Qualifying Exam Solutions: Thermal Physics and Statistical Mechanics

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Problem A

1 Solutions for Problem 1

a) $\Delta Q = 0$ for adiabatic processes, and thus the first law of thermodynamics becomes:

$$\Delta U + A = 0, \tag{1}$$

where A is the work done by gas, and U is its internal energy. Using $A = P_2 \Delta V$ and $\Delta U = C_V \Delta T$ we obtain:

$$C_V(T_2 - T_1) + P_2(V_2 - V_1) = 0. \tag{2}$$

Using the equation of state for the ideal gas $PV = RT$ and the relation between heat capacities $C_P - C_V = R$ we get (after some straightforward algebraic manipulations):

$$T_2 = \frac{C_V T_1 + P_2 V_1}{C_P}, \quad V_2 = \frac{RT_2}{P_2}. \tag{3}$$

b) Using the result from part a) we immediately obtain:

$$T_f = \frac{C_V T_2 + P_1 V_2}{C_P}, \quad V_f = \frac{RT_f}{P_1}. \tag{4}$$

The easiest way to compute the temperature difference is to use the first law of thermodynamics directly:

$$\begin{aligned} C_V(T_2 - T_1) &+ P_2(V_2 - V_1) = 0, \\ C_V(T_f - T_2) &+ P_1(V_f - V_2) = 0. \end{aligned} \tag{5}$$

Adding these equations we get:

$$C_V(T_f - T_1) = P_1(V_2 - V_f) + P_2(V_1 - V_2). \tag{6}$$

The next step is to invoke the differential version of the adiabatic equation:

$$\begin{aligned}\gamma P_2(V_2-V_1) &+ V_1(P_2-P_1)=0,\\ \gamma P_1(V_f-V_2) &+ V_2(P_1-P_2)=0.\end{aligned} \tag{7}$$

Then we can easily show that

$$T_f - T_1 = \frac{1}{C_P}(P_1-P_2)(V_2-V_1), \tag{8}$$

which is always positive. More explicitly, we can use the adiabatic equation again:

$$V_2 - V_1 = \frac{V_1}{\gamma P_2}(P_1-P_2) \tag{9}$$

to show that

$$T_f - T_1 = \frac{C_v}{C_p^2}\frac{V_1}{P_2}(P_2-P_1)^2, \tag{10}$$

which is quadratic in $P_2 - P_1$.

Thus the change in temperature is a second order correction wrt the change in pressure. It is possible to make this change as small as we want by making the weights that we add to or remove from the piston at each step very small. The change in temperature is always positive, as expected from the second law of thermodynamics.

Problem C2

Solutions for Problem 2

a) Insert $E = (p_x^2 + p_y^2 + p_z^2)/2m + V(x,y,z)$ into

$$\Phi(x,y,z,p_x,p_y,p_z)d\tau = \frac{e^{-\beta E}d\tau}{\int_{-\infty}^{\infty} e^{-\beta E}d\tau}, \tag{11}$$

and integrate over $dxdydz$ to get the distribution over momenta:

$$\begin{aligned} F(p_x,p_y,p_z) &= \int dxdydz\ \Phi(x,y,z,p_x,p_y,p_z) \\ &= \frac{e^{-\beta(p_x^2+p_y^2+p_z^2)/2m}}{\int dp_x dp_y dp_z\ e^{-\beta(p_x^2+p_y^2+p_z^2)/2m}} \end{aligned} \tag{12}$$

Note that the terms containing $V(x,y,z)$ drop out. $F(p_x,p_y,p_z)$ factorizes into 3 terms: $F(p_x,p_y,p_z) = \Psi(v_x)\Psi(v_x)\Psi(v_x)$, where

$$\Psi(v_x) = \frac{e^{-\beta m v_x^2/2}}{\int dv_x e^{-\beta m v_x^2/2}}, \quad \text{etc.} \tag{13}$$

