Problem set 1

Phy-801

January 2026

1. **The heat capacity of solids vs gases:** The heat capacity of a material characterises how easily it changes temperature due to being heated. In statistical mechanics you learned that there are two commonly used heat capacities, one at constant pressure C_P and one at constant volume C_V. Mayer's relation, which gives the difference between the two heat capacities C_P and C_V, in terms of the material's volume V, temperature T and its mechanical properties

$$C_P - C_V = \frac{TV\alpha^2}{\kappa_T} \tag{1}$$

namely the coefficient of thermal expansion α characterises the expansion of a material due to increased temperature at fixed pressure, and the compressibility κ_T characterises how easily a material is compressed by increasing the pressure at fixed temperature

$$\alpha \equiv \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P, \qquad \kappa_T \equiv -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T. \tag{2}$$

(a) In this question we will derive Mayer's relation.

i. Starting from the first law of thermodynamics

$$dU = TdS - PdV, \tag{3}$$

and the definitions of the heat capacities at constant volume and constant pressure

$$C_V \equiv \left.\frac{\partial U}{\partial T}\right|_V, \qquad C_P \equiv \left.\frac{\partial H}{\partial T}\right|_P,$$

(where here $H = U + PV$ is the enthalpy[1]) show that C_V and C_P are given by

$$C_V = T\left.\frac{\partial S}{\partial T}\right|_V, \qquad C_P = T\left.\frac{\partial S}{\partial T}\right|_P$$

ii. Use the total differential identity

$$dz = \left.\frac{\partial z}{\partial x}\right|_y dx + \left.\frac{\partial z}{\partial y}\right|_x dy. \tag{4}$$

with $(x, y, z) = (T, V, S)$ to obtain a form for $\partial S/\partial T|_P$, and substitute this into the form for $C_P - C_V$.

iii. Use the equality of mixed partial derivatives

$$\left.\frac{\partial}{\partial x}\right|_y \left.\frac{\partial z}{\partial y}\right|_x = \left.\frac{\partial}{\partial y}\right|_x \left.\frac{\partial z}{\partial x}\right|_y \tag{5}$$

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[1] The enthalpy differs from the internal energy U by the term PV, which accounts for the mechanical work required to expand the system against the external pressure. As a result, H is the appropriate energy function for processes carried out at constant pressure.

	ρ [$\mathrm{kg\,m^{-3}}$]	α [$\mathrm{K^{-1}}$]	κ_T [$\mathrm{Pa^{-1}}$]	C_P/M [J/(kg K)]
Al	2.699×10^3	6.93×10^{-5}	1.32×10^{-11}	8.99×10^2
Cu	8.960×10^3	4.95×10^{-5}	7.14×10^{-12}	3.85×10^2
Si	2.330×10^3	7.80×10^{-6}	1.00×10^{-11}	7.13×10^2

Table 1: Properties of solids at $T = 300\,\mathrm{K}$. Sources: NIST WebBook.[3]

with $(x, y, z) = (T, V, F)$ (where $F = U - TS$ is the free energy) to obtain the Maxwell relation

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

and substitute this into the relation obtained in the previous part.

iv. Make use of (4) again with $(x, y, z) = (T, P, V)$ to obtain a form for $\partial P/\partial T|_V$, and substitute this identity into your form for $C_P - C_V$.

v. Finally use the definitions of α and κ_T to hence obtain (1).

