10

Perturbations of Thermodynamic State Functions

When you come to a fork in the road, take it.

Yogi Berra

As discussed in the Chapter 9, state functions specify quantities that depend only on the small number of variables needed to characterize an equilibrium state. It turns out that state functions are strongly restricted by the postulates of thermodynamics, so that we can derive a great many non-trivial equations linking observable quantities. The power of thermodynamics is that these relations are true for *all* systems, regardless of their composition!

In Part I we used the symbol E to denote the energy of a system, which is customary in statistical mechanics. Unfortunately, it is customary in thermodynamics to use the symbol U for the energy. The reason for this deplorable state of affairs is that it is often convenient in thermodynamics to consider the energy per particle (or per mole), which is denoted by changing to lower case, $u \equiv U/N$. Since e might be confused with Euler's number, u and U have become standard. Technically, there is also a difference in meaning. The proper definition of U is $U = \langle E \rangle$. When we consider the microcanonical ensemble, for which the width of the energy distribution is zero, it does not make any difference. It will become important when we turn to quantum systems. We will follow thermodynamics convention in Part II and denote the energy by U. It is fortunate that students of thermal physics are resilient, and can cope with changing notation.

10.1 Small Changes in State Functions

In much of thermodynamics we are concerned with the consequences of small changes. Part of the reason is that large changes can often be calculated by summing or integrating the effects of many small changes, but in many cases the experimental questions of interest really do involve small changes.

Mathematically, we will approximate small changes by infinitesimal quantities. This, in turn, leads us to consider two distinct types of infinitesimals, depending on whether or not there exists a function that can be determined uniquely by integrating the infinitesimal.

10.2   Conservation of Energy

The great discovery by James Prescott Joule (English physicist, mathematician, and brewer, 1818–1889) that heat is form of energy, combined with the principle that energy is conserved, gives us the First Law of Thermodynamics.

We will usually apply the First Law to small changes in thermodynamic quantities, so that it can be written as

$$dU = đQ + đW \tag{10.1}$$

if the number of particles in the system does not change. Although dU, $đQ$, and $đW$ are all infinitesimal quantities, there is an important distinction between those written with d and those written with $đ$ that is discussed in the next section.

The change in the energy of a system during some thermal process is denoted by dU, and is positive when energy is added to the system. The energy added to the system in the form of heat is denoted by $đQ$, and the work done on the system is denoted by $đW$. The sign convention is that all three of these differentials are positive when energy is added to the system.

> Our choice of sign convention for $đW$ is by no means universal. Taking an informal survey of textbooks, I have found that about half use our convention, while the other half take $đW$ to be positive when work is done by the system. Be careful when comparing our equations with those in other books.

In many applications of thermodynamics we will have to consider transfers of energy between two or more systems. In that case, the choice of the positive directions for $đQ$ and $đW$ will be indicated by arrows in a diagram.

10.3   Mathematical Digression on Exact and Inexact Differentials

Consider an infinitesimal quantity defined by the equation

$$dF = f(x)dx, \tag{10.2}$$

where $f(x)$ is some known function. We can always—at least in principle—integrate this equation to obtain a function $F(x)$ that is unique to within an additive constant.

Now consider the infinitesimal defined by the equation

$$đF = f(x,y)dx + g(x,y)dy, \tag{10.3}$$

where $f(x,y)$ and $g(x,y)$ are known functions. Although the differential $đF$ can be integrated along any given path, the result might depend on the specific path, and not just on the initial and final points. In that case, no unique function $F(x,y)$ can be found by integrating eq. (10.3), and $đF$ is called an 'inexact' differential. The use of $đ$ instead of d indicates that an infinitesimal is an inexact differential.

Note that if two path integrals produce different values, the integral over the closed path going from the initial to the final point along one path and returning along the other will not vanish. Therefore, the failure of an integral around an arbitrary closed path to vanish is also characteristic of an inexact differential.

As an example, take the following inexact differential:

$$đF = x\,dx + x\,dy. \tag{10.4}$$

Consider the integral of this differential from $(0,0)$ to the point (x,y) by two distinct paths.

