ExamT4 - Thermal Physics II, Prof. G. Palasantzas

Date: 28-01-2026, Total number of points: 100, Points for taking the exam: 10

Problem 1 (20 points) Consider the partition function Z_N for the van der Waals (vdW) gas of N (>>1) particles in volume V at temperature T (λ_{th} is the thermal wavelength).

$$Z_N = \frac{1}{N!}\left(\frac{V-Nb}{\lambda_{th}{}^3}\right)^N e^{(\beta aN^2/V)}$$

(a: 10 points) From Z_N derive the vdW equation for P=P(T,V,N):

$$P = \frac{k_B TN}{V-Nb} - \frac{aN^2}{V^2}$$

(b: 10 points) Calculate the chemical potential μ of the vdW gas.
Tips: Consider $F=-k_B T\ln(Z_N)$, $P=-(\partial F/\partial V)_{T,N}$, $\mu=(\partial F/\partial N)_{V,T}$.

Problem 2 (25 points) In a Joule–Kelvin liquefier, the gas can be cooled by expansion through an insulated throttle. Using the viral expansion of the vdW equation $PV/RT = 1 + (1/V)[b - (a/RT)]$ (V>>b), from Eq. (1) calculate the inversion temperature T.

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T} \quad (1)$$

Problem 3 (25 points)

(a: 20 points) (i: 5 points) If we assume for simplicity a system that has only one available state, with energy cost E, then show that for fermions the Fermi–Dirac function at temperature T and chemical potential μ (>>k_BT) has the form $f(E) = 1/[e^{\beta(E-\mu)} + 1]$. What are the asymptotic expressions/values of f(E) when: (ii: 5 points) $E \ll \mu$; (iii: 5 points) $E \gg \mu$; and (vi: 5 points) $E \approx \mu$. Tip: $f(E) = (-1/\beta)(\partial \ln\Im/\partial E)$ with $\Im = \sum_{n=0}^{\infty} e^{n\beta(\mu-E)}$ the grand partition function.

(b: 5 points) If two identical fermions are in the same state $|\varphi>$ then show that $|\varphi>|\varphi>=0$.

Problem 4 (20 points)

Show that for a gas of fermions with density of states $g(E)$ and Fermi energy E_F, the chemical potential μ(T) is given by

$$\mu(T) = E_F - \frac{\pi^2}{6}(k_B T)^2 \frac{g'(E_F)}{g(E_F)} + \dots$$

where $g'(E) = dg/dE$. Use the Sommerfeld expansion formula:

$$I = \int_0^{\infty} \phi(E)f(E)\,dE, \quad I = \int_0^{\mu} \phi(E)\,dE + \frac{\pi^2}{6}(k_B T)^2 \left(\frac{d\phi}{dE}\right)_{E=\mu}$$

to expand the Fermion number N for chemical potential μ: $N = \int_0^{\infty} g(E)f(E)dE$.

Problem 1

$$Z_N = \frac{1}{N!} \left(\frac{V - Nb}{d_{th}^3} \right)^N e^{\left(\frac{\alpha N^2}{V k_B T} \right)}$$

$$\ln Z_N = -\ln N! + N \ln \left(\frac{V - Nb}{d_{th}^3} \right) + \frac{\alpha N^2}{V k_B T}$$

$$N \gg 1 \implies \ln N! = N \ln N - N$$

$$\ln Z_N = -N \ln N + N + N \ln \left(\frac{V - Nb}{d_{th}^3} \right) + \frac{\alpha N^2}{V k_B T}$$

$$F = -k_B T \ln Z_N$$

$$P = -\left(\frac{\partial F}{\partial V} \right)_{N,T} = P$$

$$P = k_B T \left(\frac{\partial \ln Z_N}{\partial V} \right)_{N,T}$$

$$P = \frac{N k_B T}{V - Nb} - \frac{\alpha N^2}{V^2}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

$$\mu = - k_B T \left(\frac{\partial \ln Z_N}{\partial N}\right)_{T,V}$$

$$\frac{\partial \ln Z_N}{\partial N} = \ln\left[\frac{V-Nb}{N d_{th}^3}\right] - \frac{Nb}{V-Nb} + \frac{2\alpha N}{V k_B T}$$

$$= ?$$

$$\mu = - k_B T \ln\left[\frac{V-Nb}{N d_{th}^3}\right] + \frac{N k_B T b}{V-Nb} - \frac{2\alpha N}{V}$$

$$= ?$$

$$\mu = - k_B T \ln\left[\frac{V_m-b}{d_{th}^3}\right] + \frac{k_B T b}{V_m - b} - \frac{2\alpha}{V_m}$$

$$V_m = V/N$$

Problem 2

For the

$$P = \frac{RT}{V} + \frac{bRT}{V^2} - \frac{\alpha}{V^2} \quad (1)$$

$$\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1 \Rightarrow$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V \Big/ \left(\frac{\partial P}{\partial V}\right)_T \quad (2)$$

