\beta\,\hbar\,\omega}\right) + \frac{\beta\,\hbar\,\omega}{2}\right) \\
&= \frac{\hbar\,\omega\, e^{-\beta\,\hbar\,\omega}}{1 - e^{-\beta\,\hbar\,\omega}} + \frac{\hbar\,\omega}{2} \\
&= \hbar\,\omega\left(\frac{1}{e^{\beta\,\hbar\,\omega}} + \frac{1}{2}\right) \\
&= \hbar\,\omega\left(\langle n \rangle + \frac{1}{2}\right) \\
\implies \langle n \rangle &= \frac{1}{e^{\beta\,\hbar\,\omega} - 1}
\end{aligned}
$$

$$
\begin{aligned}
\mathcal{P}(n) &= \frac{e^{-\beta\,E_n}}{\xi} \\
\mathcal{P}(n) &= \frac{e^{-\beta\,\hbar\,\omega\left(n+\frac{1}{2}\right)}}{\xi}
\end{aligned}
$$

$$
\begin{aligned}
\langle n \rangle &= \sum_{n=0}^{\infty} n\,\mathcal{P}(n) \\
&= \sum_{n=0}^{\infty} n\,\frac{e^{-\beta\,\hbar\,\omega\left(n+\frac{1}{2}\right)}}{\xi} \\
&= \frac{1 - e^{-\beta\,\hbar\,\omega}}{e^{-\frac{\beta\,\hbar\,\omega}{2}}} \sum_{n=0}^{\infty} n\, e^{-\beta\,\hbar\,\omega\left(n+\frac{1}{2}\right)} \\
&= \left(1 - e^{-\beta\,\hbar\,\omega}\right) \sum_{n=0}^{\infty} n\, e^{-\beta\,\hbar\,\omega\, n} \\
&= \left(e^{-\beta\,\hbar\,\omega} - 1\right) \frac{\partial}{\partial(\beta\,\hbar\,\omega)} \sum_{n=0}^{\infty} e^{-\beta\,\hbar\,\omega\, n} \\
&= \left(e^{-\beta\,\hbar\,\omega} - 1\right) \frac{\partial}{\partial(\beta\,\hbar\,\omega)} \left(\frac{1}{1 - e^{-\beta\,\hbar\,\omega}}\right) \\
&= \left(1 - e^{-\beta\,\hbar\,\omega}\right) \frac{e^{-\beta\,\hbar\,\omega}}{\left(1 - e^{-\beta\,\hbar\,\omega}\right)^2} \\
&= \frac{e^{-\beta\,\hbar\,\omega}}{1 - e^{-\beta\,\hbar\,\omega}} \\
\langle n \rangle &= \frac{1}{e^{\beta\,\hbar\,\omega} - 1}
\end{aligned}
$$

Exercise 3

1.

$$
\begin{aligned}
N &= \frac{\text{total phase space volume}}{\text{phase space volume occupied by a single particle}} \\
&= \frac{1}{h^3} \int d^3\vec{q}\, d^3\vec{p} \\
&= \frac{V}{h^3} \int p^2 \sin\theta \, dp\, d\theta\, d\phi \\
&= \frac{4\,\pi\,V}{h^3} \int p^2\, dp \\
&= \frac{4\,\pi\,V}{h^3} \int \left(\frac{\hbar\,\omega}{v}\right)^2 \frac{\hbar}{v}\, d\omega && (p = \hbar\,k = \tfrac{\hbar\,\omega}{v}) \\
&= \frac{4\,\pi\,V}{h^3\,v^3} \left(\frac{h}{2\,\pi}\right)^3 \int \omega^2\, d\omega \\
&= \frac{V}{2\,\pi^2\,v^3} \int \omega^2\, d\omega
\end{aligned}
$$

$$
\begin{aligned}
3\,N &= \int g(\omega)\, d\omega \\
\implies \int g(\omega)\, d\omega &= \frac{3\,V}{2\,\pi^2\,v^3} \int \omega^2\, d\omega \\
\implies g(\omega) &= \frac{3\,V\,\omega^2}{2\,\pi^2\,v^3}
\end{aligned}
$$

