FYS4130 - Oblig 1

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TASK 1 - BLACK BOX NUMERICAL METHOD

We want to find the isothermal compressibility at constant T and N,

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

with a black box numerical method which gives us values for P and N as function of intput parameters T, V, and μ which we may vary. The derivatives we're able to compute with our numerical method is the partial derivative of either P or N with respect to one of the input parameters, when the other two are held constant. We must therefore rewrite equation (1), such that it only contains such derivatives. To begin, we use the chain rule on the reciprocal of the partial derivative in equation (1)

$$\begin{aligned}\left(\frac{\partial P}{\partial V}\right)_{T,N} &= \frac{\partial(P,T,N)}{\partial(V,T,N)} = \frac{\partial(P,T,N)}{\partial(V,T,\mu)}\cdot\frac{\partial(V,T,\mu)}{\partial(V,T,N)} \\ &= \frac{\partial(P,N,T)}{\partial(V,\mu,T)}\cdot\frac{\partial(\mu,V,T)}{\partial(N,V,T)} = \frac{\partial(P,N,T)}{\partial(V,\mu,T)}\Big/\left(\frac{\partial N}{\partial \mu}\right)_{V,T}.\end{aligned}$$

The last factor is a partial derivative we're able to compute, by computing the change in N as we vary μ only. For the other factor, we expand the jacobian, using its definition

$$\frac{\partial(P,N,T)}{\partial(V,\mu,T)} = \left(\frac{\partial P}{\partial V}\right)_{\mu,T}\left(\frac{\partial N}{\partial \mu}\right)_{V,T} - \left(\frac{\partial P}{\partial \mu}\right)_{V,T}\left(\frac{\partial N}{\partial V}\right)_{\mu,T}. \tag{2}$$

We see that the four partial derivatives in equation (2) are taken with respect to either V, with the other input parameters held constant, or μ with the other input parameters held constant. Measuring the change in P and N with these constraints is thus something our numerical method is capable of, and we have successfully reduced κ_T into multiple partial derivatives we're able to solve. The resulting expression for κ_T becomes

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

TASK 2 - PARTIAL DERIVATIVE

We want to rewrite the partial derivative

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

In this task we will need the standard set of second derivatives given in Swendsen, and we list them here for convenience

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} \tag{3}$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} \tag{4}$$

$$c_P = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{P,N} \tag{5}$$

$$\tag{6}$$

We begin by applying the chain rule to the Jacobian, which enables us to get a partial derivative containing U and G in the denominator only.

$$\begin{aligned}\left(\frac{\partial P}{\partial U}\right)_{G,N} &= \frac{\partial(P,G,N)}{\partial(U,G,N)} = \frac{\partial(P,G,N)}{\partial(P,T,N)}\cdot\frac{\partial(P,T,N)}{\partial(U,G,N)} = \left(\frac{\partial G}{\partial T}\right)_{P,N}\frac{\partial(P,T,N)}{\partial(U,G,N)} \\ &= -S\Big/\frac{\partial(U,G,N)}{\partial(P,T,N)},\end{aligned} \tag{7}$$

where we used the differential form of the Gibbs free energy, $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}N$, to solve the first partial derivative of G with respect to T at constant P and N. The second factor was written in terms of the reciprocal such that the thermodynamic potentials in the Jacobian appear in the nominator.

We will now find an expression for $\partial(U,G,N)/\partial(P,T,N)$. To avoid partial derivatives containing U and G simultaneously, we expand the expression by using the definition of Jacobians.

$$\begin{aligned}\frac{\partial(U,G,N)}{\partial(P,T,N)} &= \left(\frac{\partial U}{\partial P}\right)_{T,N}\left(\frac{\partial G}{\partial T}\right)_{P,N} - \left(\frac{\partial U}{\partial T}\right)_{P,N}\left(\frac{\partial G}{\partial P}\right)_{T,N} \\ &= -S\left(\frac{\partial U}{\partial P}\right)_{T,N} - V\left(\frac{\partial U}{\partial T}\right)_{P,N},\end{aligned} \tag{8}$$

where the last equation follow from the definition of dG and the partial derivatives of it.

For the partial derivative of U with respect to T at constant P and N, we consider the differential form of fundamental relation in the energy representation, which at constant N becomes

$$\begin{aligned}\mathrm{d}U &= T\mathrm{d}S - P\mathrm{d}V \\ \implies \left(\frac{\partial U}{\partial T}\right)_{P,N} &= T\left(\frac{\partial S}{\partial T}\right)_{P,N} - P\left(\frac{\partial V}{\partial T}\right)_{P,N} \\ &= Nc_P - PV\alpha,\end{aligned} \tag{9}$$

where we used equations (5) and (3) for the two partial derivatives.

