

3.6: The Thermodynamic Dance

A more conventional name for this section would be “Changes of Variable in Thermodynamics”, but the changes of variable involved always remind me of an elaborate dance where partners are exchanged and where patterns seem to dissolve and then reappear, but in fact are always present, even if hidden.

3.6.1 Description in terms of variables (S, V, N)

We know that in many circumstances (e.g. pure, non-magnetic fluids) the thermodynamic state of a system is uniquely specified by giving the entropy S , the volume V , and the particle number N . The master function for this description is the energy

$$E(S, V, N) \quad (3.6.1)$$

whose total differential is

$$dE = TdS - pdV + \mu dN. \quad (3.6.2)$$

Remember that a “master function” is one from which all functions of interest can be obtained by simple differentiation. . . the equation above, for example, shows directly that

$$p(S, V, N) = -\left(\frac{\partial E}{\partial V}\right)_{S, N}. \quad (3.6.3)$$

Remember also that the variables V and N are just representative mechanical parameters. Other mechanical parameters such as particle mass m , particle radius r_{HS} , or the numbers of two different species, N_{H_2} and N_{He} , will be relevant in other circumstances.

3.6.2 Description in terms of variables (T, V, N)

For many purposes the description in terms of S, V , and N is awkward. (Entropy, for example, can be difficult to measure and to understand.) In these situations a more natural set of variables might be temperature T , volume V , and number N . We can change² to this set through a Legendre transformation (a process sometimes called “trading in an S for a T ”) obtaining the new master function

$$F(T, V, N) = E - TS, \quad (3.6.4)$$

which is called the “Helmholtz potential” (or the “Helmholtz free energy”³), and which has the associated master equation

$$dF = -SdT - pdV + \mu dN. \quad (3.6.5)$$

(In some books, the Helmholtz potential is denoted by A rather than F .)

Lots of information can be read directly from the master equation. For example, the entropy can be found through

$$S(T, V, N) = -\left(\frac{\partial F}{\partial T}\right)_{V, N}. \quad (3.6.6)$$

It is less obvious how to find the energy, but a little thought shows that

$$E(T, V, N) = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_{V, N} = \frac{\partial(F/T)}{\partial(1/T)}_{V, N}. \quad (3.6.7)$$

This equation is frequently used and carries the name “Gibbs-Helmholtz equation”.

One sometimes hears that “energy must be regarded as a function of (S, V, N) while Helmholtz potential must be regarded as a function of (T, V, N)”. This is false. The energy $E(T, V, N)$ above is a perfectly good function but it is not a master function. The energy is the master function for the description in terms of (S, V, N) but not for the description in terms of (T, V, N). Similarly, one could find the Helmholtz potential as a function of (S, V, N), but it would not be a master function.

Another immediate consequence of the master equation is that

$$p(T, V, N) = -\left(\frac{\partial F}{\partial V}\right)_{T, N}. \quad (3.6.8)$$

This equation is *extremely* well known. . . it is just the “equation of state”, relating pressure, temperature, volume, and number. Examples are the famous ideal gas equation of state

$$p(T, V, N) = \frac{Nk_B T}{V} \quad (3.6.9)$$

and the only slightly less famous van der Waals equation of state for non-ideal gases

$$p(T, V, N) = \frac{k_B T}{V/N - v_0} - \frac{e_0 v_0}{(V/N)^2}, \quad (3.6.10)$$

where v_0 and e_0 are positive empirical constants with the dimensions of volume and energy respectively.

Notice that $S(T, V, N)$, $E(T, V, N)$, and $p(T, V, N)$ are all interesting quantities, but none of them are master functions, that is, none of them contain all the thermodynamic information. It is a common misconception that the equation of state contains everything one could want to know about a substance. In fact, for example, helium and nitrogen are both nearly ideal gases at room temperature (so they obey nearly the same equation of state) but the specific heat of nitrogen is about 67% greater than that of helium (so they differ dramatically in some thermodynamic properties).

