Lecture 17 Blackbody Radiation 6 November 2008

Blackbody radiation is radiation in equilibrium with matter. So far, we have calculated the spectral energy density and the integrated energy density of blackbody radiation. What about entropy? One way might be from Helmholtz Free energy.

We can consider the energy of the cavity as an infinite number of harmonic oscillators; a system in equilibrium with a heat bath.

system - one SHO

heat bath - all the rest of the SHOs

Partition function for that system:

$$Z_1 = \sum_n e^{-E_n/kT} = \sum_n e^{-\hbar\omega(n+1/2)/kT} = \underbrace{e^{-\hbar\omega/2kT}}_{\text{Can neglect since it won't contribute to thermodynamic properties}} \sum_n e^{-\hbar\omega n/kT} = \cancel{Z_1}$$

$$Z_1 = \sum_{n=0}^{\infty} x^n \quad \text{where } x = e^{-\hbar\omega/kT}$$

$$Z_1 = 1 + x + x^2 + x^3 + \ldots = \left(\frac{1}{1-x}\right) = \frac{1}{(1-e^{-\hbar\omega/kT})}$$

partition function for one SHO in eq. with an infinite number of SHOs

The Partition Function for the photon gas or cavity radiation:

$$Z_{\substack{\text{photon}\\ \text{gas}}} = \prod_\alpha \left(\frac{1}{1-e^{-\hbar\omega_\alpha/kT}}\right)$$

Helmholtz Free Energy

$$F_{photon} = -kT \ln Z_{photon} = -kT \ln \Sigma\left(\frac{1}{1-e^{-\hbar\omega_\alpha/kT}}\right) = kT\Sigma\left(-\ln\left(\frac{1}{1-e^{-\hbar\omega/kT}}\right)\right)$$

$$F_{photon} = kT \sum_\alpha \ln(1-e^{-\hbar\omega_\alpha/kT})$$

since ω_α are closely spaced $\Sigma \to \int$. $\quad f(\omega)d\omega = \frac{V}{\pi^2 c^3}\omega^2 d\omega$

$$F_{photon} = kT\frac{V}{\pi^2 c^3}\int_0^\infty \omega^2 d\omega \ln(1-e^{-\hbar\omega/kT})$$

Convert to a dimensionless integral $x = \hbar\omega/kT$

$$F_{photon} = \frac{V}{\pi^2 c^3}\frac{(kT)^4}{\hbar^3}\underbrace{\int_0^\infty x^2 \ln(1-e^{-x})\,dx}_{\text{integrate by parts}}$$

$$\frac{x^3}{3}\ln(1-e^{-x})\Big|_0^\infty - \int_0^\infty \frac{x^3}{3}(1-e^{-x})^{-1}(-e^{-x})(-1)dx \approx \int_0^\infty \frac{x^3 dx}{e^x-1} = \frac{\pi^4}{15}$$

$$F_{photon} = \frac{-V\pi^2 k^4}{45 c^3 \hbar^3} T^4$$

Thermodynamics of Blackbody Radiation

Helmholtz Free Energy

$$F = -\frac{V\pi^2(kT)^4}{45(\hbar c)^3}$$ goes as T^4 like the total energy density

Fundamental thermodynamic Identity: $dE = TdS - PdV \rightarrow dF = -PdV - SdT$

$$F = F(V,T) \qquad dF = \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT = -PdV - SdT$$

Pressure

Cavity radiation exerts a pressure on the walls of the cavity. This is true even in classical theory.

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{\pi^2(kT)^4}{(45\ \hbar c)^3}$$

Entropy

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{4V\pi^2k^4T^3}{45(\hbar c)^3}$$ is the entropy of the photon gas.

Total Energy In the Cavity

$$E = F + TS = -\frac{V\pi^2(kT)^4}{45(\hbar c)^3} + T\left(\frac{4}{45}\frac{V\pi^2k^4T^3}{(\hbar c)^3}\right) = \frac{V\pi^2(kT)^4}{15(\hbar c)^3}$$ like before...

$$u(T) = \frac{E}{V} = \frac{\pi^2(kT)^4}{15(\hbar c)^3}$$

Relation of Pressure and Energy Density

$$P = \frac{1}{3}u(T)$$

Thermodynamics

$$E = V\cdot u(T) \qquad P = \frac{1}{3}u(T) \qquad dE = TdS - PdV = u(T)dV + V\left(\frac{du}{dT}\right)dT$$

$$dS = \frac{dE}{T} + \frac{PdV}{T} = \frac{1}{T}\left[u\,dV + V\frac{du}{dT}dT\right] + \frac{u}{3T}dV = \frac{4}{3}\frac{u\,dV}{T} + \frac{V}{T}\frac{du}{dT}dT$$

$$S = S(V,T) \quad dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT \rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \frac{4u}{3T}, \left(\frac{\partial S}{\partial T}\right)_V = \frac{V}{T}\frac{du}{dT}$$

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{\partial^2 S}{\partial V \partial T}$$

$$\frac{4}{3}\left\{\frac{1}{T}\frac{du}{dT} + u\left(\frac{-1}{T^2}\right)\right\} = \frac{1}{T}\frac{du}{dT} \rightarrow \frac{4dT}{3T} = \frac{1}{3}\frac{du}{u} \rightarrow u \propto T^4$$ got relationship

So even thermodynamics is not compatible with classical