

## Lösungen zum Übungsblatt 9

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### Problem 1: Particle number fluctuations

We consider our system as a grand canonical ensemble because the particle number  $N$  is not given exactly. We want to compute the particle number fluctuations  $\langle (N - \bar{N})^2 \rangle$  with  $\langle N \rangle = \bar{N}$  at fixed temperature  $T$ .

The following approach was splitted up in several steps. In step (i) we show the Maxwell relation ( $V$ : Volume,  $P$ : pressure):

$$\left( \frac{\partial \mu}{\partial V} \right)_{T,N} = - \left( \frac{\partial P}{\partial N} \right)_{T,V} \quad (1)$$

With this result we'll show the following relation for homogeneous systems with the isothermal compressibility  $\kappa_T$  (step(ii)):

$$\left( \frac{\partial \mu}{\partial N} \right)_{T,V} = \frac{V}{N^2} \frac{1}{\kappa_T} \quad (2)$$

*Proof to (i):*

Given is the differential for the free energy:

$$\begin{aligned} dF &= -S dT - P dV + \mu dN \\ \Rightarrow \left( \frac{\partial F}{\partial N} \right)_{T,V} &= \mu, \quad \left( \frac{\partial F}{\partial V} \right)_{T,N} = -P \\ \Rightarrow \left( \frac{\partial \mu}{\partial V} \right)_{T,N} &= \frac{\partial^2 F}{\partial V \partial N} = \frac{\partial^2 F}{\partial N \partial V} = - \left( \frac{\partial P}{\partial N} \right)_{T,V} \end{aligned}$$

In the last step we avail that the order of differentiations is equal.

q.e.d.

*Proof to (ii):*

Our system is a homogeneous system. It means, that for the pressure (for example) we can write:

$$P(T, V, N) = P(T, \alpha V, \alpha N)$$

If we make our system bigger, the volume and the particle number are growing proportional to  $\alpha$ .  $T$  and  $P$  don't. They are *intensive* variables. After differentiation to  $\alpha$  we obtain

(at the point  $\alpha = 1$ ):

$$\begin{aligned}
\frac{dP(T, V, N)}{d\alpha} &= \frac{dP(T, \alpha V, \alpha N)}{d\alpha} \\
&= \left( \frac{\partial P}{\partial T} \frac{dT}{d\alpha} + \frac{\partial P}{\partial \alpha V} \frac{d\alpha V}{d\alpha} + \frac{\partial P}{\partial \alpha N} \frac{d\alpha N}{d\alpha} \right)_{\alpha=1} \\
&= \left( \frac{\partial P}{\partial V} \right)_{T, N} V + \left( \frac{\partial P}{\partial N} \right)_{T, V} N = 0
\end{aligned} \tag{3}$$

Analogue we can show for  $\mu(T, V, N) = \mu(T, \alpha V, \alpha N)$  ( $\mu$  is also an intensive variable):

$$\left( \frac{\partial \mu}{\partial V} \right)_{T, N} V + \left( \frac{\partial \mu}{\partial N} \right)_{T, V} N = 0$$

With the definition of the isothermal compressibility  $\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T, N}$  and (1) we obtain:

$$\begin{aligned}
\left( \frac{\partial \mu}{\partial N} \right)_{T, V} &= -\frac{V}{N} \left( \frac{\partial \mu}{\partial V} \right)_{T, N} \\
&= \frac{V}{N} \left( \frac{\partial P}{\partial N} \right)_{T, N} \\
&= -\frac{V^2}{N^2} \left( \frac{\partial P}{\partial V} \right)_{T, N} \\
&= \frac{V}{N^2} \frac{1}{\kappa_T}
\end{aligned}$$

q.e.d.

Now we consider our grand canonical ensemble with the partition sum  $Z_G$ :

$$Z_G = \sum_{N=1}^{\infty} \int [d\Gamma] e^{-\beta(H - \mu N)}$$

We know for the mean of  $N$ :

$$\bar{N} = \frac{1}{\beta Z_G} \frac{\partial Z_G}{\partial \mu}$$

We compute  $\frac{\partial Z_G}{\partial \mu}$  and  $\frac{\partial^2 Z_G}{\partial \mu^2}$  because we'll need it for the next calculation:

$$\begin{aligned}
\frac{\partial Z_G}{\partial \mu} &= \beta \sum_{N=1}^{\infty} \int [d\Gamma] N e^{-\beta(H - \mu N)} = \beta \bar{N} Z_G \\
\frac{\partial^2 Z_G}{\partial \mu^2} &= \beta^2 \sum_{N=1}^{\infty} \int [d\Gamma] N^2 e^{-\beta(H - \mu N)} = \beta^2 \langle N^2 \rangle Z_G
\end{aligned} \tag{4}$$

