Problem set 1 — Solutions

Phy-801

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1. **The heat capacity of solids vs gases**

   (a) i. Using $dU = TdS - PdV$

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V = T\left.\frac{\partial S}{\partial T}\right|_V \tag{1}$$

using $dH = d(U+PV) = TdS + VdP$

$$C_P = \left.\frac{\partial H}{\partial T}\right|_P = T\left.\frac{\partial S}{\partial T}\right|_P \tag{2}$$

ii. Use the total differential identity for $S(T,V)$:

$$dS = \left.\frac{\partial S}{\partial T}\right|_V dT + \left.\frac{\partial S}{\partial V}\right|_T dV \tag{3}$$

therefore

$$\left.\frac{\partial S}{\partial T}\right|_P = \left.\frac{\partial S}{\partial T}\right|_V + \left.\frac{\partial S}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_P . \tag{4}$$

therefore

$$C_P - C_V = T\left[\left.\frac{\partial S}{\partial T}\right|_P - \left.\frac{\partial S}{\partial T}\right|_V\right] = T\left.\frac{\partial S}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_P . \tag{5}$$

iii. Using $dF = d(U - TS) = -S\,dT - P\,dV$. Thus

$$S = -\left.\frac{\partial F}{\partial T}\right|_V , \qquad P = -\left.\frac{\partial F}{\partial V}\right|_T . \tag{6}$$

differentiating again, and using the equality of mixed derivatives

$$\left.\frac{\partial S}{\partial V}\right|_T = -\frac{\partial}{\partial V}\left(\left.\frac{\partial F}{\partial T}\right|_V\right)_T = -\frac{\partial}{\partial T}\left(\left.\frac{\partial F}{\partial V}\right|_T\right)_V = \left.\frac{\partial P}{\partial T}\right|_V . \tag{7}$$

and hence

$$C_P - C_V = T\left.\frac{\partial P}{\partial T}\right|_V \left.\frac{\partial V}{\partial T}\right|_P . \tag{8}$$

iv. Use the total differential of $V = V(T,P)$:

$$dV = \left.\frac{\partial V}{\partial T}\right|_P dT + \left.\frac{\partial V}{\partial P}\right|_T dP. \tag{9}$$

with $dV = 0$ yields

$$\left.\frac{\partial P}{\partial T}\right|_V = -\frac{\left.\frac{\partial V}{\partial T}\right|_P}{\left.\frac{\partial V}{\partial P}\right|_T} . \tag{10}$$

and hence

$$C_P - C_V = -T\,\frac{\left(\left.\frac{\partial V}{\partial T}\right|_P\right)^2}{\left.\frac{\partial V}{\partial P}\right|_T} . \tag{11}$$

v. Using the definitions

$$\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P, \qquad \kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T, \qquad \left.\frac{\partial V}{\partial P}\right|_T = -\kappa_T V. \tag{12}$$

we hence obtain

$$\boxed{C_P - C_V = \frac{TV\alpha^2}{\kappa_T}} \tag{13}$$

(b) For an ideal monatomic gas, the single-particle partition function is

$$Z_1 = \frac{1}{(2\pi\hbar)^3}\int_V d^3x \int_{\mathbb{R}^3} d^3p\, e^{-\beta p^2/(2m)}. \tag{14}$$

The x-integral gives V. For the momentum integral, factorize into three identical Gaussians:

$$\int_{\mathbb{R}^3} d^3p\, e^{-\beta p^2/(2m)} = \left(\int_{-\infty}^{\infty} dp\, e^{-\beta p^2/(2m)}\right)^3 = \left(\sqrt{\frac{2\pi m}{\beta}}\right)^3 = (2\pi m k_B T)^{3/2}. \tag{15}$$

Hence

$$Z_1 = V\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}. \tag{16}$$

and hence

$$F = -k_BTN\left[\log V + \frac{3}{2}\log\left(\frac{mk_BT}{2\pi\hbar^2}\right)\right] + k_BT\log N! \tag{17}$$

(c) Using that $F = -k_{\mathrm{B}}T\log Z$

$$P = -\left.\frac{\partial F}{\partial V}\right|_T = Nk_BT\left.\frac{\partial \log Z_1}{\partial V}\right|_T = \frac{Nk_BT}{V}, \tag{18}$$

Also

$$U = -T^2\left.\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right|_V = Nk_{\mathrm{B}}T^2\left.\frac{\partial \log Z_1}{\partial T}\right|_V = \frac{3}{2}Nk_BT. \tag{19}$$