The Gaussian integral in the denominator can be taken, resulting in:

$$\Psi(v_x)dv_x = \left(\frac{\beta m}{2\pi}\right)^{1/2} e^{-\beta m v_x^2/2}. \tag{14}$$

Sketch of $\Psi(v_x)$ is a Gaussian centered on 0.

b) Calculation are identical for the x, y, and z components. We do just the x component below.

$$\bar{KE}_x = \frac{1}{2}m\bar{v_x^2}, \tag{15}$$

where

$$\bar{v_x^2} = \int_{-\infty}^{\infty} v_x^2 \Psi(v_x)dv_x = \left(\frac{\beta m}{2\pi}\right)^{1/2}\left(\frac{2}{\beta m}\right)^{3/2}\int_{-\infty}^{\infty}\xi^2 \exp^{-\xi^2} d\xi = \frac{1}{\beta m}. \tag{16}$$

Thus $\bar{KE}_x = \frac{1}{2}kT$ as expected from the equipartition theorem ($\beta = 1/kT$), and similarly for y and z.

c) Given $F(v_x, v_y, v_z)$, what is $f(v)$ - the probability that the molecule's velocity is between v and $v + dv$?

$$f(v)dv = \int_\Omega d\Omega v^2 dv F(v_x, v_y, v_z) = \left(\frac{\beta m}{2\pi}\right)^{3/2} 4\pi dv\ v^2 e^{-\beta m v^2/2}, \tag{17}$$

so that

$$f(v) = \left(\frac{\beta m}{2\pi}\right)^{3/2} 4\pi v^2 e^{-\beta m v^2/2}. \tag{18}$$

The sketch has a maximum at $\sqrt{2/\beta m}$ and a Gaussian tail.

d) Instead of integrating over x, y, and z, integrate Eq. (11) over v_x, v_y, and v_z. This results in:

$$F(x, y, z) = \frac{e^{-\beta V(x,y,z)}}{\int\int\int dxdydz\ e^{-\beta V(x,y,z)}}, \tag{19}$$

the fraction of molecules within $dxdydz$ of a given point (x, y, z). In other words, this is the spatial density:

$$n(x, y, z) = n_0 e^{-\beta V(x,y,z)}. \tag{20}$$

For a flat Earth, the potential energy of a molecule at a small height h above ground is $V = mgh$, resulting in (after integrating out the x and y components):

$$n(z) = n(0)e^{-mgh/kT}, \tag{21}$$

Problem B

Problem 2 (partition function, average energy)

(a)

$$Z = \sum_i d_i \exp\left(-\beta\varepsilon_i\right) = 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}$$

(b)

$$\langle\varepsilon\rangle = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\frac{\left(-\varepsilon\right)e^{-\beta\varepsilon} + \left(-2\varepsilon\right)e^{-2\beta\varepsilon}}{1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}} = \varepsilon\frac{e^{-\beta\varepsilon}+2e^{-2\beta\varepsilon}}{1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}}$$

(c)

$$P = \frac{e^{-2\beta\varepsilon}}{1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}} \approx \frac{1-2\beta\varepsilon}{1+1-\beta\varepsilon+1-2\beta\varepsilon} \approx \frac{1}{3}$$

all 3 levels are populated with the same probability

(d)

$$\langle\varepsilon\rangle = \varepsilon\frac{e^{-\beta\varepsilon}+2e^{-2\beta\varepsilon}}{1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}} \approx \varepsilon\frac{1+2}{1+1+1} = \varepsilon$$

Problem 2 (cont'd)

(e) $$\exp(-2\beta\varepsilon)=\frac{1}{1.1}\quad 2\beta\varepsilon=\ln 1.1\quad T=\frac{2\varepsilon}{k_B\ln 1.1}$$

