Statistical Mechanics - Homework 1

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PROBLEM 1

Part (a)

We know that $dQ = N_0 C_V \, dT$ and that thermal equilibrium will occur when $T_1 = T_2 = 2T_0$. The entropy change of the first volume is

$$\Delta S_1 = \int_{T_0}^{2T_0} dT \, \frac{5N_0^2}{2T} = \frac{5N_0^2}{2} \ln 2$$

The entropy change of the second volume is

$$\Delta S_2 = \int_{3T_0}^{2T_0} dT \, \frac{5N_0^2}{2T} = -\frac{5N_0^2}{2} \ln \frac{3}{2}$$

The total entropy change is

$$\Delta S = \Delta S_1 + \Delta S_2 = \frac{5N_0^2}{2} \left[\ln 2 - \ln \frac{3}{2} \right] = \frac{5N_0^2}{2} \ln \frac{4}{3}$$

Part (b)

PROBLEM 2

Part (a)

We will use the following Jacobian properties:

$$\frac{\partial(u, y)}{\partial(x, y)} = \left(\frac{\partial u}{\partial x} \right)_y \qquad \frac{\partial(u, v)}{\partial(x, y)} = -\frac{\partial(v, u)}{\partial(x, y)}$$

We can rewrite the given expression as

$$\frac{\partial(P, S)}{\partial(T, S)} \frac{\partial(V, T)}{\partial(S, T)} - \frac{\partial(P, T)}{\partial(S, T)} \frac{\partial(V, S)}{\partial(T, S)} = \frac{\partial(S, P)}{\partial(T, S)} \frac{\partial(T, V)}{\partial(S, T)} - \frac{\partial(T, P)}{\partial(S, T)} \frac{\partial(S, V)}{\partial(T, S)}$$

$$= \left(\frac{\partial S}{\partial T} \frac{\partial P}{\partial S} - \frac{\partial S}{\partial S} \frac{\partial P}{\partial T} \right) \left(\frac{\partial T}{\partial S} \frac{\partial V}{\partial T} - \frac{\partial T}{\partial T} \frac{\partial V}{\partial S} \right) - \left(\frac{\partial T}{\partial S} \frac{\partial P}{\partial T} - \frac{\partial T}{\partial T} \frac{\partial P}{\partial S} \right) \left(\frac{\partial S}{\partial T} \frac{\partial V}{\partial S} - \frac{\partial S}{\partial S} \frac{\partial V}{\partial T} \right)$$

$$= \left(\frac{\partial P}{\partial T} - \frac{\partial P}{\partial T} \right) \left(\frac{\partial V}{\partial S} - \frac{\partial V}{\partial S} \right) - \left(\frac{\partial P}{\partial S} - \frac{\partial P}{\partial S} \right) \left(\frac{\partial V}{\partial T} - \frac{\partial V}{\partial T} \right) = 0$$

Part (b)

Using the differential dH, we find

$$dH = TdS + VdP \implies \left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

Using G, this becomes

$$\left(\frac{\partial H}{\partial P}\right)_T = T\frac{\partial^2 G}{\partial T \partial P} + V = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

Part (c)

Using the definition of C_P as the derivative of enthalpy,

$$\left(\frac{\partial C_P}{\partial P}\right)_T = \frac{\partial}{\partial P}\left[\left(\frac{\partial H}{\partial P}\right)_T\right]_P = \frac{\partial}{\partial T}\left[T\left(\frac{\partial S}{\partial P}\right)_T + V\right]_P = \frac{\partial}{\partial T}\left[-T\left(\frac{\partial V}{\partial T}\right)_P + V\right]_P$$

$$= -\left(\frac{\partial V}{\partial T}\right)_P - T\left(\frac{\partial^2 V}{\partial T^2}\right)_P + \left(\frac{\partial V}{\partial T}\right)_P = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

The exact dependence on P is now determined by the equation of state. For an ideal gas, we have $V = \frac{NT}{P}$, so $\left(\frac{\partial C_P}{\partial P}\right)_T = 0$. For a Van der Waals gas, we have to solve