Yet another immediate consequence of the master equation is the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N}. \quad (3.6.11)$$

Each of the derivatives above is not only a mathematical expression, but also an invitation to perform an experiment. The derivative on the left is measured through an experiment like the following: A sample in a container of variable volume (such as a piston) is placed within a thermostatically controlled bath (so that the temperature doesn't change) and is heated in a slow and carefully monitored way (so that the heat absorbed quasistatically can be divided by the temperature to find the entropy change). As the substance is heated at constant temperature, the volume of the piston must change. Dividing the heat absorbed by the temperature and the volume change gives (for small volume changes) the derivative on the left. This experiment is not impossible, but clearly it is difficult and expensive.

Consider in turn the experiment on the right. The sample is in a “strong box” container of fixed volume and its pressure and temperature are measured as the temperature is changed. The change doesn't need to be controlled carefully and the heat absorbed doesn't need to be monitored: you can just blast your sample with a propane torch. Dividing the measured change in pressure by the measured change in temperature gives (for small temperature changes) the derivative on the right. It is remarkable that the results of these two very different experiments is always the same. . . and it shows how thermodynamics can save a lot of experimental labor! But it is still more remarkable—nearly unbelievable—that we know these two experiments give the same results because we know that the entropy function $S(E, V, N)$ exists, even though we might not know what that function is.⁴ (This Maxwell relation is discussed further in problem 3.23.)

3.6.3 Description in terms of variables (S, p, N)

I don't need to stop with this second description. Both of the descriptions above used volume as a variable. Most experiments executed here on Earth's surface are actually performed with a constant pressure (namely one atmosphere) rather than with a constant volume, suggesting that pressure should be one of our variables. We may start with the description in terms of (S, V, N) and then trade in a V for a p , obtaining a master function

$$H(S, p, N) = E + pV, \quad (3.6.12)$$

called the “enthalpy”, and the related master equation

$$dH = TdS + Vdp + \mu dN. \quad (3.6.13)$$

We could pause here to write down derivatives of $H(S, p, N)$, Maxwell relations, and so forth, but this would merely be repetitive of what we did in the last section. Instead, we ask for yet another description with the advantages of using both temperature instead of entropy and pressure instead of volume.

3.6.4 Description in terms of variables (T, p, N)

In this description, the master function

$$G(T, p, N) = F + pV \quad (3.6.14)$$

is called the “Gibbs potential” (or the “Gibbs free energy”⁵) and the master equation is

$$dG = -SdT + Vdp + \mu dN. \quad (3.6.15)$$

(It is most unfortunate that in some books the Gibbs potential is denoted F , the symbol that most books reserve for the Helmholtz potential.)

It is immediately obvious that

$$\mu(T, p, N) = \left(\frac{\partial G}{\partial N} \right)_{T, p}. \quad (3.6.16)$$

It is also true that G is an extensive quantity, and that it is a function of only one extensive quantity, namely N . It follows that G must increase linearly with N , whence

$$\mu(T, p) = \frac{G(T, p, N)}{N}. \quad (3.6.17)$$

Notice that μ , which appeared from equation (3.76) to depend upon N , is actually independent of N .

The chemical potential has so far been a wallflower in the thermodynamic dance. But there is no reason why we cannot trade in an N for a μ in the same way that we traded in a V for a p .

3.6.5 Description in terms of variables (T, V, μ)

Here the master function is

$$\Pi(T, V, \mu) = F - \mu N \quad (3.6.18)$$

with master equation

$$d\Pi = -SdT - pdV - Nd\mu. \quad (3.6.19)$$

You might wonder why Π doesn't have a name. This is because

$$\Pi = F - \mu N = F - G = -pV \quad (3.6.20)$$

or, to put it more formally,

$$\Pi(T, V, \mu) = -p(T, \mu)V, \quad (3.6.21)$$

so Π already has the name of "negative pressure times volume".