2.

$$
\begin{aligned}
N &= \frac{4\,\pi\,V}{h^3} \int p^2\, dp && \text{(from before)} \\
&= \frac{4\,\pi\,V}{h^3} \int \hbar^2 \left(\frac{\omega}{A}\right)^{\frac{2}{s}} \frac{\hbar}{s\,A^{\frac{1}{s}}}\, \omega^{\frac{1-s}{s}}\, d\omega && (p = \hbar\,k = \hbar\left(\tfrac{\omega}{A}\right)^{\frac{1}{s}}) \\
&= \frac{4\,\pi\,V}{h^3\,s\,A^{\frac{3}{s}}} \left(\frac{h}{2\,\pi}\right)^3 \int \omega^{\frac{3-s}{s}}\, d\omega \\
&= \frac{V}{2\,\pi^2\,s\,A^{\frac{3}{s}}} \int \omega^{\frac{3-s}{s}}\, d\omega
\end{aligned}
$$

$$
\begin{aligned}
3\,N &= \int g(\omega)\, d\omega \\
\implies \int g(\omega)\, d\omega &= \frac{3\,V}{2\,\pi^2\,s\,A^{\frac{3}{s}}} \int \omega^{\frac{3-s}{s}}\, d\omega \\
\implies g(\omega) &= \frac{3\,V\,\omega^{\frac{3-s}{s}}}{2\,\pi^2\,s\,A^{\frac{3}{s}}}
\end{aligned}
$$

3.

$$\begin{aligned}
C_V &= k \int_0^{\omega_D} d\omega \, \frac{(\beta\,\hbar\,\omega)^2\, e^{\beta\,\hbar\,\omega}}{(e\beta\,\hbar\,\omega)^2} \, \frac{3\,V\,\omega^{\frac{3-s}{s}}}{2\,\pi^2\,s\,A^{\frac{3}{s}}} \\
&= \frac{3\,k\,V}{2\,\pi^2\,s\,A^{\frac{3}{s}}} \int_0^{x_D} \frac{dx}{\beta\,\hbar} \, \frac{x^2\,e^x}{(e^x-1)^2} \left(\frac{x}{\beta\,\hbar}\right)^{\frac{3-s}{s}} && (x = \beta\,\hbar\,\omega) \\
&\approx \frac{3\,k\,V}{2\,\pi^2\,s\,(A\,\beta\,\hbar)^{\frac{3}{s}}} \int_0^{\infty} \frac{x^{\frac{3+s}{s}}\,e^x}{(e^x-1)^2}\,dx && (x_D = \tfrac{\hbar\,\omega_D}{k\,T} \to \infty \text{ as } T \to 0) \\
&= \frac{3\,k\,V}{2\,\pi^2\,s\,(A\,\beta\,\hbar)^{\frac{3}{s}}} \left(- \frac{x^{\frac{3+s}{s}}}{e^x-1}\bigg|_0^{\infty} + \int_0^{\infty} \frac{3+s}{s}\,\frac{x^{\frac{3}{s}}}{e^x-1}\,dx \right) && (u = x^{\frac{3+s}{s}},\ dv = \tfrac{e^x}{(e^x-1)^2}) \\
&= \frac{3\,k\,V}{2\,\pi^2\,s\,(A\,\beta\,\hbar)^{\frac{3}{s}}} \, \frac{3+s}{s} \int_0^{\infty} x^{\frac{3}{s}}\,e^{-x}\,\frac{1}{1-e^{-x}}\,dx \\
&= \frac{3\,k\,V}{2\,\pi^2\,s\,(A\,\beta\,\hbar)^{\frac{3}{s}}} \, \frac{3+s}{s} \int_0^{\infty} x^{\frac{3}{s}}\,e^{-x} \sum_{n=0}^{\infty} e^{-n\,x}\,dx \\
&= \frac{3\,k\,V}{2\,\pi^2\,s\,(A\,\beta\,\hbar)^{\frac{3}{s}}} \, \frac{3+s}{s} \, (-1)^{\frac{3}{s}} \sum_{n=0}^{\infty} \frac{\partial^{\frac{3}{s}}}{\partial(n-1)^{\frac{3}{s}}} \int_0^{\infty} e^{-x\,(n-1)}\,dx \\
&= \frac{3\,k\,V}{2\,\pi^2\,s\,(A\,\beta\,\hbar)^{\frac{3}{s}}} \, \frac{3+s}{s} \, (-1)^{\frac{3}{s}} \sum_{n=0}^{\infty} \frac{\partial^{\frac{3}{s}}}{\partial(n-1)^{\frac{3}{s}}} \, \frac{e^{-x\,(n-1)}}{-n-1}\bigg|_0^{\infty} \\
&= \frac{3\,k\,V}{2\,\pi^2\,s\,(A\,\beta\,\hbar)^{\frac{3}{s}}} \, \frac{3+s}{s} \, (-1)^{\frac{3}{s}} \sum_{n=0}^{\infty} \frac{\partial^{\frac{3}{s}}}{\partial(n-1)^{\frac{3}{s}}} \, \frac{1}{n+1} \\
C_V &= \frac{3\,k\,V}{2\,\pi^2\,s\,(A\,\beta\,\hbar)^{\frac{3}{s}}} \, \frac{3+s}{s} \sum_{n=0}^{\infty} \left(\frac{3}{s}\right)! \, \frac{1}{(n+1)^{\frac{3+s}{s}}} \\
&= \frac{3\,k\,V}{2\,\pi^2\,s\,(A\,\beta\,\hbar)^{\frac{3}{s}}} \left(\frac{3+s}{s}\right)! \, \zeta\!\left(\frac{3+s}{s}\right)
\end{aligned}$$

