FYS4130: Obligatory Assignment 1

Steinnes L. *

Department of physics, University of Oslo, P.O. Box 1048 Blindern, N-0316 Oslo, Norway

Abstract

The following sections attempt to give answers to Assignment 1 in the UiO course FYS4130: Statistical Mechanics. The program used to solve parts of exercise 3 can be found at my github page [2].

Problem 1

Assume there exists a method to obtain values for S, N, P as functions of T, V, μ. One could vary the input variables to find

$$c_v = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{V,N}. \tag{1}$$

First of all, note that $S(T,V,\mu)$, and V and N are the variables kept constant. Thus, there is no guarantee that μ wouldn't change with a decrease or increase in T. Based on the input variables write the total differential as

$$dS = \left(\frac{\partial S}{\partial V}\right)_{T,\mu} dV + \left(\frac{\partial S}{\partial T}\right)_{V,\mu} dT + \left(\frac{\partial S}{\partial \mu}\right)_{T,V} d\mu. \tag{2}$$

Consider the partial derivatives as independent variables. Thus, with N and V held constant, then

$$\left(\frac{\partial S}{\partial T}\right)_{V,N} = \left(\frac{\partial S}{\partial T}\right)_{V,\mu} + \left(\frac{\partial S}{\partial \mu}\right)_{T,V}\left(\frac{\partial \mu}{\partial T}\right)_{V,N}, \tag{3}$$

since $\partial T/\partial T = 1$.

Numerical derivation on a 3D mesh with discrete values for $S(T_i, V_j, \mu_k) = S_{i,j,k}$ can then be applied to solve for c_v. One must take into account that c_v most likely has divergent

*lasse.steinnes@fys.uio.no [March 10, 2021] behavior in a first order phase transition, because heat changes the state of the material rather than raising overall temperature. This can be seen mathematically from

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S, \tag{4}$$

because Helmholtz free energy, $F(T)$, has a kink where the phase transition occurs (in a point because T is an intensive variable). S will then have discontinuous "jump" at T_c. To avoid numerical overflow (from $T = 0.0$), but still describe c_v during phase transition, small enough ΔT must be applied, and a central difference is suggested. Let

$$\Delta ST_i = \frac{S_{i+1,j,k} - S_{i-1,j,k}}{T_{i+1} - T_{i+1}}, \tag{5}$$

and so on. Then eq. 3 becomes

$$\left[\left(\frac{\partial S}{\partial T}\right)_{V,N}\right]_{T=T_i,\mu=\mu_i} \approx \Delta ST_i + \Delta S\mu_k + \frac{\mu_{k+1} - \mu_{k-1}}{T_{i+1} - T_{i+1}}, \tag{6}$$

where a general expression for T_i and μ_i is

$$x_i = \frac{x_{i+1} + x_{i-1}}{2}. \tag{7}$$

c_v can be determined from eq. 6 for a particular V,N at points T_i and μ_i.

Problem 2

Want to reduce the derivative

$$\left(\frac{\partial P}{\partial U}\right)_{G,N}, \tag{8}$$

to a combination of the standard set quantities α, κ_T, c_p, c_v, T, S, P, V, μ and N. The equations for these quantities will not be given in the derivation, since they should be known from before. The general method applied is to introduce differentials of T,P,V and S, because the standard set can be expressed in term of these.

First, try to write the expression as a Jacobian, neglect the N constant and perform the typical chain rule trick. In the end rearrange variables with the rule $\partial(x,y)/\partial(z,q) = -\partial(y,x)//\partial(z,q)$.

$$\frac{\partial(P,G,N)}{\partial(U,G,N)} = \frac{\partial(P,G)}{\partial(P,T)} \cdot \frac{\partial(P,T)}{\partial(U,G)} = \frac{\partial(G,P)}{\partial(T,P)} \cdot \left[\frac{\partial(U,G)}{\partial(P,T)}\right]^{-1}. \tag{9}$$