Thus

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V = \frac{3}{2}Nk_B. \tag{20}$$

For an ideal gas $H = U + PV = \frac{3}{2}Nk_BT + Nk_BT = \frac{5}{2}Nk_BT$, hence

$$C_P = \left.\frac{\partial H}{\partial T}\right|_P = \frac{5}{2}Nk_B, \tag{21}$$

and hence

$$\boxed{C_P - C_V = Nk_B}. \tag{22}$$

(d) For an ideal monatomic gas,

$$\boxed{\frac{C_P - C_V}{C_P} = \frac{2}{5} = 0.4}. \tag{23}$$

For Helium (given mass-specific values at $T = 300$ K),

$$\frac{C_P - C_V}{C_P} = \frac{(C_P/M) - (C_V/M)}{C_P/M} = \frac{(5.193 - 3.116)\times 10^3}{5.193\times 10^3} = 0.400. \tag{24}$$

This matches the ideal-gas prediction to the quoted precision.

(e) **Solids: compute $(C_P - C_V)/C_P$ from Mayer's relation**
Substituting $V = M/\rho$ into Mayers relation dividing by C_P yields

$$\delta\tilde{C} = \frac{C_P - C_V}{C_P} = \frac{T\alpha^2}{\rho\,\kappa_T(C_P/M)}. \tag{25}$$

Using data

$$\text{Al:}\quad \delta\tilde{C} = 4.50\times10^{-2}\quad(\approx 4.5\%), \tag{26}$$
$$\text{Cu:}\quad \delta\tilde{C} = 2.98\times10^{-2}\quad(\approx 3.0\%), \tag{27}$$
$$\text{Si:}\quad \delta\tilde{C} = 1.10\times10^{-3}\quad(\approx 0.11\%). \tag{28}$$

Compared to Helium ($\approx 40\%$), the solid-state difference between C_P and C_V is typically much smaller.

(f) Plugging in $v = (\rho\kappa_T)^{-1/2}$, yields

$$\boxed{\frac{C_P - C_V}{C_P} = \frac{Tv^2\alpha^2}{C_P/M}}. \tag{29}$$

For an ideal gas, $\alpha = 1/T$ and $\kappa_T = 1/P$ and $\rho = M/V = Pm_{\text{mol}}/(RT)$, so

$$v = (\rho\kappa_T)^{-1/2} = \sqrt{\frac{P}{\rho}} = \sqrt{\frac{RT}{m_{\text{mol}}}}. \tag{30}$$

With $m_{\text{He}} = 4.0026\times10^{-3}$ kg/mol and $T = 300$ K,

$$v_{\text{He}} \simeq \sqrt{\frac{(8.314)(300)}{4.0026\times10^{-3}}} \simeq 7.89\times10^2\ \text{m/s}, \qquad \alpha_{\text{He}} = \frac{1}{T} \simeq 3.33\times10^{-3}\ \text{K}^{-1}. \tag{31}$$

For solids we have (by computation)

$$v_{\text{Al}} \simeq 5.30\times10^3\ \text{m/s}, \qquad \alpha_{\text{Al}} = 6.93\times10^{-5}\ \text{K}^{-1}, \tag{32}$$
$$v_{\text{Cu}} \simeq 3.95\times10^3\ \text{m/s}, \qquad \alpha_{\text{Cu}} = 4.95\times10^{-5}\ \text{K}^{-1}, \tag{33}$$
$$v_{\text{Si}} \simeq 6.55\times10^3\ \text{m/s}, \qquad \alpha_{\text{Si}} = 7.80\times10^{-6}\ \text{K}^{-1}. \tag{34}$$

Discussion of scales

- The speed of sound v is somewhat larger in solids (4-7km/s) than in Helium (~ 0.8 km/s)
- The thermal expansion coefficient is vastly smaller in solids ($\alpha_{\text{solid}} \sim 10^{-5}$–$10^{-6}$ K^{-1}) than in Helium ($\alpha_{\text{He}} \sim 10^{-3}$ K^{-1})
- C_P/M is approximately the same.

Therefore, as the ratio $(C_P - C_V)/C_P$ depends on α^2, α is the dominant scale in generating the discrepancy between solids and gasses.

(g) The scale $v = (\rho\kappa_T)^{-1/2}$ is the *speed of sound.*

2. **The Boltzmann solid**

There are 3 kinetic and 3 potential quadratic terms per particle.