Differentiation of  $\overline{N}$  to  $\mu$ :

$$\begin{aligned}
\left(\frac{\partial \overline{N}}{\partial \mu}\right)_{T,V} &= \beta^{-1} \left[ Z_G^{-1} \frac{\partial^2 Z_G}{\partial^2 \mu} + \frac{\partial Z_G^{-1}}{\partial \mu} \frac{\partial Z_G}{\partial \mu} \right] \\
&= \beta^{-1} \left[ Z_G^{-1} \frac{\partial^2 Z_G}{\partial^2 \mu} - Z_G^{-2} \frac{\partial Z_G}{\partial \mu} \frac{\partial Z_G}{\partial \mu} \right] \\
&= \beta \left( \langle N^2 \rangle - \overline{N}^2 \right) \\
&= \beta \langle (N - \langle N \rangle)^2 \rangle
\end{aligned} \tag{5}$$

After comparing (2) and (5) we obtain ( $\beta = k_B T$ ):

$$\kappa_T = \frac{k_B T V}{\overline{N}^2} \langle (N - \langle N \rangle)^2 \rangle$$

With this equation you can compute the variance of  $N$  by known  $V$  and  $\overline{N}$ .

### Problem 2: Thermodynamical potentials

In the considered system with Volume  $V$ , particle number  $N$  and temperature  $T$ , the free energy  $F$  is given by:

$$F(T, V) = -N k_B T \ln(C_0 V) - N k_B T \ln(C_1 [k_B T]^\alpha) \tag{6}$$

with  $C_0, C_1 = \text{const} > 1$ . We regard  $N$  as constant in the following.

(a) The entropy  $S(T, V)$  is given by:

$$\begin{aligned}
S(T, V) &= - \left( \frac{\partial F}{\partial T} \right)_V \\
&= N k_B \cdot (\ln(C_0 V) + \ln(C_1 [k_B T]^\alpha) + \alpha) \ .
\end{aligned} \tag{7}$$

(b) With the definition of the free energy

$$F(T, V) = E(T, V) - T \cdot S(T, V) \ ,$$

we obtain using (6) and (7):

$$\begin{aligned}
E(T, V) &= F(T, V) + T \cdot S(T, V) \\
&= \alpha N k_B T \ .
\end{aligned} \tag{8}$$

(c) Now we have to replace  $T$  by  $S$  in (8), what is done using (7):

$$\begin{aligned}
T &= \frac{1}{k_B} \cdot \exp\left(\frac{S}{\alpha N k_B} - 1\right) \cdot \left(\frac{1}{C_0 C_1 V}\right) \\
\Rightarrow E(S, V) &= \alpha N k_B \frac{1}{k_B} \cdot \exp\left(\frac{S}{\alpha N k_B} - 1\right) \cdot \left(\frac{1}{C_0 C_1 V}\right) \ .
\end{aligned}$$

(d) The pressure is computed using (6) as follows:

$$\begin{aligned} p(T, V) &= - \left( \frac{\partial F}{\partial V} \right)_T \\ &= \frac{Nk_B T}{V} . \end{aligned} \tag{9}$$

(e) With (9), we obtain:

$$V(T, p) = \frac{Nk_B T}{p} . \tag{10}$$

The free enthalpy is given by:

$$\begin{aligned} G(T, p) &= F + pV \\ &= -Nk_B T \cdot (\ln(C_0 V) + \ln(C_1 [k_B T]^\alpha) - 1) \\ &= Nk_B T \cdot (1 - \ln(C_0 C_1 V [k_B T]^\alpha)) \\ &= Nk_B T \cdot \left( 1 - \ln \left( C_0 C_1 \frac{N}{p} [k_B T]^{\alpha+1} \right) \right) . \end{aligned}$$

(f) To get the specific heat, we proceed as follows:

$$\begin{aligned} c_V &= \frac{T}{m} \left( \frac{\partial S}{\partial T} \right)_V \\ &= \frac{\alpha N k_B}{m} , \end{aligned}$$

where  $m$  is the mass of all  $N$  particles.

(g) With its definition, we get for the isothermal compressibility using (10):

$$\begin{aligned} \kappa_T &= - \frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \\ &= \frac{1}{p} . \end{aligned}$$

### Problem 3: A simple model of thermodynamics of lattice vibrations

#### Introduction

We look at a simple model describing the thermodynamical behaviour of solids. The so-called *Einstein model* uses the following assumptions: each atom is considered as harmonic oscillator without any interaction to other atoms, and all atoms have the same frequency of oscillation. We will discuss the validity of this system.

