

33-765 Homework 8

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29. Joule-Thomson Coefficient for the van der Waals Gas

Let's combine two subjects of inquiry: We know from class what the Joule-Thomson effect is, and we know that it is boring for the ideal gas. But now we have an equation of state for a more realistic gas! What does this say about the Joule-Thomson coefficient? We start by writing the van der Waals equation in rescaled variables:

$$V_c = 3Nb \quad k_B T_c = \frac{8a}{27b} \quad P_c = \frac{a}{27b^2}$$

and hence define

$$\tilde{T} = \frac{T}{T_c} \quad \tilde{P} = \frac{P}{P_c} \quad \tilde{V} = \frac{V}{V_c}$$

1. Show that in the reduced variables \tilde{T} , \tilde{V} , and \tilde{N} , the thermal equation of state reads $(\tilde{P} + 3\tilde{V}^{-2})(3\tilde{V} - 1) = 8\tilde{T}$.

The thermal equation of state for a van der Waals gas is

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

We can write our scaled variables in terms of the regular ones

$$\tilde{T} = \frac{27bk_B T}{8a} \quad \tilde{P} = \frac{27b^2 P}{a} \quad \tilde{V} = \frac{V}{3bN}$$

and substitute those into our equation of state:

$$\begin{aligned} \frac{a}{27b^2} \tilde{P} &= \frac{N\tilde{T} \left(\frac{8a}{27b} \right)}{bN(3\tilde{V} - 1)} - \frac{aN^2}{9b^2\tilde{V}^2 N^2} \\ &= \frac{8a\tilde{T}}{27b^2(3\tilde{V} - 1)} - \frac{a}{9b^2\tilde{V}^2} \\ \tilde{P} &= \frac{8\tilde{T}}{(3\tilde{V} - 1)} - \frac{3}{\tilde{V}^2} \\ \frac{8\tilde{T}}{(3\tilde{V} - 1)} &= (\tilde{P} + 3\tilde{V}^{-2}) \\ 8\tilde{T} &= (\tilde{P} + 3\tilde{V}^{-2})(3\tilde{V} - 1) \end{aligned}$$

2. Find the relationship between \tilde{P} and \tilde{V} (with \tilde{T} eliminated!) that holds when the Joule-Thomson coefficient $\mu_{JT} = 0$. Note, it turns out that for pressures below this so-called “inversion curve” $\tilde{P}_{\text{inv}}(\tilde{V})$, we have $\mu_{JT} > 0$.

The Joule-Thomson coefficient equation states that

$$\mu_{JT} = -\frac{\tilde{V}}{Nc_P}(\tilde{T}\alpha - 1) = 0 \implies \tilde{T} = \frac{1}{\alpha} = \tilde{V} \left. \frac{\partial \tilde{T}}{\partial \tilde{V}} \right|_{P,N}$$

We can take this derivative from the equation of state:

$$\tilde{T} = \tilde{V} \left(\frac{3(2 - 3\tilde{V} + \tilde{P}\tilde{V}^3)}{\tilde{V}^3} \right)$$

Substituting this back into the original equation and solving for \tilde{P} , we find that

$$\tilde{P}_{\text{inv}}(\tilde{V}) = \frac{9}{\tilde{V}^2}(2\tilde{V} - 1)$$

3. Using the scaled thermal equations of state, show that the volume on the inversion curve satisfies $\tilde{V}^{-1} = 3 - \sqrt{4\tilde{T}/3}$.

To do this, we just substitute the new equation we found into the original:

$$\begin{aligned} \left(\frac{9}{\tilde{V}^2}(2\tilde{V} - 1) + \frac{3}{\tilde{V}^2} \right) (3\tilde{V} - 1) &= 8\tilde{T} \\ \frac{6(1 - 3\tilde{V})^2}{\tilde{V}^2} &= 8\tilde{T} \\ \frac{(1 - 3\tilde{V})^2}{\tilde{V}^2} &= \frac{4}{3}\tilde{T} \\ \frac{1 - 3\tilde{V}}{\tilde{V}} &= -\sqrt{\frac{4}{3}\tilde{T}} \\ \frac{1}{\tilde{V}} - 3 &= -\sqrt{\frac{4}{3}\tilde{T}} \\ \frac{1}{\tilde{V}} &= 3 - \sqrt{4\tilde{T}/3} \end{aligned}$$

Here I chose the negative root because it gave me the answer I wanted, clever right?

