

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

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

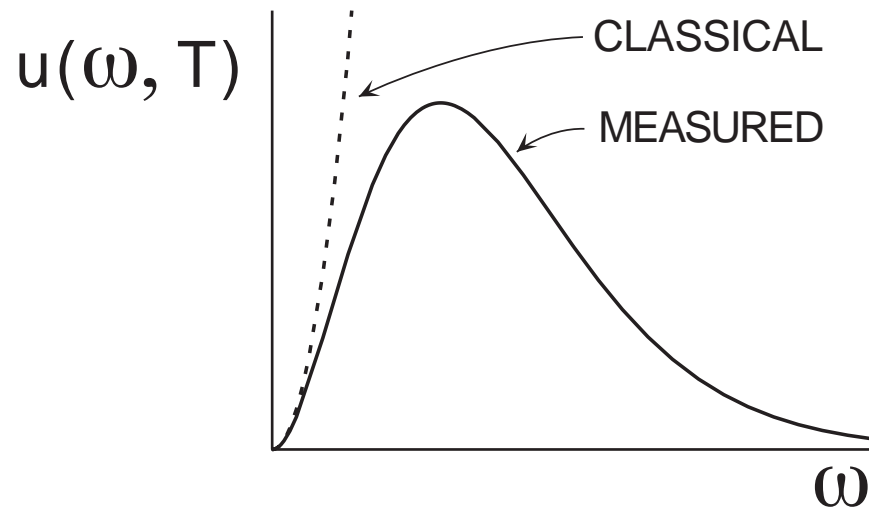
- Harmonic oscillators

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

Classical Statistical Mechanics

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

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



Quantum Statistical Mechanics

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

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

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

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

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

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

$$\begin{aligned} F(V, T) &= -kT \ln Z = -kT \sum_{\text{states } i} \ln Z_i \\ &= -kT \int_0^\infty D(\omega) [\ln Z_i] d\omega \end{aligned}$$

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

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

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

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

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

NOTE: THE ADIABATIC PATH IS $T^3V = \text{CONSTANT}$