## Methods

At first, we replace the operator  $\hat{a}_i^+ \hat{a}_i = \hat{N}$  in the Hamiltonian with its eigenvalue, since the system is in an eigenstate. Then we calculate the canonical partition sum, that is required for getting energy, average energy, free energy and specific heat. After that, we look at the behaviour of the specific heat for  $T \rightarrow 0$  and  $T \rightarrow \infty$ .

## Results

a) We get the following results:

$$\begin{aligned} Z(\beta, N) &= \left( \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} \right)^N \\ F(\beta, N) &= \frac{\hbar\omega N}{2} + \frac{N}{\beta} \ln(1 - e^{-\beta\hbar\omega}) \\ \langle E \rangle &= \frac{1}{2} N \hbar\omega + \frac{N \hbar\omega}{e^{\beta\hbar\omega} - 1} \\ c_V(T) &= \frac{N \hbar^2 \omega^2 \cdot \exp\left(\frac{\hbar\omega}{k_B T}\right)}{k_B T^2 \cdot \exp\left(\frac{\hbar\omega}{k_B T} - 1\right)^2} \\ E(T, N) &= \frac{1}{2} N \hbar\omega + \frac{N \hbar\omega}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)}. \end{aligned}$$

In Figure 1 and 2, the last two are plotted.

b) For the cases  $T \rightarrow 0$  and  $T \rightarrow \infty$ , we obtain:

$$\begin{aligned} \lim_{T \rightarrow 0} c_V(T) &= 0 \\ \lim_{T \rightarrow \infty} c_V(T) &= N k_B. \end{aligned}$$

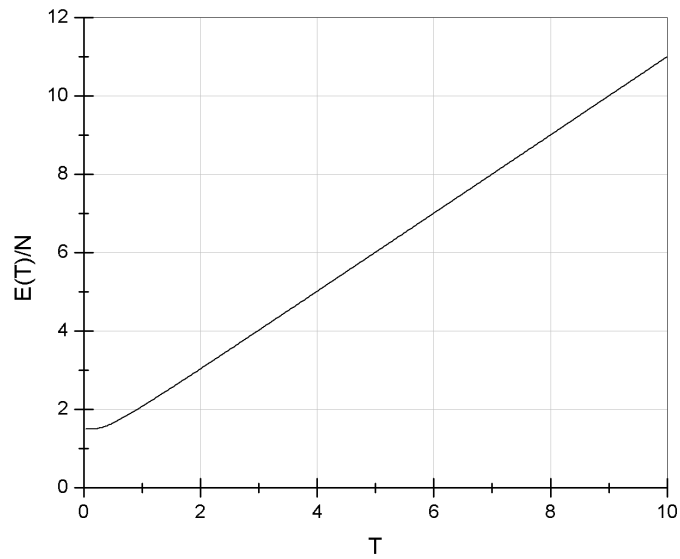


Figure 1: The energy  $E(T, N)/N$  for  $\hbar\omega = 1$  and  $k_B = 1$

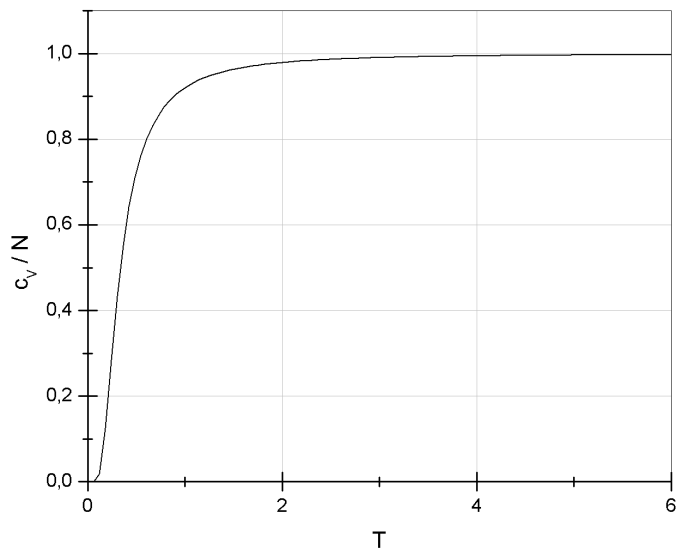


Figure 2: The specific heat  $c_V(T)/N$  for  $\hbar\omega = 1$  and  $k_B = 1$

## Discussion

For high temperatures, the equation  $c_V(T) = Nk_B$  corresponds to the experimental results. However, for temperatures  $\rightarrow 0$  the deviation increases. This comes from the assumption of no interaction between the atoms. That fact becomes important when the thermodynamic oscillation frequency is in the range of sound waves.

The collapse of this model at temperatures near absolute zero led to the *Debye modell*.