(f) $$C_V=\frac{dU}{dT}=N\frac{d\langle\varepsilon\rangle}{dT}=N\frac{d\langle\varepsilon\rangle}{d\beta}\frac{d\beta}{dT}$$

$$=N\varepsilon\left(-\frac{1}{k_BT^2}\right)\left\{\frac{(-\varepsilon)e^{-\beta\varepsilon}+(-2\varepsilon)2e^{-2\beta\varepsilon}}{1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}}-\frac{\left(e^{-\beta\varepsilon}+2e^{-2\beta\varepsilon}\right)\left[(-\varepsilon)e^{-\beta\varepsilon}+(-2\varepsilon)e^{-2\beta\varepsilon}\right]}{\left[1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}\right]^2}\right\}$$

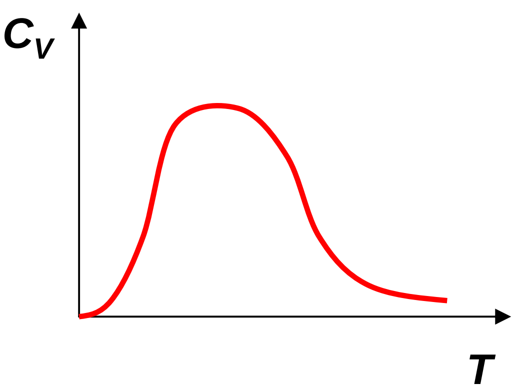
$$=\left(\frac{N\varepsilon^2}{k_BT^2}\right)\left\{\frac{\left[e^{-\beta\varepsilon}+4e^{-2\beta\varepsilon}\right]\left[1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}\right]-\left(e^{-\beta\varepsilon}+2e^{-2\beta\varepsilon}\right)\left(e^{-\beta\varepsilon}+2e^{-2\beta\varepsilon}\right)}{\left[1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}\right]^2}\right\}$$

$$=\frac{N\varepsilon^2}{k_BT^2}\left\{\frac{e^{-\beta\varepsilon}+4e^{-2\beta\varepsilon}+e^{-2\beta\varepsilon}+4e^{-3\beta\varepsilon}+e^{-3\beta\varepsilon}+4e^{-4\beta\varepsilon}-e^{-2\beta\varepsilon}-4e^{-3\beta\varepsilon}-4e^{-4\beta\varepsilon}}{\left[1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}\right]^2}\right\}$$

$$=\frac{N\varepsilon^2}{k_BT^2}\frac{e^{-\beta\varepsilon}+4e^{-2\beta\varepsilon}+e^{-3\beta\varepsilon}}{\left[1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}\right]^2}$$

Low ***T*** (β>>ε): $$C_V=\frac{N\varepsilon^2}{k_BT^2}\frac{e^{-\beta\varepsilon}+4e^{-2\beta\varepsilon}+e^{-3\beta\varepsilon}}{\left[1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}\right]^2}\approx\frac{N\varepsilon^2}{k_BT^2}e^{-\frac{\varepsilon}{k_BT}}$$

high ***T*** (β<<ε): $$C_V=\frac{N\varepsilon^2}{k_BT^2}\frac{e^{-\beta\varepsilon}+4e^{-2\beta\varepsilon}+e^{-3\beta\varepsilon}}{\left[1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}\right]^2}\approx\frac{2}{3}\frac{N\varepsilon^2}{k_BT^2}$$



Problem 1 (multiplicity, entropy)

Problem C1

(a) $$S = k_B \ln\Omega = k_B \ln f(N) + N k_B \ln V + \frac{N f}{2} k_B \ln U \qquad \frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V} = k_B \frac{N f}{2U}$$

$$T = \frac{2U}{N f k_B} \qquad U = \frac{N f}{2} k_B T$$ - in agreement with the equipartition theorem

When $\boldsymbol{T} \to 0$, $\boldsymbol{U} \to 0$, and $\boldsymbol{S} \to -\infty$ - doesn't make sense. This means that the expression for Ω holds in the "classical" limit of high temperatures, it should be modified at low $\boldsymbol{T}$.