For the partial derivative of U with respect to P with T and N held constant we apply the chain rule

$$\begin{aligned}\left(\frac{\partial U}{\partial P}\right)_{T,N} &= \frac{\partial(U,T,N)}{\partial(P,T,N)} = \frac{\partial(U,T,N)}{\partial(V,T,N)}\cdot\frac{\partial(V,T,N)}{\partial(P,T,N)} = \left(\frac{\partial U}{\partial V}\right)_{T,N}\left(\frac{\partial V}{\partial P}\right)_{T,N} \\ &= \left(\frac{\partial U}{\partial V}\right)_{T,N}(-V\kappa_T).\end{aligned} \tag{10}$$

Equation (4) was used to rewrite the second partial derivative. For the other partial derivative, we once again use the previouslly mentioned expression for dU with N held constant

$$\left(\frac{\partial U}{\partial V}\right)_{T,N} = T\left(\frac{\partial S}{\partial V}\right)_{T,N} - P. \tag{11}$$

To proceed with the final partial derivative we will first use a Maxwell relation. We notice that S is differentiated with respect to V at constant T and N, so we can use the differential form of the Helmholtz free energy to derive the Maxwell relation.

$$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N \implies -\left(\frac{\partial F}{\partial T}\right)_{V,N} = S$$

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = -\left[\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_{V,N}\right]_{T,N} = -\left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_{T,N}\right]_{V,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}.$$

We rewrite the last partial derivative using the chain rule

$$\begin{aligned}\left(\frac{\partial P}{\partial T}\right)_{V,N} &= \frac{\partial(P,V,N)}{\partial(T,V,N)} = \frac{\partial(P,V,N)}{\partial(P,T,N)} \cdot \frac{\partial(P,T,N)}{\partial(T,V,N)} = -\frac{\partial(V,P,N)}{\partial(T,P,N)} \cdot \frac{\partial(P,T,N)}{\partial(V,T,N)} \\ &= -\left(\frac{\partial V}{\partial T}\right)_{P,N} \Big/ \left(\frac{\partial V}{\partial P}\right)_{T,N} = -V\alpha/(-V\kappa_T) = \frac{\alpha}{\kappa_T},\end{aligned} \tag{12}$$

where in the last step equations (3) and (4) were used to rewrite the nominator and denominator, repsectively. Equation (10) can now be solved, by inserting equation (12) into equation (11)

$$\begin{aligned}\left(\frac{\partial U}{\partial P}\right)_{T,N} &= -V\kappa_T \left(\frac{\partial U}{\partial V}\right)_{T,N} = -V\kappa_T \left(T\frac{\alpha}{\kappa_T} - P\right) \\ &= -VT\alpha + PV\kappa_T\end{aligned}$$

Inserting equation (10) and (9) into equation (8) we get

$$\frac{\partial(U,G,N)}{\partial(P,T,N)} = -S\left(-VT\alpha + PV\kappa_T\right) - V\left(Nc_P - PV\alpha\right) = -V\left[SP\kappa_T + Nc_P - ST\alpha - PV\alpha\right] \tag{13}$$

Finally, inserting equation (13) into equation (7) we arrive at the final expression

$$\left(\frac{\partial P}{\partial U}\right)_{G,N} = -S\left[\frac{\partial(U,G,N)}{\partial(P,T,N)}\right]^{-1} = \frac{S/V}{SP\kappa_T + Nc_P - ST\alpha - PV\alpha} \tag{14}$$

TASK 3

We consider the Helmholtz free energy given by equation (15)

$$F = T\left[N_x \ln\left(\alpha l b^2 \frac{N_x}{V}\right) + N_y \ln\left(\alpha l b^2 \frac{N_y}{V}\right) + N_z \ln\left(\alpha l b^2 \frac{N_z}{V}\right) + \gamma l b^2 \frac{N_x N_y + N_y N_z + N_z N_x}{V}\right] \tag{15}$$

a) - Dimensionless volume

Using $\tilde{V} = V/lb^2$, we can rewrite the four volume terms in the expression by $lb^2/V = 1/\tilde{V}$. The expression for the Helmholtz free energy divided by T now becomes

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

b) - Equilibrium Helmholtz free energy

We will now increase the rod concentration, $n = N/V$, so slow that we always consider the system to be in equilibrium. The temperature and volume is kept constant, but we increase N by adding rods. We will set $\alpha = 1$ in all following calculations.