From the Legendre transform $G = U[T,P] = U - ST + VP \Rightarrow dG = -SdT + VdP$, then

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{10}$$

As a result the eq. 9 becomes

$$\left(\frac{\partial P}{\partial U}\right)_{G,N} = -S \cdot \left[\frac{\partial(U,G)}{\partial(P,T)}\right]^{-1}. \tag{11}$$

Now, use the Jacobian determinant

$$\frac{\partial(a,b)}{\partial(c,d)} \overset{\text{def.}}{=} \begin{vmatrix} \frac{\partial a}{\partial c} & \frac{\partial s}{\partial d} \\ \frac{\partial b}{\partial c} & \frac{\partial b}{\partial d} \end{vmatrix} = \frac{\partial a}{\partial c} \cdot \frac{\partial b}{\partial d} - \frac{\partial a}{\partial c} \cdot \frac{\partial b}{\partial c}. \tag{12}$$

Thus

$$\frac{\partial(U,G)}{\partial(P,T)} = \frac{\partial(U,T)}{\partial(P,T)} \cdot \frac{\partial(G,P)}{\partial(T,P)} - \frac{\partial(U,P)}{\partial(T,P)} \cdot \frac{\partial(G,T)}{\partial(P,T)}. \tag{13}$$

From the differential dG from before, we see that

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V \;\text{ and }\; \left(\frac{\partial G}{\partial T}\right)_{P,N} = -S. \tag{14}$$

However, there is no direct relation to get from

$$\frac{\partial(U,T)}{\partial(P,T)} \;\text{ and }\; \frac{\partial(U,P)}{\partial(T,P)}. \tag{15}$$

To derive expressions for each of them, a number of relations have to be made use of. The steps are listed below. For the first mentioned derivative in eq. 15 use the chain rule with $\partial(V,T)$, where we recognize κ_T, so that (s.t.)

$$\frac{\partial(U,T)}{\partial(P,T)} = -\kappa_T V \frac{\partial(U,T)}{\partial(V,T)}. \tag{16}$$

Now apply the chain rule with $\partial(S,V)$, so that

$$\frac{\partial(U,T)}{\partial(V,T)} = \frac{\partial(U,T)}{\partial(S,V)} \cdot \left(-\frac{c_v N}{T}\right). \tag{17}$$

Apply the Jacobian determinant (12), so that

$$\frac{\partial(U,T)}{\partial(S,V)} = \frac{\partial(U,V)}{\partial(S,V)} \cdot \frac{\partial(T,S)}{\partial(V,S)} - \frac{\partial(U,S)}{\partial(V,S)} \cdot \frac{\partial(T,V)}{\partial(S,V)}. \tag{18}$$

From $dU = TdS - PdV$, most of the derivatives are known, and we recognize c_v. For the remaining derivative, apply the maxwell relation from dU

$$\frac{\partial(T,S)}{\partial(V,S)} \overset{m.w}{=} -\frac{\partial(P,V)}{\partial(T,V)} = -\frac{\partial(P,V)}{\partial(P,T)} / \frac{\partial(T,V)}{\partial(T,V)} = \frac{\partial(V,P)}{\partial(T,P)} / \frac{\partial(V,T)}{\partial(P,T)} = -\frac{\alpha}{\kappa_T}. \tag{19}$$

Piecing the first halves together

$$\frac{\partial(U,T)}{\partial(V,T)} = -\frac{\partial(U,T)}{\partial(S,V)} \frac{c_v N}{T} = \left(\frac{T\alpha}{\kappa_T} - \frac{PT}{c_v N}\right) \frac{C_v N}{T} = \frac{c_v N \alpha}{\kappa_T} - P, \tag{20}$$

s.t.

$$\frac{\partial(U,T)}{\partial(P,T)} = -\kappa_T V \frac{\partial(U,T)}{\partial(V,T)} = -\kappa_T V \left(\frac{c_v N \alpha}{\kappa_T} - P\right) = V(P\kappa_T - c_v N \alpha). \tag{21}$$

