FYS4130 - Oblig 1

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TASK 1 - BLACK BOX NUMERICAL METHOD

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

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

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} \tag{2}$$

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

$$c_P = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{P,N} \tag{4}$$

$$\tag{5}$$

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.

$$\begin{aligned}\left(\frac{\partial P}{\partial U}\right)_{G,N} &= \frac{\partial(P,G,N)}{\partial(U,G,N)} = \frac{\partial(P,G,N)}{\partial(P,T,N)}\cdot\frac{\partial(P,T,N)}{\partial(U,G,N)} = \left(\frac{\partial G}{\partial T}\right)_{P,N}\frac{\partial(P,T,N)}{\partial(U,G,N)} \\ &= -S\Big/\frac{\partial(U,G,N)}{\partial(P,T,N)},\end{aligned} \tag{6}$$

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.

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

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

$$\begin{aligned} \mathrm{d}U &= T\mathrm{d}S - P\mathrm{d}V \\ \implies \left(\frac{\partial U}{\partial T}\right)_{P,N} &= T\left(\frac{\partial S}{\partial T}\right)_{P,N} - P\left(\frac{\partial V}{\partial T}\right)_{P,N} \\ &= Nc_P - PV\alpha, \end{aligned} \tag{8}$$

where we used equations (4) and (2) 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

$$\begin{aligned} \left(\frac{\partial U}{\partial P}\right)_{T,N} &= \frac{\partial(U,T,N)}{\partial(P,T,N)} = \frac{\partial(U,T,N)}{\partial(V,T,N)} \cdot \frac{\partial(V,T,N)}{\partial(P,T,N)} = \left(\frac{\partial U}{\partial V}\right)_{T,N}\left(\frac{\partial V}{\partial P}\right)_{T,N} \\ &= \left(\frac{\partial U}{\partial V}\right)_{T,N}(-V\kappa_T). \end{aligned} \tag{9}$$

Equation (3) 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

$$\left(\frac{\partial U}{\partial V}\right)_{T,N} = T\left(\frac{\partial S}{\partial V}\right)_{T,N} - P. \tag{10}$$

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

$$\begin{aligned} \left(\frac{\partial P}{\partial T}\right)_{V,N} &= \frac{\partial(P,V,N)}{\partial(T,V,N)} = \frac{\partial(P,V,N)}{\partial(P,T,N)} \cdot \frac{\partial(P,T,N)}{\partial(T,V,N)} = -\frac{\partial(V,P,N)}{\partial(T,P,N)} \cdot \frac{\partial(P,T,N)}{\partial(V,T,N)} \\ &= -\left(\frac{\partial V}{\partial T}\right)_{P,N} \Big/ \left(\frac{\partial V}{\partial P}\right)_{T,N} = -V\alpha/(-V\kappa_T) = \frac{\alpha}{\kappa_T}, \end{aligned} \tag{11}$$

where in the last step equations (2) and (3) were used to rewrite the nominator and denominator, repsectively.

Equation (9) can now be solved, by inserting equation (11) into equation (10)

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

Inserting equation (9) and (8) into equation (7) we get

$$\frac{\partial(U,G,N)}{\partial(P,T,N)} = -S\left(-VT\alpha + PV\kappa_T\right) - V\left(Nc_P - PV\alpha\right) = -V\left[SP\kappa_T + Nc_P - ST\alpha - PV\alpha\right] \tag{12}$$

Finally, inserting equation (12) into equation (6) we arrive at the final expression

$$\left(\frac{\partial P}{\partial U}\right)_{G,N} = -S\left[\frac{\partial(U,G,N)}{\partial(P,T,N)}\right]^{-1} = \frac{S/V}{SP\kappa_T + Nc_P - ST\alpha - PV\alpha} \tag{13}$$

TASK 3

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