(a) For one particle,

$$Z_1 = \frac{1}{(2\pi\hbar)^3}\int_{\mathbb{R}^3} d^3x \int_{\mathbb{R}^3} d^3p\ \exp\left[-\beta\left(\frac{p^2}{2m} + \frac{K}{2}(x - x_0)^2\right)\right]. \tag{35}$$

The integrals factorize:

$$\int d^3p \, e^{-\beta p^2/(2m)} = (2\pi m k_B T)^{3/2}\,, \tag{36}$$

$$\int d^3x \, e^{-\beta K x^2/2} = \left(\frac{2\pi k_B T}{K}\right)^{3/2}\,. \tag{37}$$

Thus

$$Z_1 = \frac{1}{(2\pi\hbar)^3}\,(2\pi m k_B T)^{3/2}\left(\frac{2\pi k_B T}{K}\right)^{3/2} = \left(\frac{k_B T}{\hbar\omega}\right)^3 \tag{38}$$

where $\omega = \sqrt{K/m}$.

For N independent particles,

$$\boxed{Z = Z_1^N = \left(\frac{k_B T}{\hbar\omega}\right)^{3N}} = (\beta\hbar\omega)^{-3N} \tag{39}$$

(b)

$$U = -\frac{\partial}{\partial\beta}\ln Z = -\frac{\partial}{\partial\beta}\left(-3N\log(\beta\hbar\omega)\right) = \frac{3N}{\beta} = 3Nk_{\mathrm{B}}T \tag{40}$$

(c) Using

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V = 3Nk_B. \tag{41}$$

The molar heat capacity is then

$$\boxed{c_{\mathrm{mol}} = \frac{C_V}{N_{\mathrm{mol}}} = 3\frac{N}{N_{\mathrm{mol}}}k_B = 3N_A k_B = 3R}, \tag{42}$$

(d) Per Cartesian component, by direct Gaussian integration we find

$$\sigma_x^2 = \frac{k_B T}{K}, \qquad \sigma_p^2 = m k_B T \tag{43}$$

Therefore

$$\sigma_x\sigma_p = \frac{k_B T}{\omega}, \qquad \omega = \sqrt{\frac{K}{m}}. \tag{44}$$

Heisenberg requires $\sigma_x\sigma_p \geq \hbar/2$, so classical fluctuations would violate quantum mechanics once

$$\frac{k_B T}{\omega} \lesssim \frac{\hbar}{2} \quad \Rightarrow \quad T \lesssim \frac{\hbar\omega}{2k_B} = \tfrac{1}{2}T_E. \tag{45}$$

Thus quantum effects become quantitatively important for $T \ll T_E$ (up to order-one constants).

3. **The Einstein solid**

(a) With energies $E_n = \hbar\omega(n + \frac{1}{2})$ we have partition function

$$Z = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} \tag{46}$$

rearranging we obtain

$$Z - e^{-\beta\hbar\omega}Z = e^{-\beta\hbar\omega/2} \quad \Longrightarrow \quad Z = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \tag{47}$$

The mean energy (dropping the T-independent zero-point part in C if desired) is

$$U = -\frac{\partial \ln Z}{\partial \beta} = \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right). \tag{48}$$

Differentiate to get the heat capacity:

$$\boxed{C_{1\mathrm{D}} = \frac{\partial U}{\partial T} = k_B \left(\beta\hbar\omega\right)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2}.} \tag{49}$$

(b) N particles, each particle has 3 independent 1D oscillators

$$\boxed{c_{\mathrm{mol}} = \frac{3NC_{1\mathrm{D}}}{N_{\mathrm{mol}}} = 3R \left(\beta\hbar\omega\right)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2}.} \tag{50}$$

(c) Let $x = T_E/T$

$$\frac{c_{\mathrm{mol}}}{3R} = \frac{x^2 e^x}{\left(e^x - 1\right)^2}. \tag{51}$$

For $x \ll 1$ we have $e^x \sim 1 + x$ and hence,

$$\frac{c_{\mathrm{mol}}}{3R} \sim x^2 \frac{1}{x^2} = 1, \quad \Longrightarrow \quad c_{\mathrm{mol}} \sim 3R \tag{52}$$

(d) Key features:

i. Large T: Asymptotic approach to $c_{\mathrm{mol}} \to 3R$ from below
ii. Small T: Rapid (faster than power law) approach to $c_{\mathrm{mol}} \to 0$
iii. Intermiedate T: Crossover in range $T \sim T_E$

