

Reading assignment. Schroeder, section **3.3**.

0.1 Heat

Once the equilibrium value of the parameter determining the state of the combined system, such as U_L in the last exercise, is found, we can calculate various macroscopic properties of the system in equilibrium. For example, for the mystery substance in the last exercise, the entropy was

$$S(U, V, N) = \lambda V^{1/2} (NU)^{1/4}. \quad (1)$$

Of course, the entropy itself follows, once U , V , and N are known, but we also found an expression for the temperature:

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{\lambda V^{1/2} N^{1/4}}{4U^{3/4}} = \frac{1}{T}, \quad (2)$$

or

$$T = \frac{4U^{3/4}}{\lambda V^{1/2} N^{1/4}}, \quad (3)$$

where $U = U_{\text{eq}}$ is the equilibrium value of the energy, and the value of T is the same in both subsystems in equilibrium. As well, the amount of heat transferred is obtainable directly from the final and initial energies of either subsystem.

Consider now the entropy change accompanying a small energy change with V and N fixed and with no other kinds of work done:

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial U}\right)_{V,N} dU \\ &= \frac{1}{T} dU. \end{aligned} \quad (4)$$

In the absence of any work the energy change all arises from heat transfer:

$$dU = Q - p dV = Q, \quad (5)$$

so the entropy change is just

$$dS = \frac{Q}{T}. \quad (6)$$

This formally matches the original thermodynamic definition of entropy due to Clausius, but the condition that no work is done will eventually be seen to be more restrictive than necessary.

Now that expression gives changes in entropy only for fixed temperature, and in most cases the temperature varies as heat is added. Exceptions include very large systems, which aren't affected much if a little heat is added

or removed. If you add an ice cube to a lake, you can be sure it won't affect the temperature significantly. Also, systems undergoing certain kinds of phase transitions can absorb or release heat without changing temperature, though there may be volume changes to take into consideration.

For the common case where the temperature is altered when heat is added, it is most natural to take that into account by expressing the heat transferred in terms of the heat capacity. Recall that we defined it generally as

$$C = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T}. \quad (7)$$

Under constant-volume conditions the work vanishes, and we have simply

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N}. \quad (8)$$

With this, we can express the entropy change under constant-volume conditions as

$$dS = \frac{C_V dT}{T}. \quad (9)$$

Of course, C_V itself may vary with temperature, so the change in entropy for a finite change in T requires us to leave C_V inside the integral:

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V(T)}{T} dT. \quad (10)$$

This provides a way to determine changes in entropy between two states of different temperature through experimental measurement of C_V . That's a very important tool in classical thermodynamics, where the only way to determine the entropy function is through measurements of macroscopic properties, like C_V . Of course, we only have a scheme for finding the change ΔS so far, so some sort of reference will be necessary. We'll address that shortly.

Example. Let's try this out on the mystery substance from the last exercise, for which we already have an explicit form for the entropy. We can use that to find the heat capacity, then integrate to find changes in entropy. It's all circular, to be sure, but it gives us a little practice both in calculating C_V from entropy and in finding entropy changes from C_V . As well, we can close the circle at the end to show that we haven't made any mistakes, but I'll leave that for an exercise.

Recall first the entropy:

$$S(U, V, N) = \lambda V^{1/2} (NU)^{1/4} = \gamma(V, N) U^{1/4}, \quad (11)$$

where the replacement $\gamma = \lambda V^{1/2} N^{1/4}$ will simplify later manipulations a bit. The temperature is

$$T = \left[\left(\frac{\partial S}{\partial U} \right)_{V,N} \right]^{-1} = \frac{4U^{3/4}}{\lambda V^{1/2} N^{1/4}} = \frac{4}{\gamma} U^{3/4}. \quad (12)$$

We can solve this to find the energy in terms of T , V , and N :

$$U = \left(\frac{\gamma}{4}\right)^{4/3} T^{4/3}, \quad (13)$$

and that can be used to find the heat capacity:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{4}{3} \left(\frac{\gamma}{4}\right)^{4/3} T^{1/3} = \eta(V,N)T^{1/3}. \quad (14)$$

As with γ , the substitution

$$\eta(V,N) = \frac{4}{3} \left(\frac{\gamma}{4}\right)^{4/3} \quad (15)$$

will save us some writing.

If we didn't already know $S(U, V, N)$, but we had available experimental measurements of $C_V(T, V, N)$ that had this functional form, we could calculate the entropy change for any temperature change at fixed N and V :

$$\begin{aligned} \Delta S &= \int_{T_i}^{T_f} \frac{C_V}{T} dT \\ &= \eta \int_{T_i}^{T_f} T^{-2/3} dT \\ &= 3\eta(T_f^{1/3} - T_i^{1/3}). \end{aligned} \quad (16)$$

While this ability to compute entropy changes from experimentally measurable quantities makes it possible to define $S(U, V, N)$ experimentally, there remains an ambiguity. We can only discover ΔS this way, so it is necessary to choose a reference point. That is resolved by the *third law of thermodynamics*, also called *Nernst's law*. It says simply:

$$\lim_{T \rightarrow 0} S = 0, \quad (17)$$

or in a form that more properly takes into account the natural dependence of S on energy:

$$\lim_{U \rightarrow U_{\text{gnd}}} S = 0. \quad (18)$$

That is, the entropy in the ground state vanishes. That makes good sense, since the true ground state is unique, so it has multiplicity $\Omega = 1$, leading to $S = k \ln 1 = 0$.