Problem 1 (cont'd)

(b) $$C_V = T\left(\frac{\partial S}{\partial T}\right)_{N,V} = T\,Nk_B\,\frac{f}{2}\frac{1}{T} = \frac{f}{2}Nk_B$$

(c) $$\Omega\left(U,V,N\right) = f\left(N\right)V^{N}U^{3N/2}$$

$$\Omega\left(U,V,N\right) \propto V_A^{N_A}\left(V-V_A\right)^{N_B}U_A^{3N_A/2}\left(U-U_A\right)^{3N_B/2}$$

$$\frac{\partial\Omega}{\partial U_A} \propto \frac{3N_A}{2}U_A^{\left(3N_A/2-1\right)}\left(U-U_A\right)^{3N_B/2} - \frac{3N_A}{2}U_A^{3N_A/2}\left(U-U_A\right)^{\left(3N_B/2-1\right)} = 0$$

$$\frac{3N_A}{2}\left(U-U_A\right) - \frac{3N_B}{2}U_A = 0 \qquad \frac{U_A}{N_A} = \frac{U_B}{N_B}$$

Problem D1

HARDER THERMAL PHYSICS PROBLEM SOLUTION

TP 2.

A) $$N = \int g_s \frac{V 4\pi p^2 dp}{h^3} \frac{1}{e^{\beta(\varepsilon-\mu)} \pm 1}$$ IDEAL GAS.

$$\Rightarrow \int g_s \frac{V 4\pi p^2 dp}{h^3} e^{-\beta\varepsilon} e^{\beta\mu}$$

$$N = g_s \frac{V 4\pi}{h^3} \int e^{-\frac{p^2}{2mT} - \frac{m}{T}} e^{\mu/T}$$

$$= g_s \frac{V}{\lambda_T^3} e^{(\mu-m)/T} \qquad \lambda_T^3 = \frac{h^3}{(2\pi m T)^{3/2}}$$

$$\boxed{\frac{\mu}{T} = \frac{m}{T} + \ln \frac{N}{V} \lambda_T^3 \frac{1}{g_s}}$$

NOTE BOLTZMANN $k_B = 1$

B) $$U = \frac{3}{2} N T + m N = U_K + m N$$

$$U = TS - pV + \mu N$$

$$TS = U + pV - \mu N$$

$$= \frac{3}{2} N T + m N + N k T - m N - T N \ln \frac{N}{V} \lambda_T^3 \frac{1}{g_s}$$

$$= \frac{5}{2} N T + T N \ln \frac{V}{\lambda_T^3} g_s$$

$$= N T \ln e^{5/2} \left(\frac{2\pi m T}{h^3} \right)^{3/2} \frac{V}{N} g_s$$

$$= N T \ln e^{5/2} \frac{V g_s}{N h^3} \left(2\pi m \cdot \frac{2}{3} \frac{U}{N} \right)^{3/2}$$

$$\boxed{S = N \ln \left[e^{5/2} \frac{V}{N} g_s \frac{1}{h^3} \left(\frac{4\pi}{3} m \frac{U}{N} \right)^{3/2} \right]}$$

TP2

$1p + 1n \rightleftarrows 1d \Rightarrow$

$\mu_p + \mu_n = \mu_d$

$$[N_p] = g_s(p) \frac{V}{\lambda_T^3(p)} e^{(\mu_p - m_p)/T}$$

$$[N_n] = g_s(n) \frac{V}{\lambda_T^3(n)} e^{(\mu_n - m_n)/T}$$

$$[N_d] = g_s(d) \frac{V}{\lambda_T^3(d)} e^{(\mu_d - m_d)/T}$$

$$\frac{[N_d]}{[N_p][N_n]} = \frac{g_s(d)}{g_s(p)\,g_s(n)} \frac{1}{V} \frac{\lambda_T^3(p)\lambda_T^3(n)}{\lambda_T^3(d)} e^{(-m_d + m_p + m_n)/T}$$