Since we have C_V is proportional to $T^{\frac{3}{s}}$, a smaller s corresponds to a fast increase of C_V with T.

Exercise 4

$$\begin{aligned}
F &= -k\,T \ln Z \\
&= -k\,T \left(-\beta\,\mathcal{V}_0 - \sum_{i=1}^{3\,N} \left(\frac{\beta\,\hbar\,\omega_i}{2} + \ln\!\left(1 - e^{-\beta\,\hbar\,\omega_i}\right) \right) \right) \\
&= \mathcal{V}_0 + \sum_{i=1}^{3\,N} \left(\frac{\hbar\,\omega_i}{2} + k\,T \ln\!\left(1 - e^{-\beta\,\hbar\,\omega_i}\right) \right)
\end{aligned}$$

$$\begin{aligned}
P &= -\frac{\partial F}{\partial V} \\
&= -\frac{\partial \mathcal{V}_0}{\partial V} - \sum_{i=1}^{3\,N} \left(\frac{\hbar}{2}\,\frac{\partial \omega_i}{\partial V} + \frac{k\,T}{1 - e^{-\beta\,\hbar\,\omega_i}}\,\beta\,\hbar\,e^{-\beta\,\hbar\,\omega_i}\,\frac{\partial \omega_i}{\partial V} \right) \\
&= -\frac{\partial \mathcal{V}_0}{\partial V} - \hbar \sum_{i=1}^{3\,N} \left(\frac{1}{2} + \frac{1}{e^{\beta\,\hbar\,\omega_i} - 1} \right) \frac{\partial \omega_i}{\partial V}
\end{aligned}$$

$$
\begin{aligned}
\Delta E &= \langle E\rangle - \mathcal{V}_0 \\
&= -\frac{\partial(\ln Z)}{\partial\beta} - \mathcal{V}_0 \\
&= \mathcal{V}_0 + \sum_{i=1}^{3\,N}\left(\frac{\hbar\,\omega_i}{2} + \frac{\hbar\,\omega_i\, e^{-\beta\,\hbar\,\omega_i}}{1-e^{-\beta\,\hbar\,\omega_i}}\right) - \mathcal{V}_0 \\
&= \hbar\sum_{i=1}^{3\,N}\left(\frac{1}{2} + \frac{1}{e^{\beta\,\hbar\,\omega_i}-1}\right)\omega_i
\end{aligned}
$$

