

Statistical Mechanics

Resit Version

8/5-2026

For this exam you can bring one A4 cheatsheet (writing on all sides). You can use a calculator. No communication with other people is allowed during the exam.

Location: EA 5159.0062 , Time: 15:00-17:00

Norm:

The answers must be given in English and readable handwriting. The table below shows the number of points to be given for each of the questions. For the exam score the total score, M , is converted to the mark using the max score ($M_{\max}=65$) according to the formula $\frac{9M}{M_{\max}} + 1$. This exam counts for 100% of the grade and the homework assignment 0%, but needs to be passed. If 1/2 bonus point was earned during the problem solving session this is added and if the resulting mark is above 10 the final mark will be 10.

Subquestion	Q1	Q2	Q3
A	5	5	5
B	5	5	5
C	5	5	5
D	5	5	5
E	-	-	5

1 Classical Statistical Mechanics

A. How is the classical Entropy defined in terms of the phase space volume in the microcanonical ensemble (give an equation and define the symbols that you introduce).

B. Use the general equipartition theorem to find the average energy of a system with the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^N A_i P_i^2 + \sum_{i=1}^N B_i Q_i^2.$$

Here P_i are momenta and Q_i positions and A_i and B_i are positive numbers.

C. What are the heat capacities (C_V and C_P) of an ideal monoatomic gas (exact expression) and how will internal degrees of freedom (as rotations and vibrations in a molecular gas) affect this result (no exact expression needed)?

D. Show that the expectation value of the number of particles, $\langle N \rangle$, can be expressed as $\langle N \rangle = z \frac{\partial}{\partial z} \log \mathcal{Q}(z, V, T)$ starting from the definition of the Grand Partition function:

$$\mathcal{Q}(z, V, T) = \sum_{N=0}^{\infty} z^N Q_N(V, T)$$

2 Phase Transitions

A. Consider a system described with the grand partition function

$$\mathcal{Q}(z, V) = (1 + z)^V (1 + z^{\alpha V}) (1 + (2z)^{\beta V}),$$

where α and β are positive constants, z is the fugacity and V the volume. Write down the equation of state for this system (present equations for P/kT and $1/v$).

B. What are the roots of this grand partition function?

C. In which limit will this system exhibit a phase transition and for which values of the fugacity does it happen?

D. What are the differences between a first- and a second-order phase transition?

3 Phonons in diamond

Assume a material with $3N$ phonon-modes that all have the frequency ω_E .

A. Explain why the partition function for the system is given by the equation

$$Q = \prod_{i=1}^{3N} \frac{\exp(-\beta\hbar\omega_E/2)}{1 - \exp(-\beta\hbar\omega_E)}.$$

Here, i numbers the different harmonic oscillators that all have the same energy $\hbar\omega_E$. The total energy of the system with the set of occupation numbers $\{n_i\}$ is $E(\{n_i\}) = \sum_i^{3N} (n_i + 1/2)\hbar\omega_E$. Here, n_i represents the excitation level ($n_i=0, 1, 2, \dots$) of the harmonic oscillator labeled as number i .

B. Give and explain the analytical expression for the average occupation number for each phonon mode

C. Derive the total internal energy of the system.

D. Derive the heat capacity of the system.

E. Calculate the specific heat capacity at 300 K assuming that $\omega_E/2\pi c$ is 1200 cm^{-1} (The vibrational energy of the C-C stretch vibration in diamond.)

This exam has been drafted by T. L. C. Jansen and verified by
T. A. Schlathölter.

Date: 17/4-2026

Signature:

A handwritten signature in cursive script, appearing to read 'Thomas Jansen', written in dark ink.

Date: 17/4-2026

Signature:

A handwritten signature in cursive script, appearing to read 'T. A. Schlathölter', written in dark ink.

Potentially useful equations

Maxwell relations:

$$P = - \left(\frac{\partial A}{\partial V} \right)_T$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_S$$

$$V = \left(\frac{\partial H}{\partial P} \right)_S$$

$$V = \left(\frac{\partial G}{\partial P} \right)_T$$

$$S = - \left(\frac{\partial A}{\partial T} \right)_V$$

$$S = - \left(\frac{\partial G}{\partial T} \right)_P$$

$$T = \left(\frac{\partial H}{\partial S} \right)_P$$

$$T = \left(\frac{\partial U}{\partial S} \right)_V$$

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

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

The thermal wavelength:

$$\lambda = \sqrt{2\pi\hbar^2/mkT}$$

The Ideal gas law:

$$PV = nRT$$

The van der Waas equation:

$$\left[P + a \left(\frac{n}{V} \right)^2 \right] \left(\frac{V}{n} - b \right) = RT$$

The Sackur-Tetrode equation:

$$S = k_B N \left(\log \left[\frac{V}{N} \left(\frac{4\pi m U}{3h^2 N} \right)^{3/2} \right] + \frac{5}{2} \right)$$

General equipartition theorem:

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = \delta_{ij} kT \quad (1)$$

The functions for the ideal Fermi gas including the low-fugacity expansions:

$$f_{5/2}(z) = \sum_{l=1}^{\infty} \frac{(-1)^{l+1} z^l}{l^{5/2}}$$

$$f_{3/2}(z) = \sum_{l=1}^{\infty} \frac{(-1)^{l+1} z^l}{l^{3/2}} \approx z - \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} - \frac{z^4}{4^{3/2}} + \dots$$

$$z = \frac{\lambda^3}{v} + \frac{1}{2^{3/2}} \left(\frac{\lambda^3}{v} \right)^2 + \dots$$

$$\epsilon_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2}{gv} \right)^{2/3}$$

$$U = \frac{3}{5} N \epsilon_F \left[1 + \frac{5}{12} \pi^2 \left(\frac{kT}{\epsilon_F} \right)^2 + \dots \right]$$