3.6.6 Intensive description in terms of variables (T, μ)

Putting equations (3.79) and (3.81) together gives

$$-pdV - Vdp = -SdT - pdV - Nd\mu \quad (3.6.22)$$

whence

$$dp = \frac{S}{V}dT + \frac{N}{V}d\mu. \quad (3.6.23)$$

In other words, we have produced a new master function, the pressure

$$p(T, \mu) \quad (3.6.24)$$

with master equation

$$dp = SdT + \rho d\mu \quad (3.6.25)$$

where we have used the volume densities

$$S = S/V \quad \text{and} \quad \rho = N/V. \quad (3.6.26)$$

The master function $p(T, \mu)$ differs in important ways from the others that we have seen. First, it is intensive rather than extensive. Second, it is a function of two rather than three variables, and the two variables are both intensive. It is clear that we cannot get any information about the system size out of $p(T, \mu)$. . . thus it fails the usual test of a master function, namely that it must provide all

thermodynamic information. On the other hand, $p(T, \mu)$ provides all the information about intensive quantities. The problems in this chapter demonstrate that $p(T, \mu)$ is a surprisingly useful master function.

This entire section is summarized in appendix J.

Problems

3.19 Stumbling in the thermodynamic dance

- a. From the thermodynamic assembly with variables T , p , and N , with master equation

$$dG = -SdT + Vdp + \mu dN \quad (3.6.27)$$

one is tempted to produce an assembly with variables T , p , and μ , using master function

$$\Phi = G - \mu N. \quad (3.6.28)$$

Why does this fail?

- b. Show that what is really desired is an intensive-only description in terms of the variables T and p , for which the master equation is

$$d\mu = -sdT + vdp, \quad (3.6.29)$$

where $s = S/N$ and $v = V/N$. (This result is called the “Gibbs-Duhem equation”.)

3.20 Not a master function

The function $E(S, V, N)$ is a master function: all thermodynamic quantities of interest can be obtained by taking suitable derivatives of $E(S, V, N)$. For the variables (T, V, N) the master function is the Helmholtz potential $F(T, V, N)$. While the energy $E(T, V, N)$ of course remains a function, it is no longer a master function. Prove this to yourself by considering two different substances, A and B, with Helmholtz potentials $F_A(T, V, N)$ and $F_B(T, V, N) = F_A(T, V, N) + aTV^2/N$. Show that these two substances have identical energies $E(T, V, N)$ but different equations of state $p(T, V, N)$.

3.21 Thermodynamics of a new substance

The entropy of a newly discovered gas is determined to be

$$S(E, V, N) = \left(\frac{k_B}{T_0}\right)^{1/2} \left(NE + \frac{k_B T_0 V^2}{v_0^2}\right)^{1/2}, \quad (3.6.30)$$

where the constants T_0 and v_0 are positive, intensive quantities with the dimensions of temperature and volume, respectively.

- Verify that this equation is acceptable in its dimensions and in its extensivity.
- Find $T(S, V, N)$ and $p(S, V, N)$ for this gas.
- Find $C_V(T, V, N)$ for this gas.

3.22 Energy from the Gibbs potential

The text claims that “any thermodynamic function can be obtained from a master function by taking derivatives.” To back up this claim, show that

$$E(T, p, N) = G(T, p, N) - T \left(\frac{\partial G}{\partial T}\right)_{p, N} - p \left(\frac{\partial G}{\partial p}\right)_{T, N} \quad (3.6.31)$$

$$= \frac{\partial(G/p)}{\partial(1/p)}_{T, N} - T \left(\frac{\partial G}{\partial T}\right)_{p, N} \quad (3.6.32)$$

$$= \frac{\partial(G/T)}{\partial(1/T)}_{p, N} - p \left(\frac{\partial G}{\partial p}\right)_{T, N} \quad (3.6.33)$$

Find an expression for $F(T, p, N)$ in terms of $G(T, p, N)$.

3.23 A Maxwell relation: special cases

a. Apply the Maxwell relation (3.71) to the special case of an ideal gas (equation of state $pV = Nk_B T$) to show that

$$S(T, V, N) = Nk_B \ln(V/V_0(T)), \quad (3.6.34)$$

where $V_0(T)$ is an undetermined function of integration that differs from one ideal gas to another. (The remarkable character of our Maxwell relation comes into sharp focus when applied to this special case: The “mechanical-type” experiments which uncover the equation of state enable us to determine much about the entropy function even in the absence of any “heat-type” experiments.)

b. Another special case worth examination is two-phase coexistence of liquid and gas. Verify the Maxwell relation both for “typical” two-phase coexistence—in which the low-temperature phase has higher density than the high-temperature phase—and for the unusual cases—such as the coexistence of water and ice—where the low-temperature phase has a higher density.

