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1 Energy in Thermal Physics

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Problem 1.1. (Fahrenheit temperature scale.)

(a) To take Celsius to Fahrenheit, we want a linear function that takes 0 to 32 and 100 to 212. Imagining a graph of this function, the vertical intercept must be 32 and the slope must be (212-32)/(100-0) = 9/5; therefore the function is

$$(T \text{ in } {}^{\circ}\text{F}) = \frac{9}{5}(T \text{ in } {}^{\circ}\text{C}) + 32.$$

Inverting this function is now just a matter of algebra:

$$(T \text{ in } {}^{\circ}\text{C}) = \frac{5}{9}[(T \text{ in } {}^{\circ}\text{F}) - 32].$$

(b) Plugging -273.15° C into the first formula gives the value -459.7 for absolute zero in degrees Fahrenheit.

Problem 1.2. To convert from Fahrenheit to Rankine, you would simply add 460, which raises the value of absolute zero (see the previous problem) to zero as desired. Rankine and kelvin temperatures are both measured from the same zero-point, so the conversion between them is just the factor of 9/5 found in the previous problem, with no constant term added. A kelvin degree is *biqqer* than a Rankine degree, so the conversion is

$$(T \text{ in } {}^{\circ}\mathbf{R}) = \frac{9}{5}(T \text{ in } \mathbf{K}),$$

which is equivalent to

$$1^{\circ} R = \frac{5}{9} K.$$

Room temperature, about 300 K, would therefore be $\frac{9}{5} \cdot 300 = 540$ on the Rankine scale.

Problem 1.3. (Kelvin temperature examples.)

- (a) Human body temperature is "officially" 37°C, or 310 K. (In the U.S., this official temperature is traditionally converted to 98.6°F—a classic example of failing to round off insignificant digits.)
- (b) Water is supposed to boil at 100°C, so that would be 373 K.
- (c) I remember a night in Minnesota when the temperature was reported as -29°F. That converts to -34°C, which is 239 K.
- (d) -196° C would be 77 K, so liquid nitrogen is about four times closer to absolute zero than room temperature is.
- (e) 327°C would be 600 K, to three significant figures.

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Problem 4.24. (Effect of temperatures and pressures on Rankine cycle efficiencies.)

(a) Lowering the maximum temperature to 500° C reduces the enthalpy at point 3 to 3081 kJ (per kilogram) and the entropy to 5.791 kJ/K. To find the fraction x of liquid water at point 4, set this entropy equal to the sum of the liquid and gas components:

$$5.791 = x(0.297) + (1-x)(8.667)$$
 \Rightarrow $x = 0.344.$

The enthalpy at point 4 is therefore

$$H_4 = (0.344)(84 \text{ kJ}) + (0.656)(2538 \text{ kJ}) = 1695 \text{ kJ}.$$

Thus the efficiency is

$$e \approx 1 - \frac{H_4 - H_1}{H_3 - H_1} = 1 - \frac{1695 - 84}{3081 - 84} = 0.46.$$

As expected, a lower maximum temperature gives a lower efficiency. However, the reduction from when $T_h = 600$ °C is quite small, only 2% out of 48%.

(b) Lowering the maximum pressure to 100 bar increases the enthalpy at point 3 to 3625 kJ (per kilogram) and the entropy to 6.903 kJ/K. To find the fraction x of liquid water at point 4, set this entropy equal to the sum of the liquid and gas components:

$$6.903 = x(0.297) + (1 - x)(8.667)$$
 \Rightarrow $x = 0.211.$

The enthalpy at point 4 is therefore

$$H_4 = (0.211)(84 \text{ kJ}) + (0.789)(2538 \text{ kJ}) = 2021 \text{ kJ}.$$

Thus the efficiency is

$$e \approx 1 - \frac{H_4 - H_1}{H_3 - H_1} = 1 - \frac{2021 - 84}{3625 - 84} = 0.45.$$

Again, the efficiency is slightly less. This time, however, the reason is less clear, because the extreme temperatures are the same as before. Apparently, less of the heat transfer occurs at temperatures near the extremes, since the boiling occurs at a lower temperature and there is more steam exiting the turbine.

