10.5: Blackbody Radiation

Before we forget all the equations in this chapter, let's use equation 10.2.12 (which we have already used twice – once in the derivation of the Joule-Thomson coefficient and once in the derivation of $C_P - C_V$) in a totally different application:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \tag{10.5.1}$$

This is a very general thermodynamical relation, and is by no means restricted to Joule's experiment. Let us apply it to electromagnetic radiation (rather than molecules) in an enclosure.

You may already have studied the theory of radiation in a cavity and the closely-related theory of blackbody radiation. You will know that classical electromagnetic theory failed to explain the observed characteristics of blackbody radiation, and that it was not explained fully until the advent of quantum theory. In the middle of the nineteenth century Kirchhoff argued theoretically that the energy density inside a cavity was independent of the nature of the walls of the cavity and depended only on the temperature and the wavelength. Stefan had shown experimentally that the radiation density inside a cavity integrated over all wavelengths was proportional to the fourth power of the temperature. Later on, Lummer and Pringsheim did some detailed measurements which showed how the radiation density per until wavelength varied with wavelength and temperature. It was shown by Rayleigh and Jeans that classical electromagnetic theory failed badly at short wavelengths to explain the observed distribution of the cavity radiation with wavelength. In 1900 Planck, without quite knowing why, showed that, if he regarded radiation as being made up of quanta of energy *hν*, the energy density per unit volume per unit wavelength interval would be expected to vary as $u_\lambda = \frac{C_1}{\lambda^5\left(e^{C_2/\lambda T}-1\right)}$ which agreed very well with the experimental data of Lummer and Pringsheim. You also may know that if you integrate this expression over all wavelengths (not particularly easy), you find that $\int u_\lambda d\lambda$ is proportional to T^4, thus also agreeing with the observations of Stefan.

However, although quantum theory was necessary to explain the Lummer-Pringsheim measurements of how u_λ varies with temperature, Boltzmann used classical thermodynamical theory to explain Stefan's T^4 law almost immediately after Stefan had announced his results, and long before the advent of quantum theory. The theory of radiation tells us that the radiation energy per unit volume u depends only on the temperature (this is Kirchhoff's radiation law) and that the radiation pressure P is related to the energy per unit volume by $P = \frac{1}{3}u$. The derivation of this is very similar to the expression that we derived for the pressure of molecules in a gas. For this situation, equation 10.2.12 becomes

$$u = \frac{1}{3}T\frac{du}{dT} - \frac{u}{3}, \tag{10.5.2}$$

or

$$4u = T\frac{du}{dT}. \tag{10.5.3}$$

Integration of this (do it!) shows that u ∝ T^4, without any need for quantum theory.

This is often written as u ∝ aT^4, but beware, here *a* is not what it generally known as "Stefan's constant". See Chapters 1 and 2 (especially Section 1.17) of my Stellar Atmospheres notes for more on this. Stefan's Law generally refers to the exitance of a black body surface, $M = \sigma T^4$, whereas here we are referring to the energy density of radiation in a cavity. The relation between a and Stefan's constant σ is $a = 4\sigma/c$.

Now suppose that you had some radiation at temperature *T* in an enclosure (such as The Universe) of volume *V*. And suppose that volume were to expand adiabatically, thus diluting the energy density. What would be the new temperature? In what follows, *V* means the volume (not the "specific" or "molar" volume) of the enclosure. *U* is the internal energy of the radiation inside it, and u is the radiation energy density, such that $U = uV$, and we shall be making use of $P = \frac{1}{3}u$ and of $u = aT^4$.

If the volume were to increase by *dV* at pressure *P*, the work done by the radiation would be $PdV = \frac{1}{3}udV$, and, if we assume that the expansion is adiabatic, this results (by the first law of thermodynamics) in a decrease of the internal energy. We apply the first law: $dU = -PdV$. That is

$$d(uV) = udV + Vdu = -\frac{1}{3}udV. \tag{10.5.4}$$

$$\frac{dV}{V} = -\frac{3}{4}\frac{du}{u}. \tag{10.5.5}$$

Therefore

$$V \propto u^{-3/4} \quad \text{or } u \propto V^{-4/3}. \tag{10.5.6}$$

But u ∝ T^4 and hence

$$VT^3 \text{ is constant,} \tag{10.5.7}$$

or the temperature is inversely proportional to the linear dimensions of the enclosure.