A same derivation must be performed on the right hand side derivative in eq. 15. To begin with, use the chain rule with $\partial(S,V)$,

$$\frac{\partial(U,P)}{\partial(T,P)} = \frac{\partial(U,P)}{\partial(S,V)} \cdot \frac{\partial(S,V)}{\partial(T,P)}, \tag{22}$$

where

$$\frac{\partial(S,V)}{\partial(T,P)} = \frac{\partial(S,P)}{\partial(T,P)} \cdot \frac{\partial(V,T)}{\partial(P,T)} - \frac{\partial(S,T)}{\partial(P,T)} \cdot \frac{\partial(V,P)}{\partial(T,P)}. \tag{23}$$

From the Maxwell relation from $dG = -SdT + VdP$

$$\frac{\partial(S,T)}{\partial(P,T)} \overset{m.x.}{=} -\frac{\partial(V,P)}{\partial(T,P)} = -\alpha V, \tag{24}$$

and inserting the other known standard set quantities

$$\frac{\partial(S,V)}{\partial(T,P)} = -\frac{VNc_p\kappa_T}{T} + \alpha^2 V^2. \tag{25}$$

The remaining derivative from eq. 22 is

$$\frac{\partial(U,P)}{\partial(S,V)} = \frac{\partial(U,V)}{\partial(S,V)} \cdot \frac{\partial(P,S)}{\partial(V,S)} - \frac{\partial(U,S)}{\partial(V,S)} \cdot \frac{\partial(P,V)}{\partial(S,V)}. \tag{26}$$

The derivatives of U are known from dU, and

$$\frac{\partial(P,V)}{\partial(S,V)} = \frac{\partial(P,V)}{\partial(T,V)} \cdot \frac{\partial(T,V)}{\partial(S,V)} = \frac{\partial(P,V)}{\partial(T,V)} \cdot \left[\frac{\partial(S,V)}{\partial(T,V)}\right]^{-1} = \frac{\alpha}{\kappa_T}\frac{T}{c_v N}. \tag{27}$$

The only derivative left to express in terms of standard set quantities is

$$\frac{\partial(P,S)}{\partial(V,S)} = \frac{\partial(P,S)}{\partial(T,S)} \cdot \frac{\partial(T,S)}{\partial(V,S)}. \tag{28}$$

Apply a Maxwell relation from dU and the result from above to find that

$$\frac{\partial(T,S)}{\partial(V,S)} \overset{m.x}{=} \frac{\partial(P,V)}{\partial(S,V)} = \frac{\alpha}{\kappa_T}\frac{T}{c_v N}, \tag{29}$$

and

$$\frac{\partial(P,S)}{\partial(T,S)} = \frac{\partial(P,S)}{\partial(P,T)} \cdot \frac{\partial(P,T)}{\partial(T,S)} = -\frac{\partial(S,P)}{\partial(T,P)} \cdot \frac{\partial(P,T)}{\partial(S,T)} = -\frac{N}{T}c_p \frac{\partial(P,T)}{\partial(V,T)} \cdot \frac{\partial(V,T)}{\partial(S,T)}. \tag{30}$$

From $dF = dU - d(ST) = -SdT - PdV$,

$$\frac{\partial(V,T)}{\partial(S,T)} \overset{m.x.}{=} \left[\frac{\partial(P,V)}{\partial(T,V)}\right]^{-1} = \frac{\kappa_T}{\alpha}. \tag{31}$$

Thus

$$\frac{\partial(P,S)}{\partial(V,S)} = \frac{\partial(P,S)}{\partial(T,S)} \cdot \frac{\partial(T,S)}{\partial(V,S)} = \frac{c_p}{c_v\kappa_T V}. \tag{32}$$