4. Inserting this into \tilde{P}_{inv} , you get the inversion curve in the $\tilde{T} - \tilde{P}$ diagram. Plot it! The part under the curve is the region that has a positive Joule-Thomson coefficient and will thus cool when subjected to the Joule-Thomson process.

$$\begin{aligned} \tilde{P}(\tilde{T}) &= \frac{9}{\left(3 - \sqrt{4\tilde{T}/3}\right)^2} \left(\frac{2}{3 - \sqrt{4\tilde{T}/3}} - 1 \right) \\ &= \left(\frac{6}{\sqrt{12\tilde{T}} - 9} - 1 \right) (\sqrt{12\tilde{T}} - 9)^2 \\ &= 24\sqrt{3\tilde{T}} - 12\tilde{T} - 27 \end{aligned}$$

See Figure 0.1 for the plot (I couldn't figure out how to put tildes in in Mathematica, sorry, just pretend they're there).

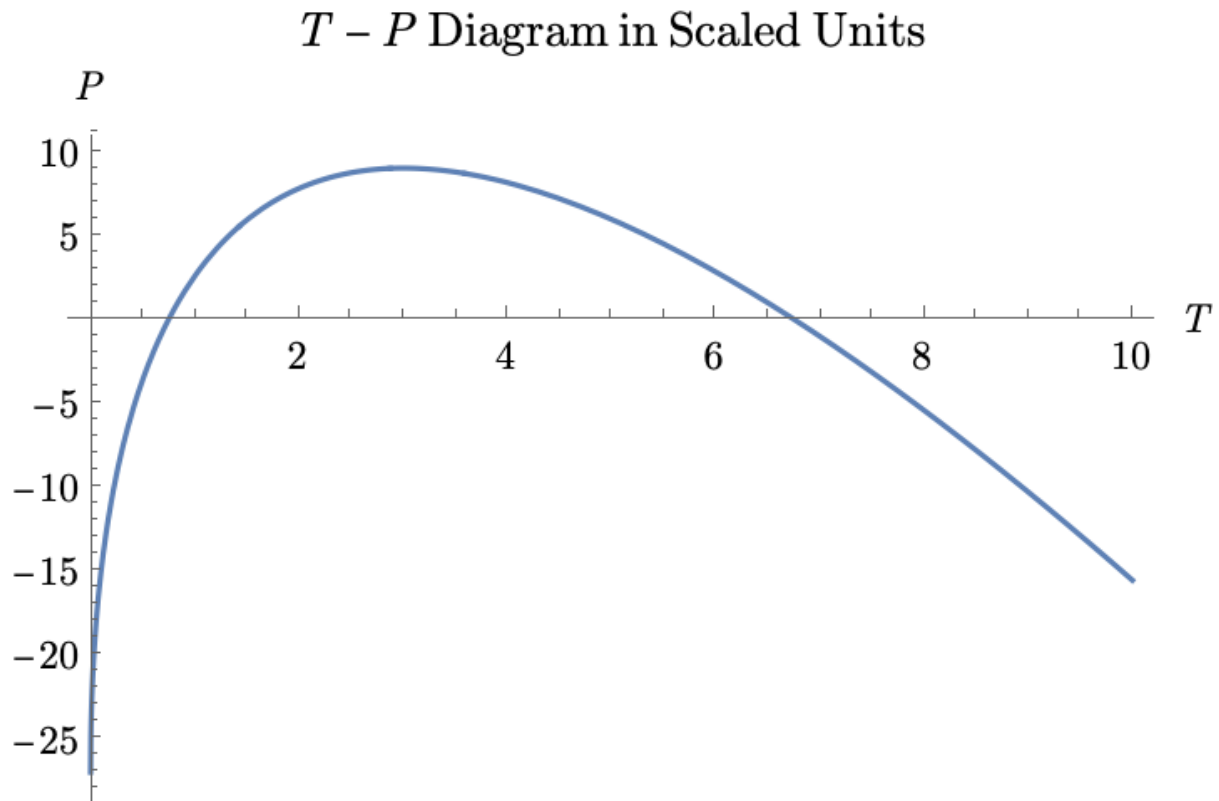


Figure 0.1: Plot for Problem 29.4

5. For hydrogen (H_2) we have $T_c = -240^\circ C$ and $P_c = 12.7 \text{ atm}$, while for carbon dioxide (CO_2) we have $T_c = 31.2^\circ C$ and $P_c = 72.8 \text{ atm}$. Do these gases heat up or cool down under a throttled expansion at room temperature and pressure?