(b) It is instructive to compare the size of the difference $C_P - C_V$ for different phases of matter. The partition function of an ideal gas of N indistinguishable non-interacting particles in a volume V is given by

$$Z = Z_1^N/N! \quad \text{where} \quad Z_1 = \frac{1}{(2\pi\hbar)^3}\int_V d^3\vec{x}\int_{\mathbb{R}^3} d^3\vec{p}\,\mathrm{e}^{-\beta H_1} \tag{7}$$

where the single particle Hamiltonian is given by the kinetic energy $H_1 = p^2/(2m)$, $\beta \equiv (k_\mathrm{B}T)^{-1}$, where k_B is the Boltzmann constant. Using the identity for Gaussian integration

$$\int_{\mathbb{R}} dt\,\mathrm{e}^{-t^2} = \sqrt{\pi} \tag{8}$$

evaluate the form for the free energy

$$F = -k_\mathrm{B}T\log Z$$

(c) Using the relations

$$U = -T^2\left.\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right|_V, \quad \text{and} \quad P = -\left.\frac{\partial F}{\partial V}\right|_T$$

obtain forms for C_P, C_V and hence Mayer's relation for an ideal gas

$$C_P - C_V = Nk_\mathrm{B}$$

(d) The ideal gas model is a quantitatively accurate model for inert monatomic gases, such as the Noble gases. Using your answer from the previous question calculate the dimensionless ratio $(C_P - C_V)/C_P$ for an ideal gas. Calculate $(C_P - C_V)/C_P$ for Helium at $T = 300\mathrm{K}$[2]

$$C_V/M = 3.116 \times 10^3\ \mathrm{J/(kg\,K)}, \quad C_P/M = 5.193 \times 10^3\ \mathrm{J/(kg\,K)} \tag{9}$$

and compare this with the ideal gas prediction.

(e) We compare the ideal gas result to data from solids. Using Table 1 and Mayer's relation (1) calculate $(C_P - C_V)/C_P$ for these materials. Compare and contrast your answer with the case of Helium in part (c).

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[2] Arp, V. D., McCarty, R. D., & Friend, D. G. (1998). Thermophysical properties of Helium-4 from 0.8 to 1500 K with pressures to 2000 MPa (NIST Technical Note 1334, revised). National Institute of Standards and Technology.

[3] Al: `https://webbook.nist.gov/cgi/inchi?ID=C7429905&Mask=2#Thermo-Condensed`;
Cu: `https://webbook.nist.gov/cgi/inchi?ID=C7440508&Mask=2#Thermo-Condensed`;
Si: `https://webbook.nist.gov/cgi/inchi?ID=C7440213&Mask=2#Thermo-Condensed`

(f) Recast Mayer's relation as

$$\frac{C_P - C_V}{C_P} = \frac{Tv^2\alpha^2}{C_P/M} \tag{10}$$

where $v = (\rho\kappa_T)^{-1/2}$ is a velocity scale, and $\rho = M/V$ is the density. Calculate v and α for both an ideal gas (Helium at $T = 300\text{K}$, you will need the molar mass $m_{\text{He}} = 4.0026 \times 10^{-3}\text{kg/mol}$) and the solids in Table 1, comment on which scale is causing the significant difference between $(C_P - C_V)/C_P$ in these two cases, and the relative importance of distinguishing between C_P and C_V for solids and gases.

(g) Based on the scale of the velocity v in part (1f), and its origin as a mechanical property of the system (i.e. it is given by a combination of the density and compressibility), suggest what physical property of material this velocity might correspond to.

2. **The Boltzmann solid:** The Boltzmann solid, (also known as *the classical Einstein solid*) consists of a system of N particles in three dimensions with the harmonic oscillator Hamiltonian

$$H = \sum_{n=1}^{N} \left(\frac{p_n^2}{2m} + \frac{1}{2} K (x_n - x_{0,n})^2 \right). \tag{11}$$

where m is the mass of each particle, the spring constant K sets the strength of the confining potential, and $x_{0,n}$ sets the equilibrium position of the nth particle.

(a) Evaluate the classical partition function (7) for the Boltzmann Hamiltonian (11) [Hint: as before use the Gaussian integral (8)].

(b) Using the partition function, calculate the internal energy U. Give a statement of equipartition theorem and show that U obeys this result. [Hint: follow the steps of the previous question: from Z Calculate F, and from F calculate U.]