$$\lambda_T^3(p) \cong \lambda_T^3(n)$$

$$\lambda_T^3(d) = \frac{h^3}{(2\pi m_d T)^{3/2}} \simeq \frac{h^3}{(2\pi \cdot 2m_p T)^{3/2}} = \frac{h^3}{2^{3/2}(2\pi m_p T)^{3/2}}$$

$$m_d = m_p + m_n - |BE|$$

$$-m_d + m_p + m_n = +BE$$

$$\boxed{\frac{[N_d]}{[N_p][N_n]} = \frac{g_s(d)}{(g_s(p))^2} \frac{2^{3/2}\lambda_T^3(p)}{V} e^{|BE|/T}}$$

Problem 3 (degenerate Fermi gas) (cont'd)

(a) Problem D2

The number of electron per unit volume: $$N = \int_0^\infty g(\varepsilon) f(\varepsilon) d\varepsilon$$

At ***T* = 0**, all the states up to ε **= *E_F*** are filled, at ε **> *E_F*** – empty: $$f(\varepsilon) = \begin{cases} 1, & \varepsilon \le E_F \\ 0, & \varepsilon > E_F \end{cases}$$

$$N = \int_0^\infty g(\varepsilon) f(\varepsilon) d\varepsilon = \int_0^{E_F} g(\varepsilon) d\varepsilon = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{E_F} \sqrt{\varepsilon}\, d\varepsilon = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} (E_F)^{3/2}$$

$$\boxed{E_F = \frac{\hbar^2}{2m}\left(3\pi^2 N\right)^{2/3} = \frac{h^2}{8m}\left(\frac{3}{\pi}N\right)^{2/3}}$$

$$E_F = \frac{h^2}{8m}\left(\frac{3}{\pi}N\right)^{2/3} \approx \frac{\left(6.6\cdot 10^{-34}\right)^2}{8\times 9.1\cdot 10^{-31}}\left(\frac{3}{\pi}8.5\cdot 10^{28}\right)^{2/3} = 1.1\cdot 10^{-18}\ \text{J} = 6.7\ \text{eV}$$

The ***total energy*** of all electrons in the conduction band (per unit volume):

$$\boxed{U_0 = \int_0^{\varepsilon_F} \varepsilon \times g(\varepsilon) d\varepsilon = \frac{3}{5} N E_F}$$

Problem 3 (degenerate Fermi gas) (cont'd)

(b)

$$\bar{n}(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - E_F}{k_B T}\right) + 1}$$

$$\frac{1}{\exp\left(\frac{\varepsilon_1 - E_F}{k_B T}\right) + 1} = 0.9 \quad \exp\left(\frac{\varepsilon_1 - E_F}{k_B T}\right) = 9 \quad \varepsilon_1 = E_F + k_B T \ln 9$$

$$\frac{1}{\exp\left(\frac{\varepsilon_2 - E_F}{k_B T}\right) + 1} = 0.1 \quad \exp\left(\frac{\varepsilon_2 - E_F}{k_B T}\right) = \frac{1}{9} \quad \varepsilon_2 = E_F - k_B T \ln 9$$

$$\Delta\varepsilon = 2k_B T \ln 9 = 0.11 \text{ eV}$$

(c)

$$N_1 = \int_{E_F - \Delta\varepsilon/2}^{E_F + \Delta\varepsilon/2} \bar{n}(\varepsilon) g(\varepsilon) d\varepsilon = \frac{3N}{2E_F^{3/2}} \sqrt{E_F} \times 0.5 \times \Delta\varepsilon = \frac{3}{4} N \frac{\Delta\varepsilon}{E_F} = N \times 0.012$$

Thus, at ***T***=300K, the ratio of the "current-carrying" electrons to all electrons in the conduction band is 0.012 or 1.2 %.