Path A: From $(0,0)$ to $(x,0)$ to (x,y).

Path B: From $(0,0)$ to $(0,y)$ to (x,y).

The path integral for Path A gives

$$\int_0^x x'\,dx'\Big|_{y'=0} + \int_0^y x'\,dy'\Big|_{x'=x} = \frac{1}{2}x^2 + xy \tag{10.5}$$

and the path integral for Path B gives

$$\int_0^y x'\,dy'\Big|_{x'=0} + \int_0^x x'\,dx'\Big|_{y'=y} = 0 + \frac{1}{2}x^2 = \frac{1}{2}x^2. \tag{10.6}$$

Since the two path integrals in eqs. (10.5) and (10.6) give different results for $y \neq 0$, there is no unique function $F(x,y)$ corresponding to the inexact differential in eq. (10.4).

10.3.1   Condition for a Differential to be Exact

We can easily determine whether a differential is exact or inexact without the necessity of performing integrals over all possible paths. If a function $F(x,y)$ exists, we can write its differential in terms of partial derivatives,

$$dF = \left(\frac{\partial F}{\partial x}\right)dx + \left(\frac{\partial F}{\partial y}\right)dy. \tag{10.7}$$

If the differential

$$dF = f(x,y)dx + g(x,y)dy \tag{10.8}$$

is exact, we can identify $f(x,y)$ and $g(x,y)$ with the corresponding partial derivatives of $F(x,y)$,

$$f(x,y) = \frac{\partial F}{\partial x} \tag{10.9}$$

$$g(x,y) = \frac{\partial F}{\partial y}. \tag{10.10}$$

By looking at partial derivatives of $f(x,y)$ and $g(x,y)$, we find that they must satisfy the following condition:

$$\frac{\partial f}{\partial y} = \frac{\partial^2 F}{\partial y \partial x} = \frac{\partial^2 F}{\partial x \partial y} = \frac{\partial g}{\partial x}. \tag{10.11}$$

The central equality follows from the fact that the order of partial derivatives can be switched without changing the result for well-behaved functions, which are the only kind we allow in physics textbooks.

10.3.2 Integrating Factors

There is an interesting and important relationship between exact and inexact differentials. Given an inexact differential,

$$đF = f(x,y)dx + g(x,y)dy \tag{10.12}$$

we can find a corresponding exact differential of the form

$$dG = r(x,y)đF \tag{10.13}$$

for a function $r(x,y)$, which is called an 'integrating factor'. The function $r(x,y)$ is not unique; different choices for $r(x,y)$ lead to different exact differentials that are all related to the same inexact differential.

The example given in eq. (10.4) is too easy. The function $r(x,y) = 1/x$ is obviously an integrating factor corresponding to $dG = dx + dy$.

A less trivial example is given by the inexact differential

$$đF = y\,dx + dy. \tag{10.14}$$

To find an integrating factor for eq. (10.14), first write the formal expression for the exact differential,

$$dG = r(x,y)đF = r(x,y)y\,dx + r(x,y)dy. \tag{10.15}$$

The condition that dG is an exact differential in eq. (10.11) gives

$$\frac{\partial}{\partial y}[r(x,y)y] = \frac{\partial}{\partial x}r(x,y) \tag{10.16}$$

or

$$r + y\frac{\partial r}{\partial y} = \frac{\partial r}{\partial x}. \tag{10.17}$$

Eq. (10.17) has many solutions, so let us restrict our search for an integrating factor to functions that only depend on x,

$$r(x,y) = r(x). \tag{10.18}$$

Eq. (10.17) then simplifies because the partial derivative with respect to y vanishes,

$$r = \frac{dr}{dx}. \tag{10.19}$$

Eq. (10.19) can be easily solved

$$r(x,y) = r(x) = \exp(x). \tag{10.20}$$

The final result for dG is

$$dG = \exp(x)đF = y\exp(x)\,dx + \exp(x)dy. \tag{10.21}$$

Naturally, any constant multiple of $\exp(x)$ is also an integrating factor.