Collecting terms

$$\frac{\partial(U,P)}{\partial(V,S)} = \frac{Tc_p}{c_v\kappa_T V} + \frac{P\alpha T}{\kappa_T c_v N}, \tag{33}$$

$$\frac{\partial(U,P)}{\partial(T,P)} = \frac{\partial(U,P)}{\partial(S,V)} \cdot \frac{\partial(S,V)}{\partial(T,P)} = \left(\frac{Tc_p}{c_v\kappa_T V} + \frac{P\alpha T}{\kappa_T c_v N}\right)\left(\alpha^2 V^2 - \frac{VNc_p\kappa_T}{T}\right). \tag{34}$$

Using all the results (see especially eq.'s 11, 13, 21 and 34) one gets in the end

$$\left(\frac{\partial P}{\partial U}\right)_{G,N} = -\left[\frac{V^2\left(P\kappa_T - c_v N\alpha\right)}{S} + \frac{1}{\kappa_T c_v}\left(\frac{Tc_p}{V} + \frac{P\alpha T}{N}\right)\left(\alpha^2 V^2 - \frac{VNc_p\kappa_T}{T}\right)\right]^{-1}. \tag{35}$$

There are probably ways to rewrite the above expression to a prettier one. Also, choosing another path would maybe lead to other dependencies, such as μ, possibly resulting in fewer steps to get an answer. However, here, no relations with μ were taken advantage of.

Problem 3

We have a container (volume V) with N rod shaped particles. Rods are oriented along the x, y and z-axes, so that the total number of rods are constrained by

$$N = N_x + N_y + N_z. \tag{36}$$

The container is held at constant $T = kT_{\text{actual}}$ with units $[J/k \cdot k = J]$, so that

$$F = T\left[N_x \ln\left(\alpha l b^2 \frac{N_x}{V}\right) + N_y \ln\left(\alpha l b^2 \frac{N_y}{V}\right) + N_z \ln\left(\alpha l b^2 \frac{N_z}{V}\right) + \gamma l b^2 \frac{N_x N_y + N_y N_z + N_z N_x}{V}\right]. \tag{37}$$

Here the volume of the rectangular rod shaped particles is $V_{\text{rod}} = lb^2$, where l denotes the length, and b the width. Let α and γ be positive dimensionless constants.

a) Dimensionless Helmholtz free energy

Want to use the dimensionless volume variable

$$\tilde{V} = \frac{V}{lb^2}, \tag{38}$$

to find $\tilde{F} = F(\tilde{V})/T$. Recognize

$$\frac{1}{V} = \frac{lb^2}{V}, \tag{39}$$

and we find directly that

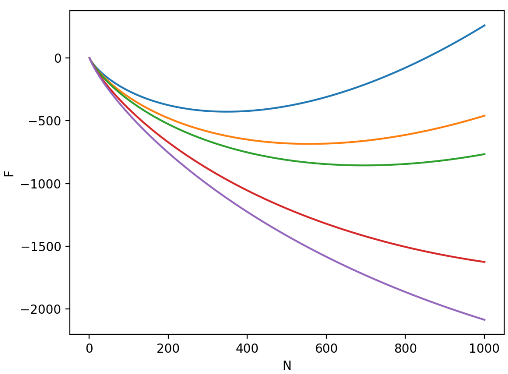
$$\tilde{F} = \left[N_x \ln\left(\alpha \frac{N_x}{\tilde{V}}\right) + N_y \ln\left(\alpha \frac{N_y}{\tilde{V}}\right) + N_z \ln\left(\alpha \frac{N_z}{\tilde{V}}\right) + \gamma \frac{N_x N_y + N_y N_z + N_z N_x}{\tilde{V}} \right]. \quad (40)$$