Room temperature and pressure are about $22^\circ C$ and 1 atm . I'll convert everything to Kelvin so that we don't run into problems with negative temperature. This means room temperature is 295 K and the critical temperatures for hydrogen and carbon dioxide are 33 K and 304.2 K respectively. This gives us

$$\tilde{P} = \frac{P}{P_c} = \frac{1}{12.7} = 0.078 \quad \tilde{T} = \frac{295}{33} = 8.94$$

for Hydrogen and

$$\tilde{P} = \frac{1}{72.8} = 0.0137 \quad \tilde{T} = \frac{295}{304.2} = 0.97$$

for carbon dioxide.

Examining the plot from the previous question, we can see that the point for Hydrogen gas falls above the curve while the point for carbon dioxide falls below it, so carbon dioxide will cool under the Joule-Thomson process while Hydrogen gas will not.

30. Ice Skating

First, a few facts: (1) Icebergs contain freshwater, and only about 10% of an iceberg is visible above the ocean's surface. (2) The density of sea water is about 1.025 g/cm^3 . (3) It takes about 334 kJ to melt one kilogram of ice (from just below freezing to just above freezing). Now here comes the problem you will be able to solve using these data:

1. What is the slope of the melting curve in the T-P diagram of water at atmospheric pressure?

First, we know from the Clausius-Clapeyron equation that

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

L is the latent heat of the transition, given in the problem as 334kJ. T is the temperature at which ice freezes/melts, which is $\sim 273\text{K}$. Finally, we can use the first and second facts to determine the density of ice to be $0.9 \times 1025\text{kg/m}^3 = 922.5\text{kg/m}^3$. The density of water is defined as 1000kg/m^3 , and we want to find the change in volume per particle, since that's what L is written in terms of. Therefore, we don't care about the mass: $\Delta V = \frac{1}{922.5\text{m}^3} - \frac{1}{1000\text{m}^3} = -8.4 \times 10^{-5}\text{m}^3$. Plugging this all in, we find that

$$\frac{dP}{dT} = \frac{334000\text{J/kg}}{273\text{K}(-8.4 \times 10^{-5}\text{m}^3)} = -1.45 \times 10^7\text{Pa/K}$$

2. Most ice rinks operate at about -7°C . How heavy would a person have to be so that the pressure exerted on the ice through the blades of that person's skates will pressure-melt the ice? (Estimate the area of an ice skate's blade.)

If we take our result from the previous section, we can recognize the units to be $\text{Pa/K} = \left(\frac{\text{N}}{\text{m}^2}\right) \text{K}$, so we need to multiply our result by $\Delta T = -7\text{K}$ to get force and area:

$$-1.45 \times 10^7\text{Pa/K} * -7\text{K} = 1.015 \times 10^8\text{N/m}^2$$

I'll make a guess that the average pair of ice skates have an area of 0.0004m^2 , so it will take

$$1.015 \times 10^8\text{N/m}^2 * 0.0004\text{m}^2 = 4.06 \times 10^4\text{N}$$

to melt it. Approximating $g = 10\text{m/s}^2$, we find that the required mass is

$$4060\text{kg} = 8950.768\text{lbs}$$

I doubt this is true, since the melting is what makes the ice skate move easily across the surface, but I don't know where I went wrong here. The average person should be able to melt the ice.

31. Equipartition Theorem

Consider a Hamiltonian $H(\{p, q\})$ on phase space. Let x_i be any of the $6N$ coordinates, for instance, it could be $p_{27,y}$ or $q_{1673536,x}$. Let $\langle \cdot \rangle$ denote the canonical average (i.e., the average over the canonical state $P_{\text{can}}(\{p, q\})$).