4. **Debye solid**

(a) In d-dimensions the number of k-space density of states per mode is

$$dN = \left(\frac{L}{2\pi}\right)^d d^d\boldsymbol{k} \tag{53}$$

using $d = 2$, polar symmetry, and $\omega = vk$ we get the frequency density of states

$$dN = \frac{L^2}{4\pi^2} \cdot 2\pi k dk = \frac{L^2}{2\pi} k dk = \frac{L^2}{2\pi v^2} \omega d\omega \quad \Longrightarrow \quad g(\omega) = \frac{L^2\omega}{2\pi v^2} \tag{54}$$

Impose a Debye cut-off ω_D. The total number of states per mode should equal the number of atoms $N = nL^2$

$$\int_0^{\omega_D} g(\omega)\, d\omega = N \quad \Rightarrow \quad \omega_D = 2v\sqrt{\pi n}, \quad \Rightarrow \quad g(\omega) = \frac{2N\omega}{\omega_D^2} \tag{55}$$

In $d = 2$ there will be two modes (one each of transverse and longitudinal) which are here degenerate

$$U(T) = \int_0^{\omega_D} d\omega\, g(\omega)\, \frac{2\hbar\omega}{e^{\beta\hbar\omega} - 1} = \frac{4\hbar N}{\omega_D^2} \int_0^{\omega_D} d\omega\; \omega^2 n_B(\beta\hbar\omega), \quad n_B(x) = \frac{1}{e^x - 1} \tag{56}$$

Differentiate to find heat capacity and change variables to $x = \beta\hbar\omega$ with

$$C = \frac{\partial U}{\partial T} = \frac{4\hbar^2 N}{k_{\mathrm{B}} T^2 \omega_D^2} \int_0^{\omega_D} d\omega\; \frac{\omega^3 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} = 4Nk_{\mathrm{B}} \frac{T^2}{T_D^2} \int_0^{T_D/T} dx\; \frac{x^3 e^x}{(e^x - 1)^2} \tag{57}$$

(b) For $T \gg T_D$, the upper limit $T_D/T \ll 1$ and

$$\frac{x^3 e^x}{(e^x - 1)^2} \sim x \quad (x \ll 1). \tag{58}$$

Hence

$$\boxed{C \sim 4Nk_\mathrm{B} \frac{T^2}{T_D^2} \int_0^{T_D/T} dx\ x = 2Nk_B}. \tag{59}$$

(c) For $T \ll T_D$, the upper limit $T_D/T \to \infty$ so

$$C(T) \sim 4Nk_B \left(\frac{T}{T_D}\right)^2 \int_0^\infty dx\, \frac{x^3 e^x}{(e^x - 1)^2}. \tag{60}$$

thus

$$\boxed{C \propto T^2 \quad \Rightarrow \quad \nu = 2.} \tag{61}$$

(d) In d dimensions with a linear acoustic dispersion $\omega = v|\boldsymbol{k}|$, the number of modes with $|\boldsymbol{k}| < k$ scales like the d-dimensional volume of a ball:

$$g(k)dk \propto k^{d-1}dk \quad \Rightarrow \quad g(\omega) \propto \omega^{d-1}. \tag{62}$$

At low T integral converges as T dependence may be scaled out

$$U(T) \sim \int_0^\infty d\omega\, g(\omega)\, \hbar\omega\, n_B(\omega) \sim \int d\omega\, \omega^d\, f(\beta\hbar\omega) \propto T^{d+1}, \tag{63}$$

and therefore

$$\boxed{C(T) = \frac{\partial U}{\partial T} \propto T^d \quad \Longrightarrow \quad \nu = d}. \tag{64}$$

(e) Now $\omega \propto k^z$ so $k \propto \omega^{1/z}$. Then

$$N(\omega) \propto k^d \propto \omega^{d/z} \quad \Rightarrow \quad g(\omega) = \frac{\mathrm{d}N}{\mathrm{d}\omega} \propto \omega^{d/z-1}. \tag{65}$$

Thus

$$U(T) \sim \int d\omega\, \omega\, g(\omega)\, n_B(\omega) \sim \int d\omega\, \omega^{d/z}\, f(\beta\hbar\omega) \propto T^{1+d/z}, \tag{66}$$

so

$$\boxed{C(T) = \frac{\partial U}{\partial T} \propto T^{d/z} \quad \Longrightarrow \quad \nu = d/z}. \tag{67}$$