With that convention, we can find the entropy at any temperature above $T = 0$ by

$$S = \int_0^T \frac{C_V}{T} dT, \quad (19)$$

though it will be necessary to interrupt the integral wherever there is a phase change in the material, since the heat capacity becomes infinite at such points, allowing the entropy to increase discontinuously with T .

HW Problem. Schroeder problem 3.10, p. 97.

HW Problem. Schroeder problem 3.11, p. 97.

HW Problem. Schroeder problem 3.14, p. 97.

Exercise. The mystery material of the last exercise, had

$$S = \lambda V^{1/2} (NU)^{1/4} = \gamma(V, N) U^{1/4}, \quad (20)$$

where we introduced

$$\gamma(V, N) = \lambda V^{1/2} N^{1/4} \quad (21)$$

to simplify later algebra. The temperature is given by

$$T = \left(\frac{\partial S}{\partial U} \right)_{V, N} = \frac{4}{\gamma} U^{3/4}, \quad (22)$$

and the heat capacity is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V, N} = \frac{4}{3} \left(\frac{\gamma}{4} \right)^{4/3} T^{1/3} = \eta(V, N) T^{1/3}, \quad (23)$$

where

$$\eta(V, N) = \frac{4}{3} \left(\frac{\gamma}{4} \right)^{4/3}. \quad (24)$$

(a) Show that the entropy change given by

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT \quad (25)$$

is the same as the directly calculated change

$$\Delta S = S(U_f, V, N) - S(U_i, V, N). \quad (26)$$

(b) Calculate the entropy changes as equilibrium is achieved in the previous exercise. Key facts from that exercise:

$$\begin{aligned} N_L &= 1 \text{ mole} & N_R &= 2 \text{ moles} \\ V_L &= 1 \text{ m}^3 & V_R &= 1 \text{ m}^3 \\ U_{L,i} &= 200 \text{ J} & U_{R,i} &= 400 \text{ J} \\ U_{R,f} &= 2^{1/3} U_{L,f} \\ U_{L,f} &= \frac{U_{L,i} + U_{R,i}}{2^{1/3} + 1} = \frac{3}{2^{1/3} + 1} U_{L,i}. \end{aligned} \quad (27)$$

Express ΔS_L and ΔS_R as multiples of $S_{L,i}$, the initial entropy on the left side. Verify that

$$\Delta S_{\text{tot}} = \Delta S_L + \Delta S_R > 0. \quad (28)$$

Are ΔS_L and ΔS_R both positive? If not, is that OK?

[EOC, Fri. 2/10/2006, #14]

Reading assignment. Schroeder, section 3.4.

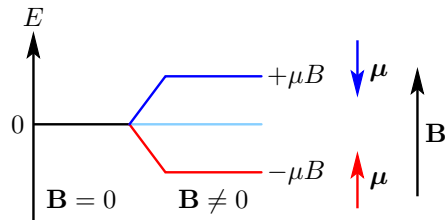
0.2 The paramagnet revisited

Now we'll explore in more detail the properties of the two-state paramagnet, one of our toy systems. It's actually much more than a toy, though, since it is physically realizable to a good approximation. One of the prime examples consists of a crystal lattice composed of atoms whose nuclei have net magnetic moments that are weakly coupled to each other and very weakly coupled to the lattice itself. This makes it possible for equilibrium to be established among the magnetic moments much faster than between the moment system and the lattice, and that makes it possible to explore the rather curious properties of this system experimentally.

Recall that the magnetic moments in a two-state paramagnet arise from the spins of particles, possibly electrons or particles in a nucleus. These spin-1/2 particles have just two possible energy states in an external magnetic field, either aligned (“up”) with the magnetic field or antialigned (“down”) with the field. The energy of a single moment is

$$E = -\boldsymbol{\mu} \cdot \mathbf{B}, \quad (40)$$

and the quantization leads to just two possible energies $E = \pm\mu B$:



The aligned (up) moments have lower energy than the antialigned moments. Notice that the energies of the two alignments become equal as the strength of the external magnetic field goes to zero, so we've chosen the zero of energy to be that state, with the quantized energies in a nonvanishing field lying symmetrically above and below that energy.

The total energy of a system of identical moments in an external field is then

$$U = \sum_i (\pm)_i \mu B = \mu B (N_\downarrow - N_\uparrow). \quad (41)$$

If the numbers of aligned and antialigned moments are not equal, the system as a whole has a net magnetic moment and is said to be magnetized. The net magnetic moment, or *magnetization*, is

$$M = \sum_i (\pm)_i \mu = \mu (N_\uparrow - N_\downarrow) = n\mu, \quad (42)$$

where $n = N_\uparrow - N_\downarrow$ is the net number of aligned moments. As you can see, the energy can be written in terms of the magnetization:

$$U = -MB = -n\mu B. \quad (43)$$

[EOC, Mon. 2/13/2006, #15; HW05 closed, due Mon. 2/20/2006]