$$\frac{P}{N}V^3 - (Pb + T)V^2 + aNV - abN^2 = 0$$

This has one real solution (which I found by computer). $\left(\frac{\partial C_P}{\partial P}\right)_T$ is plotted below, for the case of $a = b = 1$, $N = 10000$ and $T = 300$:
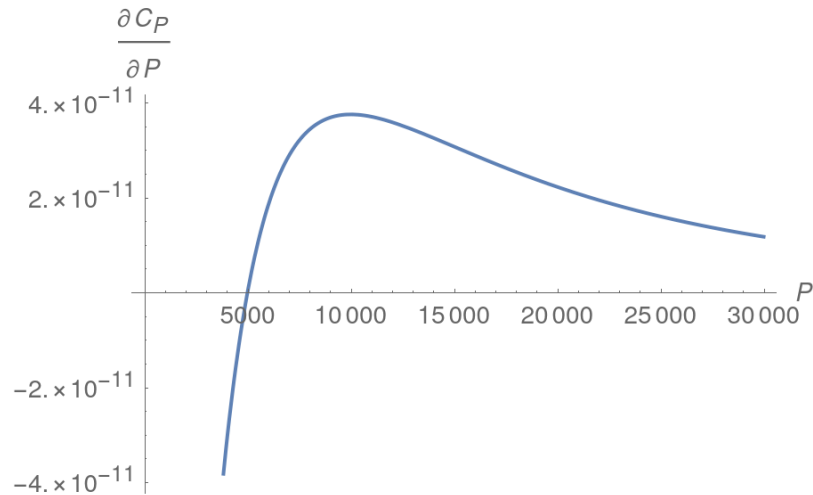
Part (d)

We have previously found that

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad \left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

Since we take E to be independent of volume and H independent of pressure, these become

$$T\left(\frac{\partial P}{\partial T}\right)_V = P \qquad T\left(\frac{\partial V}{\partial T}\right)_P = V$$

Solving for T and equating the two gives

$$V\left(\frac{\partial P}{\partial T}\right)_V = P\left(\frac{\partial V}{\partial T}\right)_P$$

Integrating both sides gives

$$VP + VC_1(V) = PV + PC_2(P)$$

so the equation of state is

$$\frac{V}{P} = const$$

PROBLEM 3

Using the fact that

$$\Delta W = -\int_{V_1}^{V_2} dV\, P$$

we find the equation of state:

$$-\int_{V_1}^{V_2} dV\, P = cT \ln \frac{V_2}{V_1} \implies P = -\frac{cT}{V}$$

To find E, we use $dE = dQ - pdV$:

$$\left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V + \frac{cT}{V}\left(\frac{\partial V}{\partial T}\right)_V \implies \int dT\left(\frac{\partial E}{\partial T}\right)_V = \int dT\, C_V$$

So we find

$$E = \frac{a}{b}e^{bT}\left(T - \frac{1}{b}\right) + c_1(V)$$

To find F, we use $dF = -SdT - PdV$. Since the expansion is isothermal, $dT = 0$ and we find

$$dF = \frac{cT}{V} \implies F = cT \ln V + c_2$$

To find H, we use $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$ to find

$$dH = TdS + VdP \implies \left(\frac{\partial H}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial T}\right)_V = aTe^{bT} - c$$

Integrating gives

$$H = \frac{a}{b}e^{bT}\left(T - \frac{1}{b}\right) - cT + c_3(V)$$

As a check on our result for E, this satisfies $H = E + PV = E - cT$. Finally, G is given by

$$G = F + PV = cT\ln V - cT + c_4$$

PROBLEM 4

Part (a)

From the differential expression for the internal energy, we can find $\left(\frac{\partial E}{\partial V}\right)_T$:

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV \implies \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\frac{\partial V}{\partial V}$$

To express this in terms of just P, V, T, we can use F:

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial^2 F}{\partial T \partial V} = \left(\frac{\partial P}{\partial T}\right)_V$$

Substituting gives

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Now we can solve the Van der Waals equation for P:

$$P = \frac{NT}{V - bN} - \frac{aN^2}{V^2}$$

so we find

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{aN^2}{V^2}$$

Part (b)

If E is constant, then we can use $0 = TdS - PdV$ to get

$$0 = T\left(\left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV\right) - PdV$$

By the definition of C_V and a Maxwell relation, this becomes

$$0 = C_V \, dT + T \left[\left(\frac{\partial P}{\partial T} \right)_V - P \right] dV$$

Using the Van der Waals equation, we finally obtain

$$\left(\frac{\partial T}{\partial V} \right)_E = -\frac{aN^2}{C_V V^2}$$

Integrating both sides gives

$$T(V_2) - T(V_1) = -\int_{V_1}^{V_2} dV \, \frac{aN^2}{C_V V^2} = \frac{aN^2}{C_V} \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

Since $V_2 > V_1$, the right had side is negative, so $T(V_2) < T(V_1)$.