Physics 467/667: Thermal Physics **Spring 2019**

Lecture 23: Maxwell Distribution, Partition Functions and Free Energy

Lecturer: Qiang Zhu *Scribes: scribe-name1,2,3*

23.1 Maxwell Speed Distribution

In the very first lecture, we briefly mentioned a microscopic model to link the speed of particles to the temperature,

$$PV = Nm\bar{v}_x^2 = NkT \tag{23.1}$$

But this is just a sort of average. Technically, the speeds of particles should follow some distribution. Let's call it $D(v)$. What's the dependence of $D(v)$?

The first factor should be just the Boltzmann factor.

$$D(v) \propto e^{E/kT} = e^{-mv^2/2kT} \tag{23.2}$$

This only accounts for an ideal gas, where the transnational motion is independent of other variables.

The second factor should be the velocity space. For a given v, it could be in any direction. The the space is $4\pi v^2$. Therefore,

$$D(v) = C \cdot 4\pi v^2 e^{-mv^2/2kT} \tag{23.3}$$

Where C is a constant. According to

$$1 = \int_0^\infty D(v)dv = C \cdot 4\pi \int_0^\infty v^2 e^{-mv^2/2kT} dv \tag{23.4}$$

Changing variables to $x = v\sqrt{m/2kT}$,

$$1 = 4\pi C(\frac{2kT}{m})^{3/2} \int_0^\infty x^2 e^{-x^2} dx \tag{23.5}$$

By using some tricks, you can find

$$\int_0^\infty x^2 e^{-x^2} dx = \sqrt{\pi}/4 \tag{23.6}$$

Therefore, $C = (m/2\pi kT)^{3/2}$.

Our final result is therefore,

$$D(v) = (\frac{m}{2\pi kT})^{3/2} 4\pi v^2 e^{-mv^2/2kT} \tag{23.7}$$

The average speed:

$$\bar{v} = \int_0^\infty vD(v)dv = \sqrt{\frac{8kT}{\pi m}} \tag{23.8}$$

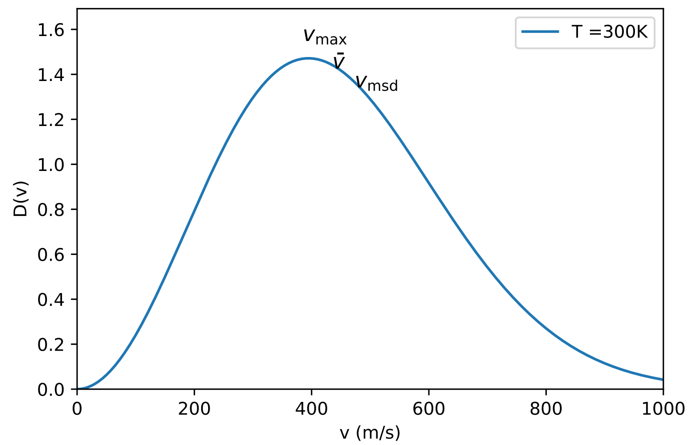

Figure 23.1: The Maxwell speed distribution and different types of characteristic speeds.

The rms speed:

$$\bar{v^2} = \int_0^\infty v^2 D(v) dv = 3kT/m \tag{23.9}$$

The most likely speed:

$$\frac{\partial D(v)}{\partial v} = 0 \quad \rightarrow \quad v_{\max} = \sqrt{\frac{2kT}{m}} \tag{23.10}$$

23.2 Partition Function and Free Energy

For a system in equilibrium with a reservoir at temperature T, the quantity most analogous to Ω is Z. Does the natural logarithm of Z have some meaning?

Recall the definition of $F = U - TS$, the partial derivative with respect to T is

$$(\frac{\partial F}{\partial T})_{V,N} = -S = \frac{F - U}{T} \tag{23.11}$$

This is a differential equation for the function $F(T)$, for any given V and N. If we use $\bar{F}$ to express the $kT\ln Z$, then

$$\frac{\partial \bar{F}}{\partial T} = \frac{\partial}{\partial T}(-kT\ln Z) = -k\ln Z - kT\frac{\partial}{\partial T}\ln Z \tag{23.12}$$

In the 2nd term, we rewrite it in terms of $\beta = 1/kT$

$$\frac{\partial}{\partial T} \ln Z = \frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta} \ln Z = \frac{-1}{kT^2}\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{U}{kT^2} \tag{23.13}$$

Therefore,

$$\frac{\partial \bar{F}}{\partial T} = -k\ln Z - kT\frac{U}{kT^2} = \frac{\bar{F} - U}{T} \tag{23.14}$$

Therefore, $\bar{F}$ obeys exactly the same differential equation as F.

At T=0, the original F is simply equal to U, the energy must be the lowest possible energy U_0, since the Boltzmann factors for all excited states will be infinitely suppressed in comparison to the ground state. Therefore,

$$\bar{F}(0) = -kT\ln Z(0) = U(0) = F(0) \tag{23.15}$$

This relation can be very useful to compute entropy, pressure, and so on.

$$S = -(\frac{\partial F}{\partial T})_{V,N} \quad P = -(\frac{\partial F}{\partial V})_{T,N} \quad \mu = (\frac{\partial F}{\partial N})_{V,T} \tag{23.16}$$