The functions for the ideal Bose gas including the low-fugacity expansions

$$g_{5/2}(z) = \sum_{l=1}^{\infty} \frac{z^l}{l^{5/2}}$$

$$g_{3/2}(z) = \sum_{l=1}^{\infty} \frac{z^l}{l^{3/2}} \approx z + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \frac{z^4}{4^{3/2}} + \dots$$

$$g_{5/2}(1) = \zeta(5/2) = 1.342 \dots$$

$$g_{3/2}(1) = \zeta(3/2) = 2.612 \dots$$

Mathematical relations

Geometric series valid for $x < 1$:

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

$$\exp(-ax) = \sum_{n=0}^{\infty} \frac{(-ax)^n}{n!}$$

$$\int_{-\infty}^{\infty} \exp(-a(x+b)^2) dx = \sqrt{\frac{\pi}{a}}$$

With $\log(x)$ the natural logarithm is considered. For $-1 < x < 1$:

$$\log(1+x) = \sum_{n=1}^{\infty} \frac{(-1)^{n+1} x^n}{n}$$

$$\int \frac{1}{x-a} dx = \log(x-a)$$

The coth function is defined

$$\coth(x) = \frac{\exp(x) + \exp(-x)}{\exp(x) - \exp(-x)}$$

For $\coth(x)$ we have (for $0 < |x| < \pi$)

$$\coth(x) = \frac{1}{x} - \frac{x}{3} + \frac{x^3}{45} - \dots - \frac{2^{2n} B_n x^{2n-1}}{(2n)!} - \dots$$

The derivative of $\coth(x)$ is

$$\frac{d \coth(x)}{dx} = \operatorname{csch}^2(x)$$

The derivative of $\cosh(x)$ is

$$\frac{d \cosh(x)}{dx} = \sinh(x)$$

The derivative of $\sinh(x)$ is

$$\frac{d \sinh(x)}{dx} = \cosh(x)$$

The derivative of $\log(x)$ is

$$\frac{d \log(x)}{dx} = 1/x$$

The hyperbolic cosecant is

$$\operatorname{csch}(x) = \frac{1}{\sinh(x)}$$

The Taylor expansion of $\operatorname{csch}^2(x)$ is

$$\operatorname{csch}^2(x) \approx \frac{1}{x^2} \left(1 - \frac{1}{3}x^2 + \dots \right)$$

The following integrals may be useful:

$$f(y) = \int_0^y dx x^2 \sqrt{1+x^2} = \frac{1}{3}y^3 \left(1 + \frac{3}{10}y^2 + \dots \right) \text{ for } y \ll 1$$

$$= \frac{1}{4}y^4 \left(1 + \frac{1}{y^2} + \dots \right) \text{ for } y \gg 1$$

$$\int_{-\infty}^{\infty} dx \exp(-ax^2) = \sqrt{\pi/a}$$

$$\int_0^{\infty} (2J+1) \exp(-aJ(J+1)) dJ = \frac{1}{a}$$

$$\int_0^{\infty} (4J+1) \exp(-2aJ(2J+1)) dJ = \frac{1}{2a}$$

$$\int_0^{\infty} (4J+3) \exp(-a(2J+1)(2J+2)) dJ = \frac{\exp(-2a)}{2a}$$

$$\int_0^{\infty} \frac{x}{\exp(x)-1} dx = \frac{\pi^2}{6}$$

$$\int_0^{\infty} \frac{x^2}{\exp(x)-1} dx = 2\zeta(3) \approx 2.40411$$

$$\int_0^{\infty} \frac{x^3}{\exp(x)-1} dx = \frac{\pi^4}{15}$$

Brownian Dynamics

Kramers-Kronig relation:

$$\tilde{\chi}'(\omega) = \mathcal{P} \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\tilde{\chi}''(\omega')}{\omega' - \omega}$$

Reverse Kramers-Kronig relation:

$$\tilde{\chi}''(\omega) = -\mathcal{P} \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\tilde{\chi}'(\omega')}{\omega' - \omega}$$

Fluctuation-Dissipation theorem:

$$\bar{C}_{xx}(\omega) = 2k_B T \frac{\tilde{\chi}''(\omega)}{\omega}$$

Potentially useful constants

$$m_e = 9.10938356 \times 10^{-31} \text{ kg}$$

$$m_n = 1.674929 \times 10^{-27} \text{ kg}$$

$$m_p = 1.672623 \times 10^{-27} \text{ kg}$$

$$N_A = 6.022140857 \times 10^{23} \text{ 1/mol}$$

$$\hbar = 1.0545718 \times 10^{-34} \text{ Js}$$

$$k_B = 1.38064852 \times 10^{-23} \text{ J/K}$$

$$k_B = 8.617333262145 \times 10^{-5} \text{ eV/K}$$

$$c = 2.99792458 \times 10^8 \text{ m/s}$$

$$e = 1.60217662 \times 10^{-19} \text{ C}$$

$$R = 8.31446261815324 \text{ J/(mol K)}$$