

Exercise sheet N. 9

Statistical Physics

University of Heidelberg

<http://www.thphys.uni-heidelberg.de/~amendola/teaching.html>

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Indicate your name, your UNI-ID and your exercise group on each page of the answer sheets.

Please hand in your solution on Tuesday 7th January during the lecture.

1 The von Neumann equation [5pt]

The density matrix for an ensemble of states k characterized in a complete (orthogonal) basis $|n\rangle$ by the wavefunctions

$$|\psi^k\rangle = \sum_n a_n^k |n\rangle \quad (1)$$

is

$$\rho_{nm} = \sum_{k=1}^{\mathcal{N}} \lambda_k a_n^k(t) a_m^{k*}(t) \quad (2)$$

Show first that the coefficients obey the equation

$$i\hbar \dot{a}_n^k(t) = \sum_m H_{nm} a_m^k(t), \quad (3)$$

where H_{mn} denote the matrix elements $H_{mn} = \langle m|H|n\rangle$ and then derive the Von Neumann equation

$$i\hbar \dot{\rho}_{mn} = (\hat{H}\rho - \rho\hat{H})_{mn} \quad (4)$$

2 Rigid rotator [15pt]

Consider a molecule, such as carbon monoxide, which consists of two different atoms, one carbon and one oxygen, separated by a distance d . Such a molecule can exist in quantum states of different orbital angular momentum. Each state has the energy

$$\epsilon_l = \frac{\hbar^2}{2I} l(l+1) \quad (5)$$

where $I = \mu d^2$ is the moment of inertia of the molecule about an axis through its centre of mass and μ is the reduced mass defined by $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$. $l = 0, 1, 2, \dots$ is the quantum number associated with the orbital angular momentum. Each energy level of the rotating molecule has the degeneracy $g_l = 2l + 1$.

1. Find the general expression for the canonical partition function Z .
2. Prove that for high temperatures Z can be approximated by the integral

$$Z \approx \int_0^\infty \exp\left(-\frac{(\hbar^2/2I)y}{k_B T}\right) dy. \quad (6)$$

Hint: Find an approximate integral representation for the summands at given l for high T and demonstrate that this can be extended to an integral over the complete summation range.

3. Evaluate the high temperature mean energy E and the heat capacity C_V .
4. Find the low-temperature approximations to the canonical partition function, the mean energy E and the heat capacity C_V .

Hint: at low temperatures you can only consider the ground and first excited states, when computing the partition function.

3 Anharmonic correction to quantum oscillator [20pt]

The energy of the vibrational states of a diatomic molecule is given by

$$\epsilon_n = \hbar\omega \left[\left(n + \frac{1}{2} \right) - \delta \left(n + \frac{1}{2} \right)^2 \right] \quad \text{where } n = 0, 1, 2, \dots \quad (7)$$

Do the following calculations up to the first order in the small parameter $\delta \ll 1$ by using Taylor expansions.

1. Determine the partition sum z_{vib} of a single molecule.

HINT: The result should be

$$z_{\text{vib}} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \left\{ 1 + \delta \left(\frac{\beta\hbar\omega}{4} \right) \frac{1 + 6e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega}}{[1 - e^{-\beta\hbar\omega}]^2} \right\} \quad (8)$$

2. Use z_{vib} to determine the average vibrational energy E_{vib} of N independent molecules.