$$\frac{F}{T} = N_x \ln\left(\frac{N_x}{\tilde{V}}\right) + N_y \ln\left(\frac{N_y}{\tilde{V}}\right) + N_z \ln\left(\frac{N_z}{\tilde{V}}\right) + \gamma \frac{N_x N_y + N_y N_z + N_z N_x}{\tilde{V}} \tag{16}$$

We compute the Helmholtz free energy numerically, and choose $\tilde{V} = 400$ for the dimensionless volume. For the number of particles, we consider $N \in [N_0, \tilde{V}]$ For each value of N we compute the helmholtz free energy for all combinations of $N_x, N_y \in [1, N-1]$ and find the corresponding value for N_z from the constraint $N = N_x + N_y + N_z$. From this, we find the values of N_x, N_y and N_z that minimizes F.

We plot the helmholtz free energy for a given

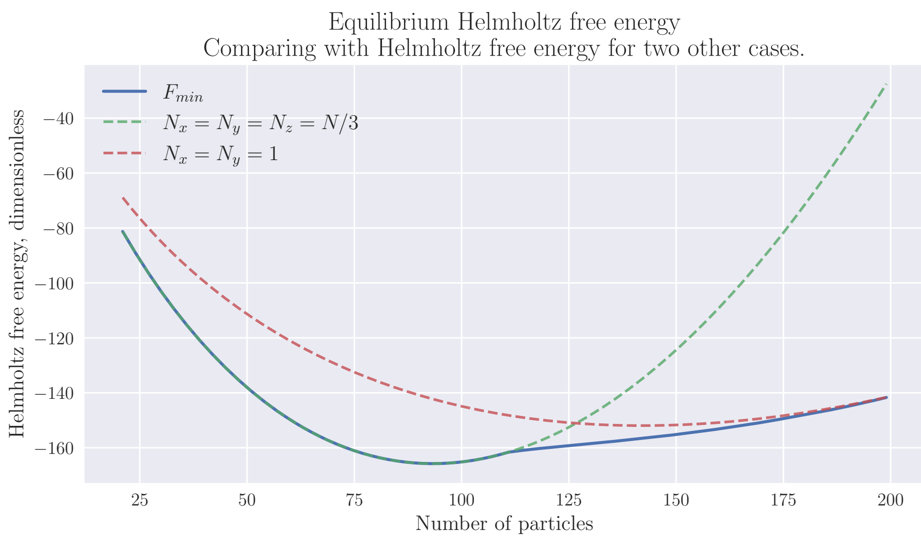

Figure 1. Helmholtz

PRESSURE

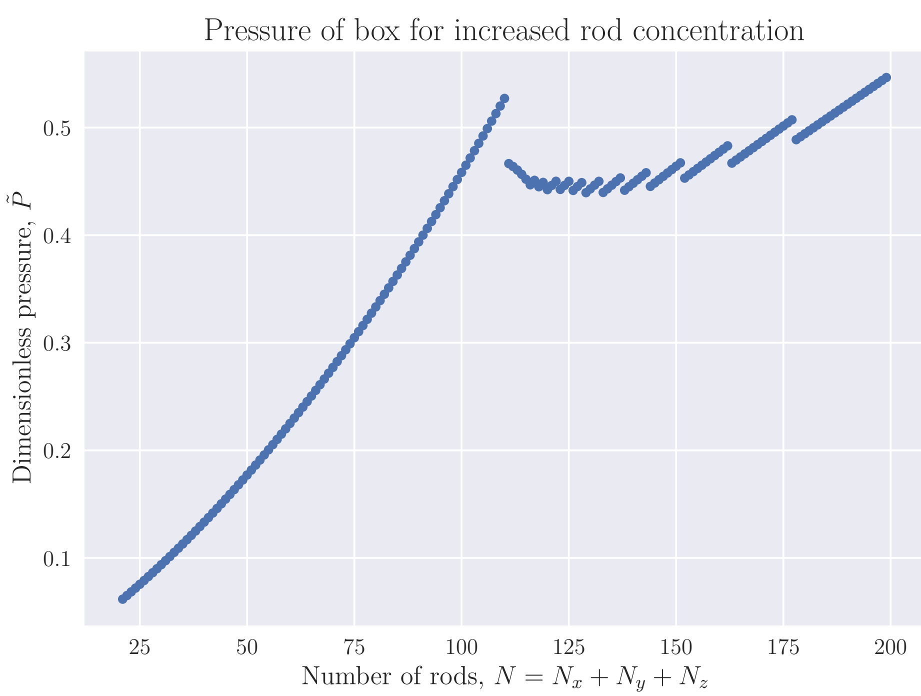

Figure 2. Helmholtz

NUMBER DENSITY

c) - Equilibrium Gibbs free energy

The Gibbs free energy is given as $G = F + PV$. We find an expression for the pressure, by taking the partial derivative of F with respect to volume, at constant T and N

