33-765 — Statistical Physics

Department of Physics, Carnegie Mellon University, Spring Term 2020, Deserno

Problem sheet #8

29. Joule-Thomson coefficient for the van der Waals gas *(6 points)*

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 ("reduced", "critically scaled") variables:

$$V_{\rm c} = 3Nb \quad , \quad k_{\rm B}T_{\rm c} = \frac{8a}{27b} \quad , \quad P_{\rm c} = \frac{a}{27b^2} \qquad \text{and hence define} \qquad \tilde{T} = \frac{T}{T_{\rm c}} \quad , \quad \tilde{P} = \frac{P}{P_{\rm c}} \quad , \quad \tilde{V} = \frac{V}{V_{\rm c}} \, . \tag{1}$$

1. Show that in the reduced variables $\tilde{T}$, $\tilde{V}$ and $\tilde{N}$ the thermal equation of state reads $(\tilde{P} + 3\,\tilde{V}^{-2})(3\,\tilde{V} - 1) = 8\,\tilde{T}$.
2. Find the relationship between $\tilde{P}$ and $\tilde{V}$ (with $\tilde{T}$ eliminated!) that holds when the Joule-Thomson coefficient $\mu_{\rm JT} = 0$. *(Note: It turns out that for pressures below this so-called "inversion curve" $\tilde{P}_{\rm inv}(\tilde{V})$, we have $\mu_{JT} > 0$.)*
3. Using the scaled thermal equation of state, show that the volume on the inversion curve satisfies $\tilde{V}^{-1} = 3 - \sqrt{4\tilde{T}/3}$.
4. Inserting this into $\tilde{P}_{\rm inv}(\tilde{V})$, 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.)
5. For hydrogen (H_2) we have $T_{\rm c} = -240\,^\circ$C and $P_{\rm c} = 12.7\,$atm, while for carbon dioxide (CO_2) we have $T_{\rm c} = 31.2\,^\circ$C and $P_{\rm c} = 72.8\,$atm. Do these gases heat up or cool down under a throttled expansion at room temperature and pressure?

30. Ice skating *(4 points)*

First a few facts: (1) Icebergs consist of freshwater, and only about 10% of an iceberg is visible above the ocean's surface. (2) The density of sea water is about $1.025\,{\rm g/cm^3}$. (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?
2. Most ice rinks operate at about $-7\,^\circ$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.)

31. Equipartition theorem *(4 points)*

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 $P_{\rm can}(\{p, q\})$).

1. Prove that the following is true: $\big\langle x_i \frac{\partial H}{\partial x_j} \big\rangle = k_{\rm B}T\;\delta_{ij}$. *(Hint: Parameter differentiation. Integration by parts.)*
2. If the Hamiltonian contains a term Ax^n, and this is the only occurrence of x, prove that $\langle Ax^n \rangle = \frac{1}{n}\,k_{\rm B}T$.
3. For the "standard" kinetic energy, and p_i one of the (scalar) momentum coordinates, prove that $\big\langle \frac{p_i^2}{2m} \big\rangle = \frac{1}{2}\,k_{\rm B}T$.

32. Hypervirial and temperature *(6 points)*

Let $\boldsymbol{\Gamma} = \{\boldsymbol{p}_1, \ldots, \boldsymbol{p}_N, \boldsymbol{q}_1, \ldots, \boldsymbol{q}_N\}$ denote a point in $6N$-dimensional phase space and let $\boldsymbol{B}(\boldsymbol{\Gamma})$ be a vector field in phase space. Let us furthermore denote the *gradient (operator) in phase space* by $\nabla_{\boldsymbol{\Gamma}} = \big(\frac{\partial}{\partial p_{1x}}, \frac{\partial}{\partial p_{1y}}, \frac{\partial}{\partial p_{1z}}, \frac{\partial}{\partial p_{2x}}, \ldots\ldots, \frac{\partial}{\partial q_{Nz}}\big)$.

1. Use Gauss' theorem to argue that $\int {\rm d}\boldsymbol{\Gamma}\;\nabla_{\boldsymbol{\Gamma}} \cdot \big\{\boldsymbol{B}(\boldsymbol{\Gamma})\,{\rm e}^{-\beta H(\boldsymbol{\Gamma})}\big\} \;=\; 0$.
2. Prove the amazing fact that every choice of $\boldsymbol{B}$ leads to an expression for the temperature: $k_{\rm B}T = \big\langle \boldsymbol{B} \cdot \nabla_{\boldsymbol{\Gamma}} H \big\rangle \big/ \big\langle \nabla_{\boldsymbol{\Gamma}} \cdot \boldsymbol{B} \big\rangle$.
3. For a standard Hamiltonian, $H = K + \Phi = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} + \Phi(\boldsymbol{q}_1, \ldots, \boldsymbol{q}_N)$, calculate $\nabla_{\boldsymbol{\Gamma}} K$, $\nabla_{\boldsymbol{\Gamma}} \Phi$, and $\nabla_{\boldsymbol{\Gamma}} H$.
4. Choosing $\boldsymbol{B}(\boldsymbol{\Gamma}) = \nabla_{\boldsymbol{\Gamma}} K$, calculate the temperature implied by the new equation. This is called the "*kinetic temperature*".
5. Repeat, but for the choice $\boldsymbol{B}(\boldsymbol{\Gamma}) = \nabla_{\boldsymbol{\Gamma}} \Phi$. This is called the "*configurational temperature*".

Note: These formulas are often used in computer simulations. The configurational temperature in particular is useful in Monte Carlo simulations, for which one usually ignores momenta and hence the more familiar kinetic temperature is not defined.