(c) Lowering the minimum temperature to 10° C reduces H_1 to 42 kJ (per kilogram). Point 3 is the same as in the example in the text, but we must redo the calculation of the fraction of liquid at point :

$$6.233 = x(0.151) + (1-x)(8.901)$$
 \Rightarrow $x = 0.305.$

The enthalpy at point 4 is therefore

$$H_4 = (0.305)(42 \text{ kJ}) + (0.695)(2520 \text{ kJ}) = 1764 \text{ kJ},$$

and so the efficiency is

$$e \approx 1 - \frac{H_4 - H_1}{H_2 - H_1} = 1 - \frac{1764 - 42}{3444 - 42} = 0.49.$$

Since we've widened the range of temperatures, the efficiency increases, as expected.

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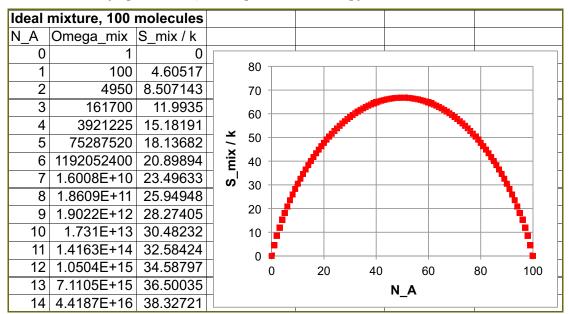
Problem 5.56. Starting from equation 5.60, we have

$$\frac{d}{dx}\Delta S_{\text{mixing}} = -R \left[\ln x + x \cdot \frac{1}{x} + (-1)\ln(1-x) - (1-x) \cdot \frac{1}{1-x} \right]$$

= $-R \left[\ln x - \ln(1-x) \right].$

The first term in this expression goes to ∞ as $x \to 0$, while the second term goes to ∞ as $x \to 1$.

Problem 5.57. I created an Excel spreadsheet with a row for each possible value of N_A from 0 to 100. The "multiplicity" of mixing is then the number of ways of choosing N_A molecules out of 100, computed in Excel as COMBIN(100,A3), for example, and the entropy of mixing, in units of k, is the natural logarithm of the multiplicity. Here are the first several rows of my spreadsheet, and a plot of the entropy:



Notice that if all the molecules are initially of the same type, converting one of them to the other type creates 4.6 units of entropy, but converting a second one creates only 3.9 units, and a converting a third creates only 3.5 units. These differences may not be huge, but they are quite significant: they indicate that the graph of S vs. N_A continues to steepen even when one is already very close to the endpoint. In the thermodynamic limit where the number of molecules is large, the slope of S vs. x becomes infinite as x goes to 0 or 1.

Problem 5.58. (A simple model of a nonideal mixture.)

(a) When the system is unmixed, the potential energy due to the interaction of each neighboring pair is u_0 . There are N molecules, each with n nearest neighbors, so you might think that the total potential energy is Nnu_0 . However, this formula counts every pair interacting pair twice, so we need to divide by 2 to obtain $U = \frac{1}{2}Nnu_0$.

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The plus sign gives the physically relevant solution, since the minus sign would give a value of s that actually decreases with increasing t. Squaring this expression then gives

$$q = \frac{\pi^2 t^2}{24} \left(1 + 1 - \frac{24}{\pi^2 t} + 2\sqrt{1 - \frac{24}{\pi^2 t}} \right) = \frac{\pi^2 t^2}{12} - t + \frac{\pi^2 t^2}{12} \sqrt{1 - \frac{24}{\pi^2 t}}$$
$$= \frac{\pi^2 t^2}{12} - t + \frac{\pi^2 t^2}{12} \left(1 - \frac{12}{\pi^2 t} + \cdots \right) = \frac{\pi^2 t^2}{6} - 2t + \cdots.$$

In the second line I've approximated the square root under the assumption that $t \gg 1$, which is true whenever the RH formula applies in the first place. The energy U is just $q\eta$, so the heat capacity is

$$C = \frac{dU}{dT} = k\frac{dq}{dt} \approx k\left(\frac{\pi^2 t}{3} - 2\right) = k\left(\frac{\pi^2 kT}{3} - 2\right).$$

The predicted heat capacity is linear in T, as expected, but offset downward by a constant term. This prediction is plotted as the solid line in the graph above. As you can see, it agrees beautifully with the exact numerical calculation as t becomes large.