1. Prove that the following is true: $\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = k_B T \delta_{ij}$. (Hint: Parameter differentiation and integration by parts)

$$\begin{aligned} \left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle &= \int d\Gamma x_i \frac{\partial H}{\partial x_j} P_{\text{can}}(\Gamma) \\ &= \int x_i d \left(-\frac{1}{\beta} P_{\text{can}}(\Gamma) \right) \\ &= x_i \left(-\frac{1}{\beta} P_{\text{can}}(\Gamma) \right) \Big|_{\partial\Gamma} + \int d\Gamma \frac{1}{\beta} P_{\text{can}}(\Gamma) \frac{\partial x_i}{\partial x_j} \end{aligned}$$

Since the variables don't depend on each other, $\frac{\partial x_i}{\partial x_j}$ will give us a δ -function. The first term is zero because the probability distribution must vanish at the boundary.

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{1}{\beta} \int P_{\text{can}}(\Gamma) \delta_{ij} d\Gamma = k_B T \delta_{ij}$$

since $\int P_{\text{can}}(\Gamma) d\Gamma = 1$ by normalization.

2. If the Hamiltonian contains a term Ax^n and this is the only occurrence of x , prove that $\langle Ax^n \rangle = \frac{1}{n} k_B T$.

We can rewrite

$$\langle Ax^n \rangle = \left\langle \left(\frac{1}{n} x \right) (Anx^{n-1}) \right\rangle = \frac{1}{n} \langle x Anx^{n-1} \rangle$$

Noticing that $\frac{\partial H}{\partial x} = Anx^{n-1}$, we use part 1 to write:

$$\langle Ax^n \rangle = \frac{1}{n} \left\langle x \frac{\partial H}{\partial x} \right\rangle = \frac{k_B T}{n}$$

3. For the “standard” kinetic energy and p_i , one of the (scalar) momentum coordinates, prove that $\left\langle \frac{p_i^2}{2m} \right\rangle = \frac{1}{2} k_B T$.

The “standard” kinetic energy term makes the Hamiltonian have the form $H = \frac{p^2}{2m} + \Phi(\{q\})$, so this problem has the same form as the previous problem with $n = 2$.

32. Hypervirial and Temperature

Let $\Gamma = \{\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{q}_1, \dots, \mathbf{q}_N\}$ denote a point in $6N$ -dimensional phase space, and let $\mathbf{B}(\Gamma)$ be a vector field in phase space. Let us furthermore denote the gradient operator in phase space by $\vec{\nabla}_\Gamma = \left(\frac{\partial}{\partial p_{1x}}, \frac{\partial}{\partial p_{1y}}, \frac{\partial}{\partial p_{1z}}, \frac{\partial}{\partial p_{2x}}, \dots, \frac{\partial}{\partial q_{Nz}} \right)$.

1. Use Gauss' theorem to argue that $\int d\Gamma \vec{\nabla}_\Gamma \cdot \{\mathbf{B}(\Gamma) e^{-\beta H(\Gamma)}\} = 0$.

I don't understand how this follows. Converting to the surface integral we get a unit vector pointing outward from the surface, but I don't really know what to do with that.

2. Prove the amazing fact that every choice of \mathbf{B} leads to an expression for the temperature: $k_B T = \langle \mathbf{B} \cdot \vec{\nabla}_\Gamma H \rangle / \langle \vec{\nabla}_\Gamma \cdot \mathbf{B} \rangle$.

$$\begin{aligned} \langle \mathbf{B}(\Gamma) \cdot \vec{\nabla}_\Gamma H \rangle &= \int d\Gamma \mathbf{B}(\Gamma) \cdot \left(\vec{\nabla}_\Gamma P_{\text{can}}(\Gamma) \right) \\ &= \int d\Gamma \mathbf{B}(\Gamma) \cdot \vec{\nabla}_\Gamma \left(-\frac{1}{\beta} P_{\text{can}}(\Gamma) \right) \\ &= \mathbf{B}(\Gamma) \cdot \vec{\nabla}_\Gamma (H(\Gamma) P_{\text{can}}(\Gamma)) \Big|_{\partial\Gamma} + \int \frac{1}{\beta} \vec{\nabla}_\Gamma \cdot \mathbf{B}(\Gamma) P_{\text{can}}(\Gamma) d\Gamma \\ &\quad + \int \frac{1}{\beta} \vec{\nabla}_\Gamma \cdot (\mathbf{B}(\Gamma) P_{\text{can}}(\Gamma)) d\Gamma \end{aligned}$$