## Appendix

a) The Hamiltonian is given by:

$$\hat{H} = \sum_{i=1}^N \hbar\omega \left( \hat{a}_i^\dagger \hat{a}_i + \frac{1}{2} \right) = \sum_{i=1}^N \hbar\omega \left( \hat{N}_i + \frac{1}{2} \right) = \sum_{i=1}^N \hbar\omega \left( n_i + \frac{1}{2} \right) , \quad (11)$$

where the last step uses, that the system state is an eigenstate. With (11), we get the partition sum:

$$\begin{aligned} Z(\beta, N) &= \text{Tr} e^{-\beta\hat{H}} = \sum_{j=0}^{\infty} e^{-\beta\hbar\omega \sum_{i=0}^N n_i + \frac{1}{2}} = \prod_{i=1}^N \sum_{j=0}^{\infty} e^{-\beta\hbar\omega (n_i + \frac{1}{2})} \\ &= \prod_{i=1}^N \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} = \left( \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} \right)^N . \end{aligned} \quad (12)$$

We compute the free energy:

$$F(\beta, N) = -\frac{1}{\beta} \ln Z(\beta, N) = \frac{\hbar\omega N}{2} + \frac{N}{\beta} \ln (1 - e^{-\beta\hbar\omega})$$

and the average energy:

$$\begin{aligned} \langle E \rangle &= -\frac{\partial}{\partial\beta} \ln Z(\beta, N) \\ &= N \frac{\partial}{\partial\beta} \frac{\beta\hbar\omega}{2} + N \frac{\partial}{\partial\beta} \ln (1 - e^{-\beta\hbar\omega}) \\ &= \frac{1}{2} N \hbar\omega + \frac{N \hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2} N \hbar\omega + \frac{N \hbar\omega}{e^{\beta\hbar\omega} - 1} . \end{aligned}$$

With that, we compute the specific heat (with  $\beta = \frac{1}{k_B T}$ ):

$$\begin{aligned}
c_V(T) &= \frac{\partial \langle E \rangle}{\partial T} \\
&= \frac{\partial}{\partial T} \frac{N \hbar \omega}{\exp\left(\frac{\hbar \omega}{k_B T} - 1\right)} \\
&= -N \hbar \omega \cdot \frac{\exp\left(\frac{\hbar \omega}{k_B T}\right) \left(-\frac{\hbar \omega}{k_B T^2}\right)}{\left(\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1\right)^2} \\
&= \frac{N \hbar^2 \omega^2 \cdot \exp\left(\frac{\hbar \omega}{k_B T}\right)}{k_B T^2 \cdot \exp\left(\frac{\hbar \omega}{k_B T} - 1\right)^2} .
\end{aligned}$$

As the energy, that has to be plotted, is given by:

$$E(T, N) = F(T, N) + T \cdot S(T, N) ,$$

we need to calculate  $S(T, N)$ :

$$\begin{aligned}
S(T, N) &= -\frac{\partial F(\beta, N)}{\partial T} \\
&= -N k_B \ln \left(1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right)\right) - \frac{N k_B T \cdot \left(-\frac{\hbar \omega}{k_B T^2}\right)}{1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right)} \\
&= \frac{N \hbar \omega}{T} \frac{1}{1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right)} - N k_B \cdot \ln \left(1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right)\right) .
\end{aligned}$$

This leads to:

$$E(T, N) = \frac{1}{2} N \hbar \omega + \frac{N \hbar \omega}{1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right)} .$$

b) We consider the two cases  $T \rightarrow 0$  and  $T \rightarrow \infty$  for  $c_V(T)$ .

$$\begin{aligned}\lim_{T \rightarrow 0} c_V(T) &= \lim_{T \rightarrow 0} \frac{N\hbar^2\omega^2 \cdot \exp\left(\frac{\hbar\omega}{k_B T}\right)}{k_B T^2 \cdot \exp\left(\frac{\hbar\omega}{k_B T} - 1\right)^2} \\ &\approx \lim_{T \rightarrow 0} \frac{N\hbar^2\omega^2}{k_B T^2 \cdot \exp\left(\frac{\hbar\omega}{k_B T}\right)} \\ &= 0 \\ \lim_{T \rightarrow \infty} c_V(T) &= \lim_{T \rightarrow 0} \frac{N\hbar^2\omega^2 \cdot \exp\left(\frac{\hbar\omega}{k_B T}\right)}{k_B T^2 \cdot \exp\left(\frac{\hbar\omega}{k_B T} - 1\right)^2} \\ &\approx \lim_{T \rightarrow 0} \frac{N\hbar^2\omega^2}{k_B T^2} \cdot \left(\frac{k_B T}{\hbar\omega}\right)^2 \\ &= Nk_B\end{aligned}$$