8.044 Statistical Physics I
Spring 2008

Normal modes of the radiation field in a rectangular cavity with conducting walls

$$\vec{E}_{n_x,n_y,n_z,\vec{\epsilon}}(\vec{r},t) \qquad\qquad \omega = \left(\frac{\pi c}{L}\right)\sqrt{n_x^2+n_y^2+n_z^2}$$

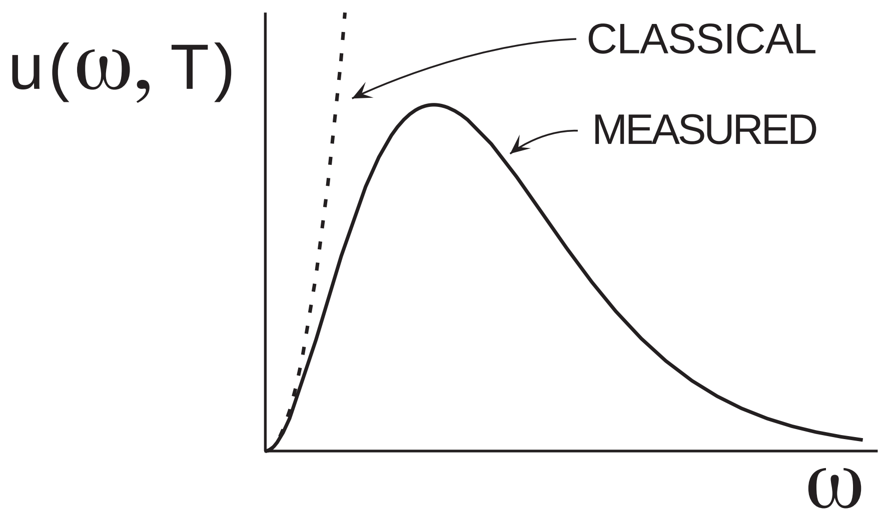
- Harmonic oscillators

- $D(\omega) = \frac{V}{\pi^2 c^3}\,\omega^2, \quad \omega \geq 0$

Classical Statistical Mechanics

$$< \epsilon(\omega) >= k_B T \quad \Rightarrow \quad u(\omega, T) =< \epsilon(\omega) > \frac{D(\omega)}{V} = \frac{k_B T}{\pi^2 c^3}\,\omega^2$$

$$u(T) = \int_0^\infty u(\omega, T)\, d\omega = \infty$$



Quantum Statistical Mechanics

$$< \epsilon(\omega) > = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} + \hbar\omega/2$$

$$u(\omega, T) = < \epsilon(\omega) > \frac{D(\omega)}{V} = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/kT} - 1} + \text{z. p. term}$$

To find the location of the maximum, set $\frac{du(\omega, T)}{d\omega} = 0$.

The maximum occurs at $\hbar\omega/kT \approx 2.82$.

$$Z = \prod_{\text{states } i} Z_i \qquad\qquad Z_i = e^{-\hbar\omega/2kT}(1 - e^{-\hbar\omega/kT})^{-1}$$

The first factor in the expression for Z_i comes from the zero-point energy.

$$F(V,T) = -kT \ln Z = -kT \sum_{\text{states } i} \ln Z_i$$

$$= -kT \int_0^\infty D(\omega) \left[\ln Z_i\right] d\omega$$

$$
\begin{aligned}
F(V,T) &= -kT \int_0^\infty D(\omega) \left[-\ln(1 - e^{-\hbar\omega/kT}) \right] d\omega + \cdots \\
&= \frac{kTV}{\pi^2 c^3} \int_0^\infty \omega^2 \ln(1 - e^{-\hbar\omega/kT})\, d\omega \\
&= \frac{V}{\pi^2 c^3 \hbar^3} (kT)^4 \underbrace{\int_0^\infty x^2 \ln(1 - e^{-x})\, dx}_{-\frac{\pi^4}{45}} \\
&= \underline{-\frac{1}{45} \frac{\pi^2}{c^3 \hbar^3} (kT)^4 V}
\end{aligned}
$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{1}{45}\frac{\pi^2}{(c\hbar)^3}(kT)^4$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{4}{45}\frac{\pi^2}{(c\hbar)^3}k^4T^3V$$

$$E = F + TS = \left(-\frac{1}{45} + \frac{4}{45}\right)(\cdots) = \frac{1}{15}\frac{\pi^2}{(c\hbar)^3}(kT)^4 V$$

Note: $P = \frac{1}{3}E/V = \frac{1}{3}u(T)$ independent of V.

NOTE: THE ADIABATIC PATH IS T^3V=CONSTANT