10.4   Conservation of Energy Revisited

Since the energy U is a state function, the differential of the energy, dU, must be an exact differential. On the other hand, neither heat nor work is a state function, so both $đQ$ and $đW$ are inexact.

10.4.1 Work

For simplicity, first consider an infinitesimal amount of work done by using a piston to compress the gas in some container. Let the cross-sectional area of the piston be A, and let it move a distance dx, where positive dx corresponds to an increase in the volume, $dV = A\,dx$. The force on the piston due to the pressure P of the gas is $F = PA$, so that the work done on the gas is $-F\,dx$ or

$$\text{\dj}W = -F\,dx = -P\,dV. \tag{10.22}$$

The volume of the system is obviously a state function, so the differential dV is exact. Eq. (10.22) shows a relationship between an inexact and an exact differential, with the function $1/P$ playing the role of an integrating factor. To see that $\text{\dj}W$ is indeed an inexact differential, integrate it around any closed path in the P,V-plane. The result will not vanish.

10.4.2 Heat

The heat transferred to a system turns out to be closely related to the change in entropy of the system. Consider the change in entropy due to adding a small amount of heat $\text{\dj}Q$ to the system,

$$dS = S(E + \text{\dj}Q, V, N) - S(E, V, N) = \left(\frac{\partial S}{\partial E}\right)_{V,N} \text{\dj}Q = \frac{\text{\dj}Q}{T}. \tag{10.23}$$

Again we see an equation relating exact and inexact differentials. In this case, the function $1/T$ is the integrating factor.

Eq. (10.23) is extremely important for a number of reasons. It can be used to numerically integrate experimental data to calculate changes in entropy. It is also important for our purposes in the next section when written slightly differently,

$$\text{\dj}Q = T\,dS. \tag{10.24}$$

10.5 An Equation to Remember

Eqs. (10.22) and (10.24) can be used to rewrite eq. (10.1) in a very useful form,

$$dU = T\,dS - P\,dV. \tag{10.25}$$

This equation is, of course, only valid when there are no exchanges of particles with another system, so that the total number of particles in the system of interest is held constant.

Curiously enough, in Section 8.10 on the fundamental relation in the entropy representation, we have already derived the generalization of eq. (10.25) to include a

change dN in the number of particles. Rewriting eq. (8.38) with dU instead of dE, we have

$$dS = \left(\frac{1}{T}\right) dU + \left(\frac{P}{T}\right) dV - \left(\frac{\mu}{T}\right) dN. \qquad (10.26)$$

Solving this equation for dU, we find one of the most useful equations in thermodynamics:

$$dU = TdS - PdV + \mu dN. \qquad (10.27)$$

The reason that the differential form of the fundamental relation is equivalent to the First Law of Thermodynamics (energy conservation) is that energy conservation was used in its derivation in Part I.

> If there is one equation in thermodynamics that you must memorize, it is eq. (10.27). In the following chapters you will see why this is so.

> Eq. (10.27) provides another interpretation of the chemical potential μ. It is the change in the energy of a system when a particle is added without changing either the entropy or the volume. The difficulty with this explanation of the meaning of μ is that it is far from obvious how to 'add a particle without changing the entropy'. Apologies.

10.6   Problems

PROBLEM 10.1
Integrating factors for inexact differentials

We showed that the inexact differential

$$\bar{d}F = y\,dx + dy$$

is related to an exact differential by an integrating function

$$r(x,y) = r_x(x).$$

1. Show that $đF$ is also related to another (different) exact differential by an integrating function of the form

$$r(x,y) = r_y(y).$$

2. Derive an explicit expression for $r_y(y)$ and show that the new differential is exact.
3. For the new differential and $x, y > 1$, calculate and compare the path integral from the point $(1,1)$ to $(1,y)$, from there to (x,y), with the path integral from the point $(1,1)$ to $(x,1)$, from there to (x,y).

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