(1) & (2) we have $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} + \frac{bR}{V^2}$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2} - \frac{2bRT}{V^3} + \frac{2\alpha}{V^3}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T} = -\left(\frac{\partial P}{\partial T}\right)_V \Big/ \left(\frac{\partial P}{\partial V}\right)_T \Rightarrow$$

$$V\left(-\frac{RT}{V^2} - \frac{2bRT}{V^3} + \frac{2\alpha}{V^3}\right) = -T\left(\frac{R}{V} + \frac{bR}{V^2}\right)$$

$$-\frac{RT}{V} - \frac{2bRT}{V^2} + \frac{2\alpha}{V^2} = -\frac{RT}{V} - \frac{bRT}{V^2}$$

$$\frac{2\alpha}{V^2} = \frac{bRT}{V^2} \Rightarrow \qquad 2\alpha = bRT \Rightarrow$$

$$\boxed{T = \frac{2\alpha}{bR}}$$

Problem 3 (25 points)

(a)

(i) <u>Fermions:</u> n = 0 and n = 1 (Pauli exclusion principle)

$$\mathcal{Z} = \sum_{n=0}^{1} e^{n\beta(\mu-E)} = 1 + e^{\beta(\mu-E)} \qquad \ln \mathcal{Z} = \ln(1 + e^{\beta(\mu-E)})$$

Then the derivative yields

$$f(E) = \left(-\frac{1}{\beta}\right)\left(\frac{\partial \ln \mathcal{Z}}{\partial E}\right) = \left(-\frac{1}{\beta}\right)\frac{-\beta e^{\beta(\mu-E)}}{[1 + e^{\beta(\mu-E)}]} = \frac{1}{[e^{\beta(E-\mu)} + 1]}$$

$\beta \mu \gg 1$

(ii)

$$E \ll \mu: \quad f(E) \simeq \frac{1}{e^{-\beta\mu}+1} \underset{\beta\mu\gg 1}{\simeq} 1$$

(iii)

$$E \gg \mu: \quad f(E) \simeq \frac{1}{e^{\beta E}+1} \underset{\beta E \gg \mu\beta \gg 1}{\simeq} 0$$

(vi)

$$(iii) \quad E \simeq \mu: \quad e^{\beta(E-\mu)}+1 \simeq 1+\beta(E-\mu)+1 = 2 + \beta(E-\mu)$$

$$f(E) \simeq \frac{1}{2+\beta(E-\mu)} = \frac{1}{2}\frac{1}{1+\frac{\beta}{2}(E-\mu)} \simeq \frac{1}{2}\left(1 - \frac{1}{2}(E-\mu)\beta\right)$$

(b)

for fermions, the requirement that $\hat{P}_{12}|\psi\rangle = -|\psi\rangle$ means

if $\psi = |\varphi\rangle|\varphi\rangle \longrightarrow \hat{P}_{12}|\varphi\rangle|\varphi\rangle = |\varphi\rangle|\varphi\rangle = -|\varphi\rangle|\varphi\rangle \implies |\varphi\rangle|\varphi\rangle = 0$

In your book you can see in more detail this:

In general, for fermions, the requirement that $\hat{P}_{12}|\psi\rangle = -|\psi\rangle$ means that if $|\psi\rangle$ is a two-particle state consisting of two particles in the *same* quantum state, i.e. if $\psi = |\varphi\rangle|\varphi\rangle$, then

$$\hat{P}_{12}|\varphi\rangle|\varphi\rangle = |\varphi\rangle|\varphi\rangle = -|\varphi\rangle|\varphi\rangle, \tag{29.13}$$

so that

$$|\varphi\rangle|\varphi\rangle = 0, \tag{29.14}$$

i.e. the doubly-occupied state cannot exist. This, again, illustrates the Pauli exclusion principle, namely that two identical fermions cannot coexist in the same quantum state.

Problem 4

Using the Sommerfeld expansion we have

$$N = \int_0^\infty g(E)\, f(E)\, dE = \int_0^M g(E)\, dE + \frac{\pi^2}{6}(k_B T)^2 \left(\frac{dg}{dE}\right)_{E=M\,(\simeq E_F)} \quad (1)$$

We perform 1st order Taylor expansion of $\int_0^M g(E)\, dE$

$$\int_0^M g(E)\, dE = \int_0^{E_F} g(E)\, dE + (M - E_F) \frac{d}{dM}\left[\int_0^M g(E)\, dE\right]_{M=E_F} \quad (2)$$

$$\frac{d}{dM}\left[\int_0^M g(E)\, dE\right]_{M=E_F} = g(M=E_F) = g(E_F)$$

Thus, $\int_0^M g(E)\, dE = \int_0^{E_F} g(E)\, dE + (M - E_F)\, g(E_F) \quad (3)$

$$\int_0^{E_F} g(E)\, dE = N \,(T=0\,k) \quad (4)$$

$(3) - (4) \Rightarrow \int_0^M g(E)\, dE = N + (M - E_F)\, g(E_F) \quad (5)$

$(1) \,\&\, (5)$ we have

$$N = N + (M - E_F)\, g(E_F) + \frac{\pi^2}{6}(k_B T)^2 \, g'(E_F) \Rightarrow$$

$$M - E_F = -\frac{\pi^2}{6}\frac{g'(E_F)\,(k_B T)^2}{g(E_F)} \Rightarrow$$

$$\boxed{M = E_F - \frac{\pi^2}{6}(k_B T)^2 \frac{g'(E_F)}{g(E_F)}}$$