3.11: Thermodynamics Applied to Light

Another non-fluid system (see section 3.7).

See Robert E. Kelly, “Thermodynamics of blackbody radiation,” Am. J. Phys. 49 (1981) 714–719, and Max Planck, *The Theory of Heat Radiation*, part II.

How do you get a “box of light?” This is blackbody (cavity) radiation: meaning radiation in thermal equilibrium. (Usually it’s also in equilibrium with the cavity walls, but you could imagine a container with mirror walls. . .)

3.11.1 Fundamentals

The fundamental thermodynamic equation for this system involves the master function $E(S, V)$. It is

$$dE = TdS - pdV. \tag{3.11.1}$$

This equation differs from previously encountered master equations in that there is no term for $\mu\ dN$. From the classical perspective, this is because radiation is made up of fields, not particles. From the quantal perspective, this is because photon number is not conserved.

Thermodynamics binds one quantity to another, but it must use experiment (or statistical mechanics) to find the values being bound. For example, thermodynamics tells us that

$$C_p = C_V + TV\frac{\beta^2}{\kappa_T}, \tag{3.11.2}$$

but it cannot calculate either C_p, or C_V, or β, or κ_T: these quantities must be found by experiment (or through a statistical mechanical calculation). The empirical result that we will employ is that for blackbody radiation,

$$p = \frac{1}{3}\frac{E}{V} = \frac{1}{3}u. \tag{3.11.3}$$

This equation of state is the parallel for blackbody radiation to $pV = Nk_BT$ for ideal gases. It was discovered by experiment, but it can be derived from electrodynamics as well.

3.11.2 Energy density as a function of temperature

Consider the energy as a function of volume and temperature. Because $E(V, T)$ is extensive, but in the argument list only V is extensive (recall that N doesn’t appear in the argument list), we must have

$$E(V,T) = Vu(T). \tag{3.11.4}$$

That is, the energy density u depends only upon temperature. What is this dependence?

We seek a differential equation for $u(T)$. Compare

$$dE = d(Vu) = Vdu + udV = V\frac{du}{dT}dT + udV \tag{3.11.5}$$

with

$$dE = TdS - pdV = TdS - \frac{1}{3}udV. \tag{3.11.6}$$

Together these give us a formula for dS:

$$dS = \left(\frac{V}{T}\frac{du}{dT}\right)dT + \left[\frac{4}{3}\frac{u}{T}\right]dV. \tag{3.11.7}$$

The Maxwell relation associated with this differential is

$$\frac{\partial(\quad)}{\partial V})_T = \frac{\partial[\quad]}{\partial T})_V \tag{3.11.8}$$

or

$$\frac{1}{T}\frac{du}{dT} = \frac{4}{3}\frac{d[u/T]}{dT} = \frac{4}{3}\left[\frac{1}{T}\frac{du}{dT} - \frac{1}{T^2}u\right]. \tag{3.11.9}$$

A rearrangement gives

$$\frac{du}{dT} = 4\frac{u}{T} \tag{3.11.10}$$

The solution is

$$4\ln T = \ln u + \text{const} \tag{3.11.11}$$

whence

$$u(T) = \sigma T^4. \tag{3.11.12}$$

The Stefan-Boltzmann law!

3.11.3 Quasistatic adiabatic expansion of radiation

Consider a sample of radiation undergoing quasistatic adiabatic change of volume. The entropy is a constant during this process, although the value of that constant will of course depend on the particular sample that's expanding.

$$dE = TdS - pdV \tag{3.11.13}$$

but $dS = 0$, $E = uV$, and $p = u/3$ so

$$\begin{aligned} udV + Vdu &= -\frac{1}{3}udV \\ Vdu &= -\frac{4}{3}udV \\ \ln u &= -\frac{4}{3}\ln V + \text{const} \\ u &= KV^{-4/3} \end{aligned}$$

Recognizing that this constant will depend upon which adiabat is taken, i.e. that it will depend on the entropy, we write

$$u(S,V) = K(S)V^{-4/3}. \tag{3.11.14}$$

Using the Stefan-Boltzmann result $u = \sigma T^4$ we find that

$$T(S,V) = \frac{C(S)}{V^{1/3}}. \tag{3.11.15}$$

This explains the cooling of the universe as it expands from the initial "hot big bang" to the current "3^o K microwave background."

3.11.4 Thermodynamics of the energy spectrum

What if we consider not just the energy density per volume, but the energy density per volume and wavelength? Let

$$\overline{u}(T,\lambda)d\lambda \tag{3.11.16}$$

represent the energy per volume due to that radiation with wavelength between λ and λ + *d*λ. As you know, quantum mechanics was discovered through Planck's efforts to find a theoretical explanation for the measured function $\overline{u}(T,\lambda)$. This is not the place to describe Planck's work. Instead I want to focus on a purely thermodynamic result that was known long before Planck started his investigations.