b) Equilibrium Helmholtz free energy and phases

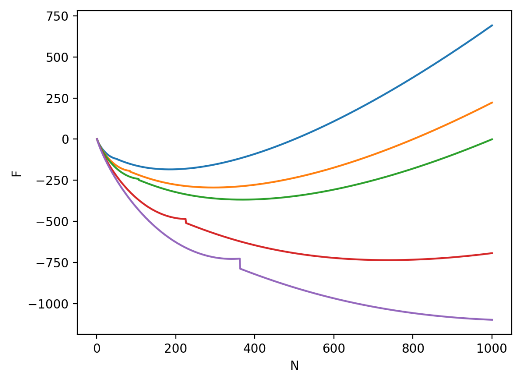
At equilibrium, there is no change in $\tilde{F}$, so that if we have two identical subsystems

$$\Delta\tilde{F} = \tilde{F}(T,V,N+\Delta N) + \tilde{F}(T,V,N-\Delta N) - 2F(T,V,N) = 0. \quad (41)$$

Here, the scientific python module `scipy.optimize.minimize` [1] is applied to find the Helmholtz free energy at equilibrium. That is, for a given $\tilde{V}$, α and γ and N, under the constraint in eq. 36. Then imagine we increase N quasi-statically, so the system is always in a state of equilibrium. In this way, one can obtain $\tilde{F}$ as a function of N (fig. 1).



(a) Case 1: $\gamma = 1$



(b) Case 2: $\gamma = 30.0$

Figure 1: **Numerical solution to F(N)**: **a)** No phase transition with $\gamma = 1$. **b)** With $\gamma = 30.0$, there is a phase transition. Dimensionless volumes ($\tilde{V}$) from top to bottom line: $500, 800, 1000, 2000, 3000$. $\alpha = 1.0$

The stability criteria for $\tilde{F}$ is

$$\left(\frac{\partial \tilde{F}}{\partial N}\right)_{T,V} = 0, \text{ and } \left(\frac{\partial^2 \tilde{F}}{\partial N^2}\right)_{T,V} \geq 0, \quad (42)$$

since N is an extensive quantity. From fig. 1a, we can see that if $\gamma >> 1$ it results in an unstable region where the criteria is not satisfied. Here the curves of each phase meet.

From fig. 1a one can find where

$$\left(\frac{\partial \tilde{F}}{\partial N}\right)_{T,V} = 0, \quad \text{and} \quad \left(\frac{\partial^2 \tilde{F}}{\partial N^2}\right)_{T,V} = 0, \tag{43}$$

to determine critical quantities. Table 1 gives an overview of the results.

Table 1: **Critical quantities**: Critical quantities for Helmholtz free energy in the phase transition. For $\tilde{V} = 3000$, $\gamma = 30.0$

N_c	n_c	N_x	N_y	N_z	$\tilde{P}_c$
362	0.11	13	13	336	-3.4

P_c was determined from the Gibbs Duheim equation. If one assumes the system to be extensive (homogeneous, and not interacting with any surfaces (bulk system)), then

$$d\mu = -\left(\frac{S}{N}\right) dT + \left(\frac{V}{N}\right) dP. \tag{44}$$

When $dT = 0$ (T constant), and n_c is also constant, one can integrate the above equation s.t.

$$P = \mu n_c. \tag{45}$$

By considering the thermodynamic relation

$$\left(\frac{\partial \tilde{F}}{\partial N}\right)_{T,V} = \mu, \tag{46}$$

we see that the chemical potential μ is the quantity changing discontinuously in the phase transition. From fig. 1, we also observe that when the volume increase, then there is a more negative slope to F. Since

$$\left(\frac{\partial \mu}{\partial V}\right)_{T,N} \overset{m.x}{=} -\left(\frac{\partial \tilde{P}}{\partial N}\right)_{T,V}, \tag{47}$$

then the change in P due to N must be positive for the equality to hold. The last equality uses a maxwell relation.

c) Gibbs Free energy as pressure increases

I used a long time look at this task, however, so far, the only suggested solution is to use the result

$$G = \mu N = \int V dP. \tag{48}$$

Thus, instead of integrating with respect to P, the relation μN was used as a substitute. See fig. 2.