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\left(\frac{\partial \tilde{V}}{\partial V}\right)_{T,N}\left(\frac{\partial F}{\partial \tilde{V}}\right)_{T,N} = -\frac{1}{lb^2}\left(\frac{\partial F}{\partial \tilde{V}}\right)_{T,N}$$

We now define the dimensionless pressure, $\tilde{P} \equiv Plb^2/T$, and can then differentiate equation (16) with respect to $\tilde{V}$.

$$\begin{aligned}\tilde{P} &= -\left[-\frac{N_x}{\tilde{V}} - \frac{N_y}{\tilde{V}} - \frac{N_z}{\tilde{V}} - \gamma\frac{N_xN_y + N_yN_z + N_zN_x}{\tilde{V}^2}\right] \\ &= \frac{N}{\tilde{V}} + \gamma\frac{N_xN_y + N_yN_z + N_zN_x}{\tilde{V}^2}\end{aligned}$$

We can now find the dimesnionless Gibbs free energy, G/T

$$\begin{aligned}\frac{G}{T} &= \frac{F}{T} + \frac{PV}{T} = \frac{F}{T} + \tilde{P}\tilde{V} \\ &= N_x \ln\left(\frac{N_x}{\tilde{V}}\right) + N_y \ln\left(\frac{N_y}{\tilde{V}}\right) + N_z \ln\left(\frac{N_z}{\tilde{V}}\right) + 2\gamma\frac{N_xN_y + N_yN_z + N_zN_x}{\tilde{V}} + N\end{aligned}$$

TASK 4

$$E = J(N_+ - N_-) \tag{17}$$

a)

The system we're considering is analogous to a toin coss, and we find the number of different micrstates from the binomial coefficient, where the constrain $N_+ + N_- = N$ can be used to eliminate N_-

$$\Omega(N, N_+) = \frac{N!}{N_+!N_-!} = \frac{N!}{N_+!(N - N_+)!}$$

b)

To find the entropy as a function for T and N where we assume large N, we start by taking the logarithm of $\Omega(N, N_+)$ and use Stirling's approximation on the different terms.

$$\begin{aligned}\ln\Omega(N, N_+) &= \ln(N!) - \ln(N_+!) - \ln(N - N_+)! \\ &\approx N\ln N - N_+\ln N_+ - (N - N_+)\ln(N - N_+) - N + N_+ + (N - N_+) \\ &= N\ln N - N_+\ln N_+ - (N - N_+)\ln(N - N_+)\end{aligned}$$

We want to eliminate N_+ from the expression in favor of temperature. To do this, we will take the partial derivative of S with respect to E

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \left(\frac{\partial N_+}{\partial E}\right)_{V,N}\left(\frac{\partial S}{\partial N_+}\right)_{V,N}$$

Rewriting equation (17) in terms of N_+ and N yields an expression for the derivative of N_+ with respect to E

$$E = J(2N_+ - N) \implies N_+ = \frac{1}{2}\left(\frac{E}{J} + N\right)$$

$$\left(\frac{\partial N_+}{\partial E}\right)_{V,N} = \frac{1}{2J}$$

Using the definition of entropy, $S = k_B \ln \Omega(N, N_+)$, we differentiate that with respect to N_+, where we use the approximated expression for $\ln \Omega(N, N_+)$

$$\begin{aligned}
\left(\frac{\partial S}{\partial N_+}\right)_{V,N} &= k_B \frac{\partial}{\partial N_+} \left[N \ln N - N_+ \ln N_+ - (N - N_+) \ln(N - N_+)\right] \\
&= k_B \left[-\ln N_+ - 1 + \ln(N - N_+) + 1\right] \\
&= k_B \ln\left(\frac{N - N_+}{N_+}\right)
\end{aligned}$$

Putting the pieces back together, we get

$$\begin{aligned}
\frac{1}{T} &= \frac{1}{2J} k_B \ln\left(\frac{N - N_+}{N_+}\right) \\
\ln\left(\frac{N - N_+}{N_+}\right) &= \frac{2J}{k_B T} \\
\implies N_+ &= \frac{N}{1 + e^{2J/k_B T}}
\end{aligned}$$

For simplicity, we now define $x \equiv \frac{2J}{k_B T}$. Before we start inserting our expression for N_+ to obtain the entropy function we find expressions for $\ln N_+$, $N - N_+$ and $\ln(N - N_+)$ in terms of N and x.