The first term is zero because the probability density vanishes on the boundary. The second term is zero because of what we know from question 32.1. Finally

$$\begin{aligned}\langle \mathbf{B}(\Gamma) \cdot \vec{\nabla}_{\Gamma} H \rangle &= \frac{1}{\beta} \int \vec{\nabla}_{\Gamma} \cdot \mathbf{B}(\Gamma) P_{\text{can}}(\Gamma) d\Gamma \\ &= \frac{1}{\beta} \langle \vec{\nabla}_{\Gamma} \mathbf{B}(\Gamma) \rangle \\ \Rightarrow k_B T &= \langle \mathbf{B} \cdot \vec{\nabla}_{\Gamma} H \rangle / \langle \vec{\nabla}_{\Gamma} \cdot \mathbf{B} \rangle\end{aligned}$$

3. For a standard Hamiltonian, $H = K + \Phi = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \Phi(\mathbf{q}_1, \dots, \mathbf{q}_N)$, calculate $\vec{\nabla}_{\Gamma} K$, $\vec{\nabla}_{\Gamma} \Phi$, and $\vec{\nabla}_{\Gamma} H$.

$$\begin{aligned}\vec{\nabla}_{\Gamma} K &= \left\{ \frac{\partial}{\partial p_{1x}} \left[\left(\frac{(\sqrt{p_{1x}^2 + p_{1y}^2 + p_{1z}^2})^2}{2m} + \dots \right), \dots, \underbrace{\frac{\partial}{\partial q_{1x}} K}_{0}, \dots \right] \right\} = \frac{1}{m} \{p_{1x}, \dots, 0, \dots\} \\ \vec{\nabla}_{\Gamma} \Phi &= \left\{ \underbrace{\frac{\partial}{\partial p_{1x}} \Phi}_0, \dots, \frac{\partial}{\partial q_{1x}} \Phi, \dots \right\} \\ \vec{\nabla}_{\Gamma} H &= \vec{\nabla}_{\Gamma} (K + \Phi) = \vec{\nabla}_{\Gamma} K + \vec{\nabla}_{\Gamma} \Phi = \left\{ \frac{p_{1x}}{m}, \dots, \frac{\partial}{\partial q_{1x}} \Phi, \dots \right\}\end{aligned}$$

4. Choosing $\mathbf{B}(\Gamma) = \vec{\nabla}_{\Gamma} K$, calculate the temperature implied by the new equation. This is called the “kinetic temperature”.

$$\begin{aligned}k_B T &= \frac{\left\langle \frac{1}{m^2} \sum_{p_{ni}} p_{ni}^2 \right\rangle}{\left\langle \sum_{p_{ni}} \frac{\partial}{\partial p_{ni}} \frac{p_{ni}}{m} \right\rangle} \\ &= \frac{\left\langle \frac{1}{m^2} \sum_{p_{ni}} p_{ni}^2 \right\rangle}{\left\langle \sum_{p_{ni}} \frac{1}{m} \right\rangle} \\ &= \frac{\left\langle \frac{2}{m} \sum_{p_{ni}} \frac{p_{ni}^2}{2m} \right\rangle}{\frac{3N}{m}} \\ &= \frac{\frac{2}{m} \langle K \rangle}{\frac{3N}{m}} \\ &= \frac{2}{3N} \langle K \rangle \\ T &= \frac{2 \langle K \rangle}{3N k_B}\end{aligned}$$

5. Repeat, but for the choice $\mathbf{B}(\Gamma) = \vec{\nabla}_{\Gamma} \Phi$. This is called the “configurational temperature”.

$$k_B T = \frac{\left\langle \sum_{q_{ni}} (\partial_{q_{ni}} \Phi)^2 \right\rangle}{\left\langle \sum_{q_{ni}} \partial_{q_{ni}}^2 \Phi \right\rangle}$$

I'm not sure how to simplify this at all.