(c) Calculate the heat capacity C, and hence the molar heat capacity $c_{\text{mol}} = C/N_{\text{mol}}$ where N_{mol} is the number of moles in the system

$$c_{\text{mol}} = 3R$$

where R is the ideal gas constant. This is the Dulong-Petit law. [Hint: calculate C_V from your value of U in the previous result. In accordance with the results of the previous question you need not distinguish between C, C_P and C_V for a solid.]

(d) Calculate $\sigma_x^2 = \langle x_n^2 \rangle - \langle x_n \rangle^2$ and $\sigma_p^2 = \langle p_n^2 \rangle - \langle p_n \rangle^2$. Let's consider whether using quantum harmonic oscillators rather than classical harmonic oscillators will lead to different results. The Heisenberg uncertainty relation states that for quantum harmonic oscillator

$$\sigma_x \sigma_p \geq \hbar/2 \tag{12}$$

Consequently, show that quantum effects must become quantitatively important for temperatures T far below the Einstein temperature

$$T_{\text{E}} \equiv \hbar\omega/k_{\text{B}} \tag{13}$$

where $\omega = \sqrt{K/m}$ is the oscillator frequency.

3. **The Einstein Solid:** Einstein recognised that deviations from the Dulong-Petit law could be explained by effects due to quantum mechanics. Specifically, by using quantum harmonic oscillators in place of classical harmonic oscillators.

As a reminder, a one-dimensional quantum harmonic oscillator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} K \hat{x}^2. \tag{14}$$

is obtained from the classical oscillator by promoting x and p to operators with commutation relations $[\hat{x}, \hat{p}] \equiv \hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar$. The eigenvalues of this operator are found to be

$$E_n = \hbar\omega(n + \tfrac{1}{2}) \tag{15}$$

where $\omega = \sqrt{K/m}$ is the oscillator's natural frequency.

(a) Evaluate the partition function of a single one-dimensional quantum harmonic oscillator

$$Z \equiv \mathrm{tr}[\mathrm{e}^{-\beta H}] \tag{16}$$

for the energy eigenvalues (15), and consequently find an expression for the heat capacity of the single oscillator.

(b) Using your result, find the heat capacity C of a system of N quantum harmonic oscillators in three dimensions (11), each with hamiltonian

$$\hat{H} = \sum_{\alpha=1}^{3} \left(\frac{\hat{p}_\alpha^2}{2m} + \frac{1}{2} K \hat{x}_\alpha^2 \right) \tag{17}$$

(c) Show that for $T \gg T_\mathrm{E}$ we recover the Dulong-Petit law.

(d) Sketch C/C_DP as a function of T/T_E (see Eq. (13)) where C_DP is the Dulong-Petit value of the heat capacity.

4. **Debye Solid:** Debye recognised that the flaw in Einstein's calculation was quantising the motion of individual decoupled atoms. His corrected treatment instead quantises the collective motion of the coupled atoms, i.e. sound waves.

(a) Assuming a single branch of phonons with dispersion $\omega(\vec{k}) = v|\vec{k}|$, derive the Debye heat capacity of a *two-dimensional* solid as a function of temperature. This may be achieved by following the approach followed in lectures, making changes where necessary to account for the different dimensionality. You will need to leave your answer in terms of an integral that one cannot do analytically.

(b) At high T, show the heat capacity goes to a constant and find that constant.

(c) At low T, show that $C \sim T^\nu$ and find ν.

(d) Show that in a d-dimensional harmonic crystal, the low-frequency density of states of normal modes varies as $g \sim \omega^{d-1}$. Deduce from this that the low-temperature specific heat of a harmonic crystal vanishes as $C \sim T^\nu$ and find ν.

(e) Furthermore, consider the case where the normal mode frequencies did not vanish linearly with $|\vec{k}|$, but as $\omega(\vec{k}) = c|\vec{k}|^z$. Derive the low temperature heat capacity exponent $C \sim T^\nu$ in this case too.