3.24 Chemical potential for mixtures

If a system contains a mixture of two chemical substances, say N_A molecules of substance A and N_B molecules of substance B, then the list of mechanical parameters must be expanded, and the entropy is a function

$$S(E, V, N_A, N_B). \quad (3.6.35)$$

In this case the chemical potential of substance A is

$$\mu_A(E, V, N_A, N_B) = -T(E, V, N_A, N_B) \left(\frac{\partial S}{\partial N_A} \right)_{E, V, N_B} \quad (3.6.36)$$

and similarly for B. Notice that the chemical potential of substance A depends upon the number of molecules of B present.

a. Perform the thermodynamic dance down to the function $F(T, V, N_A, N_B)$ to show that

$$\mu_A(T, V, N_A, N_B) = \partial F / \partial N_A \quad (3.96)$$

and similarly for B.

b. Argue that, because μ_A and μ_B are intensive, their functional dependence on V , N_A , and N_B , must be through the number densities $\rho_A = N_A/V$ and $\rho_B = N_B/V$, i.e. that

$$\mu_A(T, V, N_A, N_B) = \mu_A(T, \rho_A, \rho_B). \quad (3.6.37)$$

c. Consider the Gibbs potential $G(T, p, N_A, N_B)$ and modify the extensivity argument that produced equation (3.77) to show that

$$G(T, p, N_A, N_B) = \mu_A(T, p, N_A/N_B) N_A + \mu_B(T, p, N_A/N_B) N_B, \quad (3.6.38)$$

where the chemical potentials are independent of the overall numbers N_A and N_B but may depend on their ratio.

3.25 More parameters

What is the generalization of

$$dE = TdS - pdV + \mu dN \quad (3.6.39)$$

for systems that can be lifted and tossed? (That is, for systems in which height h and velocity \mathbf{v} are mechanical parameters.)

3.26 Another mechanical parameter

Recall expression (2.32) for the entropy of a monatomic ideal gas, and recall that $E = \frac{3}{2} Nk_B T$. Find expressions for the change in entropy and in volume if the masses of the particles are varied at constant p , T , and N . Suggest experiments that could verify these relations.

3.27 Which variables to exchange?

In carrying out the thermodynamic dance, we have exchanged the variable S for the function $T(S, V, N)$, and we have exchanged the variable V for the function $p(T, V, N)$, and more. Why would it never be appropriate to exchange the volume for the temperature? (Clue: Consider the volume of water at temperatures just above and below freezing.)

²When we changed variable from (S, V, N) to (E, V, N) (equation 3.1), I argued that this inversion was mathematically legitimate. Here I will not be so formal and just assume that everything will come out all right. (See, however, problem 3.27.) Clifford

Truesdell has called this “the principle of thoughtless invertibility”.

³The term “free” in this name is of only historical significance. Its origin lies in the fact that F is related to the maximum amount of energy that is available (“free”) for conversion into work through an isothermal process.

⁴If a material existed for which these two experiments did not give identical results, then we could use that substance to build a perpetual motion machine.

⁵I prefer the name “Gibbs potential” because it is like electrostatic potential — the quantity itself is not of intrinsic interest, but one can find many interesting things by taking its derivatives. The name “free energy” is particularly inappropriate: What do you buy from a power company? You’ve been told “Turn off the lamps to conserve energy”, but this is silly: energy is conserved whether the lamps are on or off. There’s plenty of thermal energy in any room, but you can’t get work out of that energy because the room has uniform temperature. So you don’t buy energy from a power company, you in fact buy Gibbs potential. For this reason it should be called “Gibbs expensive energy”. I am trying to get the federal government to change the name of the Department of Energy to the Department of Gibbs Potential, but so far I’ve had no success.

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