

§9. Heat Capacity and Equation of State

So, what do we want to know now?

We have seen in the above that

because the basic situation of interest is system in contact with a reservoir at T

The basically useful and fundamental variables we'd like to operate with are T and V , both easily measurable (sometimes p is more useful than V , this we will encounter later).

We would then like to be able to calculate from them U (and its changes)

p (and hence work)

S (and, by requiring its increase, the direction of travel)

How do we do this? We know so far that

$$U = - \frac{\partial \ln Z}{\partial \beta} \rightarrow U(V, T)$$

$$S = \frac{U}{T} + k_B \ln Z \rightarrow S(V, T)$$

$$dU = TdS - PdV \rightarrow p(V, T) = - \left(\frac{\partial U}{\partial V} \right)_S$$

This means that if we know the partition function

$$Z = \sum_{\alpha} e^{-\beta E_{\alpha}}$$

then we can calculate absolutely everything.

This is the main task of statistical mechanics and involves two ~~two~~ challenges

- calculate E_α 's (\leftarrow QM)

- do the sum (this involves correctly counting ~~the~~ microstates)

We will do many such calculations in what follows, but first let us introduce some general tools that will be helpful.

Note: $p_\alpha = \frac{e^{-\beta E_\alpha}}{Z} = e^{-\beta E_\alpha - \ln Z} = e^{-\beta(E_\alpha + F)}$

9.1 Free energy

Let us introduce a new function of state, called Helmholtz free energy:

equiv. to \checkmark knowing Z

so its natural variables are V and T

$$F = U - TS = -k_B T \ln Z$$

It is useful because

$$dF = dU - TdS - SdT = -PdV - SdT$$

Hence we can calculate

$U = F + TS$

$S = -\left(\frac{\partial F}{\partial T}\right)_V$

entropy directly from part. funct.

and $p = -\left(\frac{\partial F}{\partial V}\right)_T$

this is much more convenient than $p = -(\partial U / \partial V)_S$ because holding T const is much more straightforward than S !

Since $-pdV = \left(\frac{\partial F}{\partial V}\right)_T dV$, F used to be called work content.

From this follows $p = p(V, T)$ equation of state

9.2 Heat Capacity

Another useful quantity is heat capacity - amount of heat needed to change temperature by unit:

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$

↑
at const volume

(heat not a diff. so have to specify path)

This can also be calculated from free energy:

$$C_V = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V$$

This is an example of the sort of thing thermodynamics is interested in - how various therm. quantities change with others (usually T, V, p) while yet others are kept constant. This is usually parametrised in the form of response functions like C_V .

Analogously one can introduce

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p \quad \text{heat capacity @ const } p$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad \text{isothermal compressibility}$$

(calculate from eq. of state)

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad \text{thermal expansion coefficient}$$

(ditto)

$$\chi = \frac{1}{V} \left(\frac{\partial M}{\partial B} \right)_T \quad \text{magnetic susceptibility etc. etc.}$$

Note. It can be shown that $C_V > 0$ (and related to mean sq. energy fluctuation) \Rightarrow follows thermal stability Ex. (HW)

One can develop a whole thermodynamic calculus to calculate these sort of things - this will be done later in the course.

Many useful relations can be derived in general, but in the end, to compute anything specific, we will need to know, at a minimum, the eq. of state and heat capacity. And to calculate them, (as function of T, V , e.g.)

we'll need free energy or, equivalently, partition function.

Shortly, we will ~~rederive~~ calculate these for the monatomic classical ideal gas - at which point we will be in position to prove ~~that~~ the equivalence between thermodynamic and kinetic definitions of p, T, U .

Later on, we'll carry out the same programme for a number of other systems:

- magnets (spins)
- rods and strings
- radiation (photons)
- diatomic gases
- solids (phonons)
- quantum gases (Fermi-Dirac and Bose)
- "real gases" (i.e. ^{eg.} gases where particles can crowd each other)