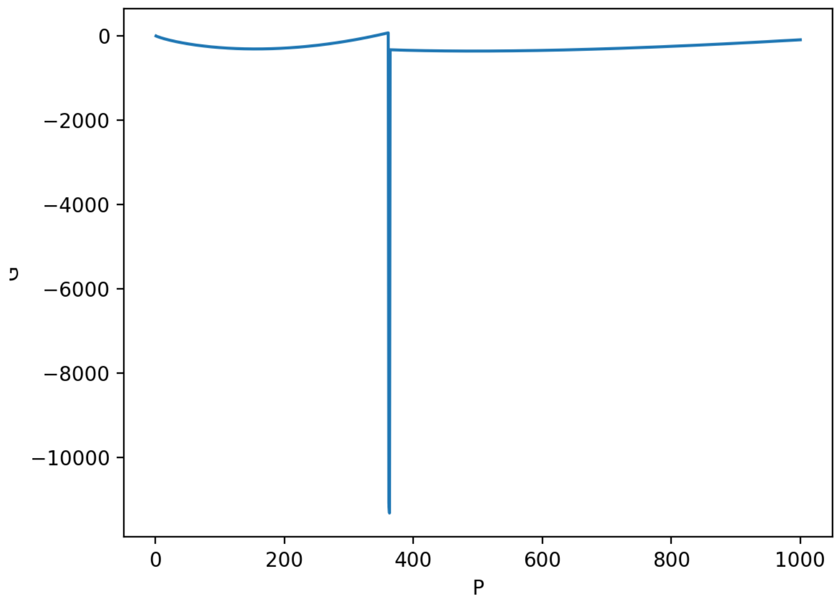


Figure 2: **Numerical solution to G(P)**. Gibbs free energy as a function of pressure.

The thermodynamic relation

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V, \tag{49}$$

suggests that $\tilde{V}$ changes discontinuosly when as P is changed.

Problem 4

Consider a one dimensional (1D) lattice of N 1D harmonic oscillators (HOs). Energy levels exist as quanta of $\hbar\omega$, where $\hbar$ is the reduced Planck constant and ω is the frequency of each oscillator.

Total energy for non-interacting HOs

$$E = \hbar\omega \sum_{i=1}^{N} \left(n_i + \frac{1}{2} \right), \tag{50}$$

where $n_i \in \mathbb{N}$ denotes the number of quanta. Total number of quanta, M, is constrained by

$$M = \sum_{i=1}^{N} n_i. \tag{51}$$

a) Microstates

Want to find number of microstates, or configurations, of the system as function of M and N. We have in total M identical quanta we can distribute among N oscillators. Take into the fact that oscillators play the role as $N-1$ partitions between a given amount of quanta. Then partitions and quanta can be ordered in $(N-1+M)!$ ways. However, since quanta and partitions are indistinguishable on their own, the final number of *distinguishable* arrangements becomes

$$\Omega(N,M) = \binom{N-1+M}{M} = \frac{(N-1+M)!}{((N-1+M)-M)!M!} = \frac{(N-1+M)!}{(N-1)!M!}. \tag{52}$$

b) S(T,N)

Want to find entropy S as a function of T and N assuming many HOs (N large) and large energy (E). For the microcanonical ensemble (NVE constant) ($k = k_b$, boltzmann constant)

$$S = k \ln \Omega(N,M) = k \ln \frac{(N-1+M)!}{(N-1)!M!} \overset{N>>1}{\approx} k \ln \frac{(N+M)!}{N!M!}. \tag{53}$$

Now apply Stirling's approximation $\ln x! = x \ln x - x$ with $O\left(ln(x)/x\right)$, s.t.

$$S = k\left[\ln(N+M)! - \ln N! - \ln M!\right]$$

$$\overset{stirl.}{\approx} k\left[(N+M)\ln(N+M) \; - N\ln N - M\ln M - (N+M) - (-N-M)\right]. \tag{54}$$