$$\begin{aligned}
\ln N_+ &= \ln\left(\frac{N}{1 + e^x}\right) = \ln N - \ln(1 + e^x) \\
N - N_+ &= N\left(1 - \frac{1}{1 + e^x}\right) = N\left(\frac{e^x}{1 + e^x}\right) = \frac{N}{1 + e^{-x}} \\
\ln(N - N_+) &= \ln\left(\frac{N}{1 + e^{-x}}\right) = \ln N - \ln\bigl(1 + e^{-x}\bigr)
\end{aligned}$$

Inserting these values for $\ln \Omega(N, N_+)$ yields

$$\begin{aligned}
S = k_B \ln \Omega(N, N_+) &= k_B \left[N \ln N - \frac{N}{1 + e^x}\left(\ln N - \ln(1 + e^x)\right) - \frac{N}{1 + e^{-x}}\left(\ln N - \ln\bigl(1 + e^{-x}\bigr)\right)\right] \\
&= k_B \left[N \ln N \left(1 - \frac{1}{1 + e^x} - \frac{1}{1 + e^{-x}}\right) + N\left(\frac{\ln(1 + e^x)}{1 + e^x} + \frac{\ln(1 + e^{-x})}{1 + e^{-x}}\right)\right] \\
&= N k_B \left[\frac{\ln(1 + e^x)}{1 + e^x} + \frac{\ln(1 + e^{-x})}{1 + e^{-x}}\right]
\end{aligned}$$

To proceed, we simplify further by considering the logarithm in the last term

$$\begin{aligned}
\ln\bigl(1 + e^{-x}\bigr) &= \ln\bigl(e^{-x}(1 + e^x)\bigr) = -x + \ln(1 + e^x) \\
\implies \frac{1}{1 + e^{-x}} \ln\bigl(1 + e^{-x}\bigr) &= \frac{\ln(1 + e^x)}{1 + e^{-x}} - \frac{x}{1 + e^{-x}}
\end{aligned}$$

Having two common factors of $\ln(1 + e^x)$, the entropy expression simplifies even further

$$\begin{aligned}
S &= N k_B \left[\left(\frac{1}{1 + e^x} + \frac{1}{1 + e^{-x}}\right) \ln(1 + e^x) - \frac{x}{1 + e^{-x}}\right] \\
&= N k_B \left[\ln(1 + e^x) - \frac{x}{1 + e^{-x}}\right]
\end{aligned}$$

Inserting the expression for x yields the final entropy expression as a function of T and N

$$S(T, N) = N k_B \left[\ln\left(1 + e^{2J/k_B T}\right) - \frac{2J/k_B T}{1 + e^{-2J/k_B T}}\right] \tag{18}$$

c)

To find the heat capacity, we use the chain rule to ease the computation

$$
\begin{aligned}
C_V &= T\left(\frac{\partial S}{\partial T}\right)_{V,N} = T\left(\frac{\partial x}{\partial T}\right)_{V,N}\left(\frac{\partial S}{\partial x}\right)_{V,N} = -T\frac{2J}{k_B T^2}\left(\frac{\partial S}{\partial x}\right)_{V,N} \\
\left(\frac{\partial S}{\partial x}\right)_{V,N} &= Nk_B\left[\frac{e^x}{1+e^x} - \frac{1}{1+e^{-x}} - x\frac{e^{-x}}{(1+e^{-x})^2}\right] \\
&= -Nk_B x\frac{e^x}{(1+e^x)^2} = -Nk_B\frac{2J}{k_B T}\frac{e^{2J/k_B T}}{\left(1+e^{2J/k_B T}\right)^2}
\end{aligned}
$$

Putting it all together, we finally arrive at

$$
C_V = \frac{4J^2 N}{k_B}\frac{1}{T^2}\frac{e^{2J/k_B T}}{\left(1+e^{2J/k_B T}\right)^2}
$$

Without any explicit calculation, we rewrite the exponential factor in terms of a hyperbolic function

$$
\begin{aligned}
\frac{e^x}{(1+e^x)^2} &= \frac{1}{4\cosh^2(\frac{x}{2})} \\
\implies \frac{e^{2J/k_B T}}{\left(1+e^{2J/k_B T}\right)^2} &= \frac{1}{4\cosh^2\left(\frac{J}{k_B T}\right)}
\end{aligned}
$$

And our final expression for the heat capacity becomes

$$
C_V = \frac{J^2 N}{k_B}\frac{1}{T^2}\frac{1}{\cosh^2\left(\frac{J}{k_B T}\right)} \tag{19}
$$