Why is the heat capacity of this system independent of N? This may seem like quite a paradox, since heat capacity must be extensive. However, this model system has no explicitly specified volume, so the notion of an extensive vs. intensive quantity is not really meaningful. In real systems, the spacing between energy levels would decrease with increasing volume. So if you like, you can imagine that there is a hidden volume dependence in the constant η . In formula 7.48 for the heat capacity of a Fermi gas in a three-dimensional box, the factor of N really comes from the energy level spacing as well; see equations 7.51 and 7.54.

Problem 7.28. (Two-dimensional Fermi gas.)

(a) In two dimensions, the allowed energy levels are

$$\epsilon = \frac{h^2}{8mL^2}(n_x^2 + n_y^2).$$

At T=0, fermions settle into the lowest unfilled levels, so in two-dimensional n-space, they fill a quarter-circle with radius $n_{\rm max}$. The Fermi energy is the highest filled level, $\epsilon_{\rm F}=h^2n_{\rm max}^2/8mA$. But the total number of fermions in the system is $N=2\cdot\pi n_{\rm max}^2/4$, assuming that the fermions have spin 1/2 and hence two allowed states for each spatial wavefunction. Solving for $n_{\rm max}^2$ and plugging into the formula for $\epsilon_{\rm F}$ gives

$$\epsilon_{\rm F} = \frac{h^2}{8mA} \bigg(\frac{2N}{\pi}\bigg) = \frac{h^2N}{4\pi mA}.$$

To compute the total energy, we add up the energies of all filled states and convert the sum to an integral over a quarter-circle in polar coordinates:

$$U = 2 \sum_{n_{\rm o}} \sum_{n_{\rm o}} \epsilon(\vec{n}) = 2 \int_0^{n_{\rm max}} dn \int_0^{\pi/2} d\phi \, n \, \epsilon(\vec{n}) = \pi \int_0^{n_{\rm max}} n \, \frac{h^2 n^2}{8mA} \, dn = \frac{\pi h^2 n_{\rm max}^4}{32mA}.$$

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Chapter 8 Systems of Interacting Particles

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Problem 8.15. This 4×4 lattice has 24 "bonds" joining neighboring dipoles, of which 10 (highlighted in the illustration at right) are between antiparallel dipoles and the other 14 are between parallel dipoles. Therefore the total energy is



$$U = 10\epsilon + 14(-\epsilon) = -4\epsilon.$$

Problem 8.16. A system of 100 two-state dipoles has 2^{100} , or 1.27×10^{30} , possible microstates. That's the total number of terms in the partition function, so if we could calculate a billion terms per second, it would take us

$$\frac{1.27 \times 10^{30}}{10^9}$$
 seconds = 1.27×10^{21} seconds = 4.0×10^{13} years

to calculate all the terms. The age of the known universe is approximately 15 billion years, so this is about 2700 times the age of the known universe.

Problem 8.17. For an Ising model of just two elementary dipoles, the energy is just $-\epsilon$ if the dipoles are parallel and ϵ if the dipoles are antiparallel. The states of the system and their Boltzmann factors are:

$$\uparrow \uparrow \colon \ e^{\epsilon/kT}; \qquad \uparrow \downarrow \colon \ e^{-\epsilon/kT}; \qquad \downarrow \uparrow \colon \ e^{-\epsilon/kT}; \qquad \downarrow \downarrow \colon \ e^{\epsilon/kT}.$$

The partition function is therefore

$$Z = 2e^{\epsilon/kT} + 2e^{-\epsilon/kT} = 4\cosh(\epsilon/kT).$$

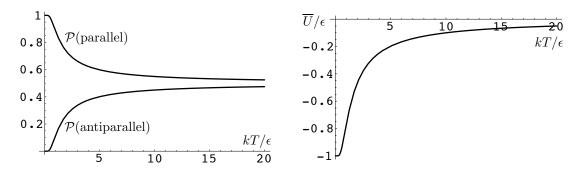
The probability of the two dipoles being parallel is

$$\mathcal{P}(\text{parallel}) = \frac{2e^{\epsilon/kT}}{2e^{\epsilon/kT} + 2e^{-\epsilon/kT}} = \frac{1}{1 + e^{-2\epsilon/kT}},$$

while the probability of them being antiparallel is

$$\mathcal{P}(\text{antiparallel}) = \frac{2e^{-\epsilon/kT}}{2e^{\epsilon/kT} + 2e^{-\epsilon/kT}} = \frac{1}{1 + e^{2\epsilon/kT}}.$$

These formulas are plotted in the figure below (left).



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