$$
\begin{aligned}
\frac{\partial\omega_i}{\partial V} &= \omega_i\,\frac{\partial(\ln\omega_i)}{\partial V} \\
&= \omega_i\,\frac{\partial(\ln\omega_i)}{\partial(\ln V)}\,\frac{\partial(\ln V)}{\partial V} \\
&= \frac{\omega_i}{V}\,\frac{\partial(\ln\omega_i)}{\partial(\ln V)} \\
&= -\frac{\gamma\,\omega_i}{V}
\end{aligned}
$$

$$
\begin{aligned}
\implies P &= -\frac{\partial\mathcal{V}_0}{\partial V} + \hbar\sum_{i=1}^{3\,N}\left(\frac{1}{2} + \frac{1}{e^{\beta\,\hbar\,\omega_i}-1}\right)\frac{\gamma\,\omega_i}{V} \\
&= -\frac{\partial\mathcal{V}_0}{\partial V} + \frac{\gamma\,\Delta E}{V}
\end{aligned}
$$

$$
C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V
$$

$$
\begin{aligned}
-1 &= \left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial T}{\partial P}\right)_V \\
\implies \left(\frac{\partial V}{\partial T}\right)_P &= -\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial P}{\partial V}\right)_T^{-1}
\end{aligned}
$$

$$
\implies C_P - C_V = -T\left(\frac{\partial P}{\partial T}\right)_V^2\left(\frac{\partial P}{\partial V}\right)_T^{-1}
$$

$$
\begin{aligned}
\left(\frac{\partial P}{\partial T}\right)_V &= -\frac{\partial^2\mathcal{V}_0}{\partial T\,\partial V} + \frac{\gamma}{V}\left(\frac{\partial\Delta E}{\partial T}\right)_V \\
&= 0 + \frac{\gamma}{V}\left(\frac{\partial(\langle E\rangle - \mathcal{V}_0)}{\partial T}\right)_V \\
&= \frac{\gamma}{V}\,(C_V - 0) \\
&= \frac{\gamma\,C_V}{V}
\end{aligned}
$$

$$
\begin{aligned}
\left(\frac{\partial P}{\partial V}\right)_T &= -\left(\frac{\partial^2\mathcal{V}_0}{\partial V^2}\right) + \frac{\gamma}{V}\left(\frac{\partial\Delta E}{\partial V}\right)_T + \gamma\,\Delta E\,\frac{\partial\frac{1}{V}}{\partial V} \\
&= -\frac{1}{\kappa\,b} + \frac{\gamma}{V}\left(\frac{\partial(\langle E\rangle - \mathcal{V}_0)}{\partial V}\right)_T - \frac{\gamma\,\Delta E}{V^2} \\
&= -\frac{1}{\kappa\,b} + \frac{\gamma}{V}\left(-P - \frac{\partial\mathcal{V}_0}{\partial V}\right) - \frac{\gamma\,\Delta E}{V^2} \\
&= -\frac{1}{\kappa\,b} + \frac{\gamma}{V}\left(\frac{\partial\mathcal{V}_0}{\partial V} - \frac{\gamma\,\Delta E}{V} - \frac{\partial\mathcal{V}_0}{\partial V}\right) - \frac{\gamma\,\Delta E}{V^2} \\
&= -\frac{1}{\kappa\,b} - \frac{\gamma^2+\gamma}{V^2}\,\Delta E \\
&= -\frac{b}{\kappa\,V^2}\left(\frac{V^2}{b^2} + \frac{\gamma^2+\gamma}{b}\,\kappa\,\Delta E\right) \\
&\approx -\frac{b}{\kappa\,V^2} \qquad\qquad (V \text{ same order as } b,\ b \gg \kappa)
\end{aligned}
$$

$$
\begin{aligned}
\implies C_P - C_V &= -T\left(\frac{\gamma\,C_V}{V}\right)^2\left(-\frac{\kappa\,V^2}{b}\right) \\
&= \frac{\gamma^2\,\kappa\,C_V^2\,T}{b}
\end{aligned}
$$