This is Wien's law[8], which states that the function $\overline{u}(T,\lambda)$, which you'd think could have any old form, must be of the form

$$\overline{u}(T,\lambda) = T^5 f(\lambda T). \tag{3.11.17}$$

An immediate consequence of Wien's law is the Wien displacement theorem: The wavelength λ^ which maximizes $\overline{u}(T,\lambda)$ is inversely proportional to temperature:

$$\hat{\lambda}(T) = \frac{\text{constant}}{T}, \tag{3.11.18}$$

where the constant is the value of x that maximizes f(x). The consequences of the Wien displacement theorem are familiar from daily life: low temperature objects (such as people) radiate largely in the infrared, moderate temperature objects (such as horseshoes in the forge) radiate largely in the red, while high temperature objects (such as the star Sirius) radiate largely in the blue.

I stated earlier that Wien's law is a purely thermodynamic result. That's almost true, but it also relies on one more fact from electrodynamics, a result called "no mode hoping":

> If the volume makes a quasistatic, adiabatic change from V_1 to V_2, then the light of wavelength in the range λ_1 to $\lambda_1 + d\lambda_1$ shifts into the range λ_2 to $\lambda_2 + d\lambda_2$ where
>
> $$\frac{\lambda_1}{V_1^{1/3}} = \frac{\lambda_2}{V_2^{1/3}}. \tag{3.11.19}$$

(This result may be derived rigorously from Maxwell's equations, but it's reasonable through this analogy: A string of length L vibrating in, say, its third mode, has wavelength $\lambda = \frac{3}{2}L$. If the length of the string is slowly changed, then the wave remains in its third mode, so λ/L is constant.)

Now we're ready to begin the derivation. Consider the quasistatic adiabatic expansion of light, and while that expansion is going on focus your attention on the light in wavelength range λ to $\lambda + d\lambda$. According to the "no mode hopping" result, during this expansion the quantity

$$\lambda/V^{1/3} \tag{3.11.20}$$

remains constant during the expansion. Furthermore, according to equation (3.203) the quantity

$$TV^{1/3} \tag{3.11.21}$$

also remains constant. Multiplying these two equations, we find that the volume-independent quantity

$$T\lambda \tag{3.11.22}$$

remains constant during the expansion: this number characterizes the expansion.

Another such volume-independent constant can be found by repeating the reasoning of subsection 3.11.3, Quasistatic adiabatic expansion of radiation, but considering not the energy of all the radiation, but the energy of the radiation with wavelengths from λ to $\lambda + \Delta\lambda$. This energy is $E = \bar{u}V\Delta\lambda$, and the pressure due to this segment of the radiation is $p = \frac{1}{3}\bar{u}\Delta\lambda$. During a quasistatic adiabatic expansion, $dE = -pdV$, so

$$(V\Delta\lambda)d\bar{u} + (\bar{u}\Delta\lambda)dV + (\bar{u}V)d[\Delta\lambda] = -\frac{1}{3}\bar{u}\Delta\lambda dV. \tag{3.11.23}$$

During the expansion the volume and wavelengths are changing through (see equation 3.207)

$$\begin{aligned}
\lambda &= cV^{1/3} \\
d\lambda &= c\frac{1}{3}V^{-2/3}dV = \frac{1}{3}\frac{\lambda}{V}dV \\
d[\Delta\lambda] &= \frac{1}{3}\frac{\Delta\lambda}{V}dV
\end{aligned}$$

so we have

$$(V\Delta\lambda)d\bar{u} = -\frac{5}{3}\bar{u}\Delta\lambda dV. \tag{3.11.24}$$

Thus

$$\begin{aligned}
Vd\bar{u} &= -\frac{5}{3}\bar{u}dV \\
\ln\bar{u} &= -\frac{5}{3}\ln V + \text{const} \\
\bar{u} &= KV^{-5/3}
\end{aligned}$$

But equation (3.203) shows how a larger volume is related to a lower temperature, so the quantity

$$\frac{\bar{u}(T,\lambda)}{T^5} \tag{3.11.25}$$

remains constant during the expansion.

Thus we have two volume-independent ways to characterize the particular curve taken by this expansion. In the thermodynamics of light, a state is specified by two variables, so a curve is specified by only one parameter. Hence these two characterizations cannot be independent: one must be a function of the other. Thus

$$\frac{\bar{u}(T,\lambda)}{T^5} = f(\lambda T) \tag{3.11.26}$$

or

$$\bar{u}(T,\lambda) = T^5 f(\lambda T). \tag{3.11.27}$$

Wein's law.

[8]Wien is pronounced like the English “veen”.

Problems

3.42 Heat capacity of light

Show that, for blackbody radiation, $C_V = 4E/T$.

Resources

Thermodynamic tables. (G.N. Lewis and M. Randall) Zemansky. Practical heat engines. Callen. Fermi.

Math book. e.g. Taylor and Mann?

Picture of Smithsonian crystal on www?

Thermodynamic data (e.g. steam tables) on www?