PH127a Problem Set 1

Patryk Kozlowski

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1 Problem 1: Minimal experimental data to recover all thermodynamics

1.1 A

To begin, let's express dU and dS in terms of dT and dV. Given the relationship:

$$TdS = dU + pdV \tag{1}$$

We can write dU as:

$$dU = TdS - pdV \tag{2}$$

Now, let's represent dU in terms of dT and dV as follows:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{3}$$

Equating the two expressions for dU, we get:

$$TdS - pdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{4}$$

Rearranging and expressing dS in terms of dT and dV, we find:

$$dS = \left(\frac{\partial U}{\partial T}\right)_V \frac{1}{T} dT + \left(\frac{\partial U}{\partial V}\right)_T \frac{1}{T} dV + p\frac{1}{T} dV \tag{5}$$

$$dS = \left(\frac{\partial U}{\partial T}\right)_V \frac{1}{T} dT + \left(\left(\frac{\partial U}{\partial V}\right)_T + p\right) \frac{1}{T} dV \tag{6}$$

Now, we can write the partial derivatives of S with respect to T and V when the opposite perimeter is fixed:

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \frac{1}{T} \tag{7}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\left(\frac{\partial U}{\partial V}\right)_T + p\right) \frac{1}{T} \tag{8}$$

Now we consider the mixed derivatives. Since the order of the ventilation does not matter, they are equal:

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)\right)=\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)\right) \tag{9}$$

First, we consider the left and side:

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)\right)=\frac{1}{T}\left(\frac{\partial}{\partial V}\left(\left(\frac{\partial U}{\partial T}\right)\right)\right) \tag{10}$$

Next, we consider the right hand side:

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V=\left(\frac{\partial}{\partial T}\left(\frac{1}{T}\left(\left(\frac{\partial U}{\partial V}\right)_T+p\right)\right)\right)_V \tag{11}$$

Differentiating with respect to T, we get:

$$\left(\frac{\partial^2 S}{\partial V\partial T}\right)=\frac{1}{T}\left(\frac{\partial^2 U}{\partial V\partial T}\right)-\frac{1}{T^2}\left(\left(\frac{\partial U}{\partial V}\right)_T+p\right)+\frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_V \tag{12}$$

Using the fact that the mixed derivatives are equal to each other:

$$\frac{1}{T}\left(\frac{\partial^2 U}{V\partial T}\right)=\frac{1}{T}\left(\frac{\partial^2 U}{\partial V\partial T}\right)-\frac{1}{T^2}\left(\left(\frac{\partial U}{\partial V}\right)_T+p\right)+\frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_V \tag{13}$$

We simplify and by multiplying through by T^2 to get the identity that we want, which is:

$$\left(\frac{\partial U}{\partial V}\right)_T=T\left(\frac{\partial p}{\partial T}\right)_V-p \tag{14}$$

So:

$$dU=C_V+\left(T\left(\frac{\partial p}{\partial T}\right)_V-p\right)dV \tag{15}$$

Integrating, we get that:

$$U(T_2,V_2)-U(T_1,V_1)=\int_{V_1}^{V_2}\left(C_V+\left(T\left(\frac{\partial p}{\partial T}\right)_V-p\right)dV\right) \tag{16}$$

Similarly, for the entropy:

$$TdS=C_V+\left(T\left(\frac{\partial p}{\partial T}\right)_V-p\right)dV+pdV \tag{17}$$

Isolating the derivative of entropy and simplifying, we get:

$$dS=\frac{C_V}{T}+\left(\left(\frac{\partial p}{\partial T}\right)_V\right)dV \tag{18}$$

Now, integrating:

$$S(T_2,V_2)-S(T_1,V_1)=\int_{V_1}^{V_2}\left(\frac{C_V}{T}+\left(\left(\frac{\partial p}{\partial T}\right)_V\right)dV\right) \tag{19}$$

1.2 B

We want to take the temperature derivative of

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{20}$$

We can write this as:

$$\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T = \frac{\partial}{\partial T}\left(T\left(\frac{\partial p}{\partial T}\right)_V - p\right) = \left(\frac{\partial p}{\partial T}\right)_V + T\left(\frac{\partial^2 p}{\partial T^2}\right)_V - \left(\frac{\partial p}{\partial T}\right)_V \tag{21}$$

So, we get:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V \tag{22}$$

Similarly, we can express this as in integral:

$$C_V(V,T) - C_V(V_0,T) = \int_{V_0}^{V}\left(T\left(\frac{\partial^2 p}{\partial T^2}\right)_V\right)dV \tag{23}$$

1.3 C

We will begin by calculating the specific heat according to:

$$C_V(V,T) = C_V(V_0,T) + \int_{V_0}^{V}\left(T\left(\frac{\partial^2 p}{\partial T^2}\right)_V\right)dV \tag{24}$$

We are using the equation of state for the van der Waals gas and reference specific heat for the ideal gas:

$$C_V(V,T) = \frac{3}{2}Nk_B + \int_{V_0}^{V}\left(T\left(\frac{\partial^2 p}{\partial T^2}\right)_V\right)dV \tag{25}$$

Solving for the pressure in the vander wall equation of state:

$$p = \frac{Nk_BT}{V - Nb} - \frac{aN^2}{V^2} \tag{26}$$

We want to find the second derivative of the pressure with respect to temperature at a fixed volume. First, we start by taking one reverie:

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{Nk_B}{V - Nb} \tag{27}$$

Next, we take the derivative again:

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_V = -\frac{Nk_B}{(V - Nb)^2} \tag{28}$$

Now the second derivative of pressure with respect to temperature is:

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_V = \frac{Nk_B}{V - Nb}\left(\frac{a}{k_BT}\right)^2 \tag{29}$$

2 Problem 2: Thermodynamics of a model classical paramagnet

First we want to compute the partition function of our system. Defining $\beta = \frac{1}{k_B T}$, we can write the partition function as:

$$Z = \int e^{-\beta E} d\Omega \tag{30}$$

where we have to find the deferential solid angle $d\Omega = sin\theta d\theta d\phi$. Given that we have the following expression for the energy:

$$E = E[\{\vec{m}_i\}] = -\sum_{i=1}^{N} \vec{m}_i \cdot \vec{B} \tag{31}$$

Gevent that $\mathbf{m} = \mu(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$ and $\mathbf{B} = (0, 0, B)$ We can write the energy as:

$$E = -\mu B \sum_{i=1}^{N} \cos\theta_i \tag{32}$$

So in spherical coordinates the partition some integral becomes:

$$Z = \int_0^{2\pi} \int_0^{\pi} e^{\beta\mu B \sum_{i=1}^{N} \cos\theta_i} \sin\theta_i d\theta_i d\phi_i = 2\pi \int_0^{\pi} e^{\beta\mu B \sum_{i=1}^{N} \cos\theta_i} \sin\theta_i d\theta_i \tag{33}$$

We can bring the summation down from the exponent and convert it into a product:

$$Z = 2\pi \int_0^{\pi} \prod_{i=1}^{N} e^{\beta\mu B \cos\theta_i} \sin\theta_i d\theta_i = 2\pi \prod_{i=1}^{N} \int_0^{\pi} e^{\beta\mu B \cos\theta_i} \sin\theta_i d\theta_i = 2\pi \left(\int_0^{\pi} e^{\beta\mu B \cos\theta} \sin\theta d\theta \right)^N \tag{34}$$

Recognizing this integral as a vessel function with $x = \beta\mu B$:

$$I(x) = \int_0^{\pi} e^{x\cos\theta} \sin\theta d\theta \tag{35}$$