Thus, collecting terms of products of N and M

$$S \approx k\left[N\ln\frac{N+M}{N} + M\ln\frac{N+M}{M}\right]. \tag{55}$$

From the energy equation (eq. 50), recognize that the sum can be split into two independent parts, where one corresponds to M (see eq. 51), s.t.

$$E = \frac{1}{2}N\hbar\omega + \hbar\omega M. \tag{56}$$

From the above equation,

$$M = \frac{E}{\hbar\omega} - \frac{N}{2}, \tag{57}$$

and

$$N + M = \frac{E}{\hbar\omega} + \frac{N}{2}. \tag{58}$$

Thus

$$\begin{aligned} S/k = N\left(\frac{E}{\hbar\omega} + \frac{N}{2}\right)\ln\left(\frac{E}{\hbar\omega} + \frac{N}{2}\right) - N\ln N + \left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)\ln\left(\frac{E}{\hbar\omega} + \frac{N}{2}\right) \\ - \left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)\ln\left(\frac{E}{\hbar\omega} - \frac{N}{2}\right). \end{aligned} \tag{59}$$

Adding and eliminating common terms results in

$$S/k = N\left(\frac{E}{\hbar\omega} + \frac{N}{2}\right)\ln\left(\frac{E}{\hbar\omega} + \frac{N}{2}\right) - N\ln N + \left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)\ln\left(\frac{E}{\hbar\omega} - \frac{N}{2}\right). \tag{60}$$

If we can find E as a function of T, then $S(E,N) \Rightarrow S(T,N)$. Fortunately, we know that

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}. \tag{61}$$

Apply both the product rule ($(uv)' = u'v + uv'$) and the chain rule

$$\frac{\partial}{\partial x} \ln\left(\frac{x}{a} + \frac{n}{2}\right) = \frac{1}{a} \frac{1}{\left(\frac{x}{a} + \frac{n}{2}\right)}, \tag{62}$$

s.t. from eq. 60,

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{k}{\hbar\omega} \ln\left(\frac{\frac{E}{\hbar\omega} + \frac{N}{2}}{\frac{E}{\hbar\omega} - \frac{N}{2}}\right) = \frac{1}{T}. \tag{63}$$

Rewriting the above expression yields

$$\frac{\frac{E}{\hbar\omega} + \frac{N}{2}}{\frac{E}{\hbar\omega} - \frac{N}{2}} = \exp\left(\frac{\hbar\omega}{kT}\right) \Longleftrightarrow E(T) = N\hbar\omega\left(\frac{1}{2} + \frac{1}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1}\right) \tag{64}$$

At high oscillator energies, $T \to \infty$. If $x = \hbar\omega/(kT)$, the use the expansion around $x = 0$ for small x

$$e^x \approx [e^x]_{x=0} + x\left[\frac{\partial e^x}{\partial x}\right]_{x=0} = 1 + x. \tag{65}$$

Then

$$E(T) = \left(\frac{1}{2} + \frac{1}{1+x-1}\right) = \frac{N\hbar\omega}{2} + NkT. \tag{66}$$

Inserting for E in eq. 60 results in

$$S(N,T) = kN\left[\left(\frac{k}{\varepsilon}T + 1\right)\ln\left(N\left(\frac{kT}{\varepsilon} + 1\right)\right) - \frac{kT}{\varepsilon}\ln\frac{NkT}{\varepsilon}\right], \tag{67}$$

where $\varepsilon = \hbar\omega$.

c) Heat capacity

The heat capacity can be defined as

$$c_v = \left(\frac{\partial E}{\partial T}\right)_V, N, \tag{68}$$

which for the high T and high N approximation (eq. 66) yields

$$c_v = Nk, \tag{69}$$

as we would expect from the equipartition theorem.

References

[1] scipy-minimize-documentation, 2021.

[2] Lasse Steinnes. Assignment1-GIT, 2020.