Lecture 1: Failure of Classical Statistical Mechanics

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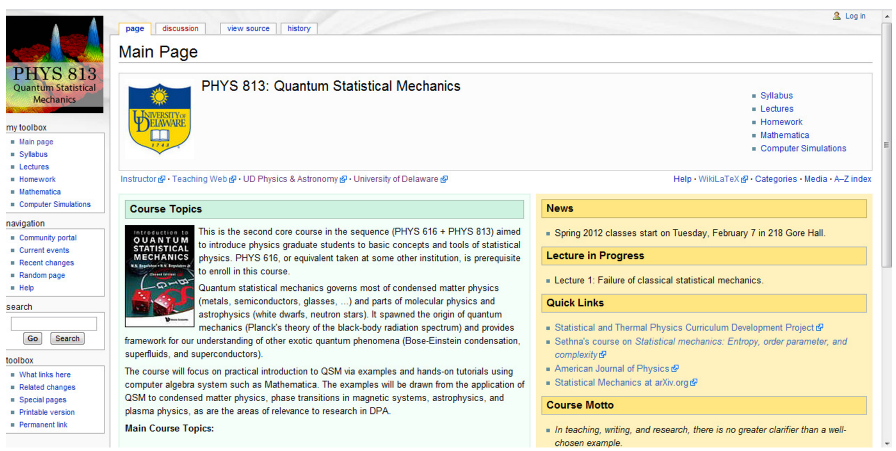
PHYS 813: Quantum Statistical Mechanics

http://wiki.physics.udel.edu/phys813



The Algorithm of Classical Statisical Mechanics for Canonical Ensemble

① CM $\vec{F} = m \cdot \vec{a}$ MD

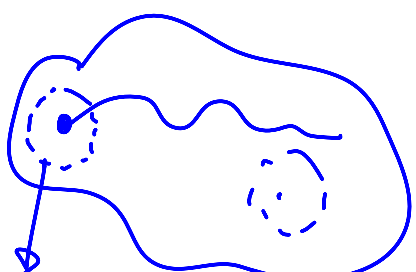
$\vec{v}$, $\vec{r}$, N

② CM $\dim = 6N$

PHASE SPACE

1. $H(p,q)$
2. $Z = \dfrac{1}{h^{3N} N!} \int e^{-\beta H(p,q)} d^{3N}p \, d^{3N}q$
3. $F = -k_B T \ln Z$
4. $P = -\partial F / \partial V, \ldots$

③ CSM



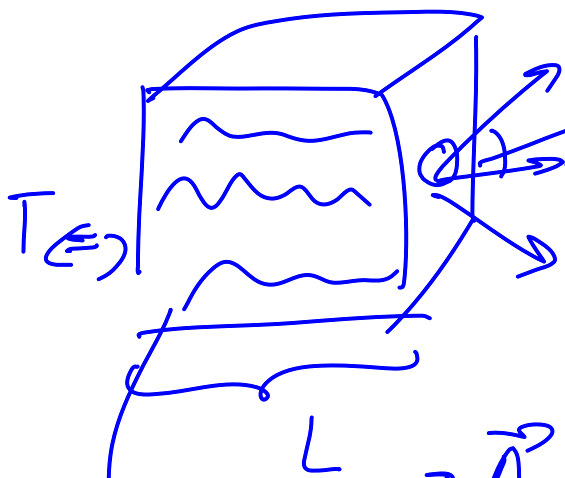
$\rho(p,q) \cdot d^{3N}p \, d^{3N}q$

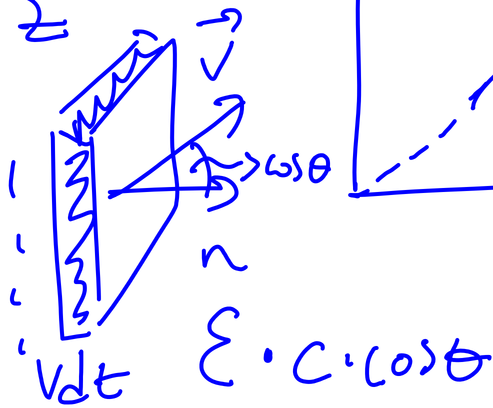
$\rho(p,q,t) = ?$ NEQ

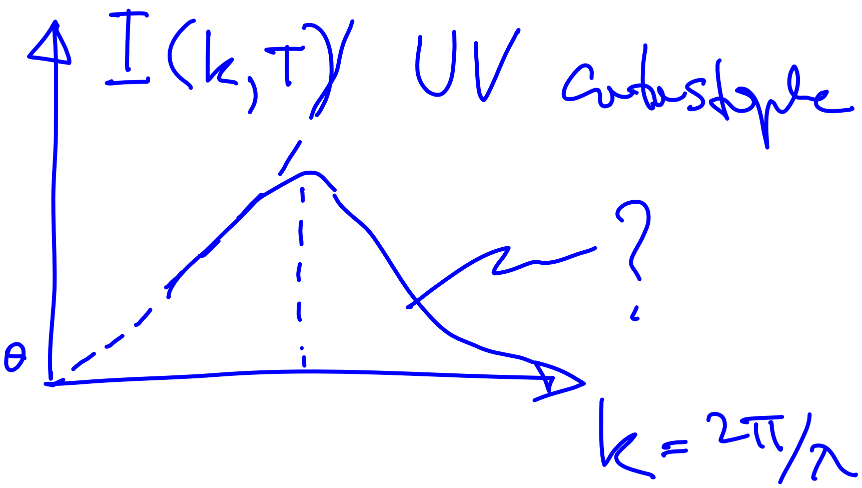
Eq $\neq f(t)$

CE: $\rho(p,q) = \dfrac{e^{-\beta H(p,q)}}{Z}$

Electromagnetic Field in Cavity at Temperature T







$$\vec{E}, \vec{B} \Rightarrow H(\vec{E}, \vec{B})$$

$$W_{EM} = W_E + W_B = \frac{1}{2}\varepsilon_0 \int_{\text{cube}} E^2\, dV + \frac{1}{2\mu_0}\int_{\text{cube}} B^2\, dV$$

$$\vec{E} = \frac{\partial \vec{A}}{\partial t}, \quad \vec{B} = \nabla \times \vec{A}\ ; \quad \vec{A} = A(x+L, y, z, t) = A(x, y+L, z, t) = \ldots$$

Decomposition of EM Field into Normal Modes

$$\vec{A}(\vec{r},t) = \sum_{\vec{k},\alpha}{}' \left(a_{\vec{k},\alpha}(t)\, e^{i\vec{k}\cdot\vec{r}} + a^{*}_{\vec{k},\alpha}\, e^{-i\vec{k}\cdot\vec{r}} \right)$$

$$\nabla \cdot \vec{E} = 0 \Rightarrow \vec{k}\cdot\vec{E} = 0 \,, \quad \alpha = 1,2$$

$$\longrightarrow \propto \left(a_{\vec{k},\alpha} + a^{*}_{\vec{k},\alpha}\right)$$

$$W_{EM} = \frac{1}{2} \sum_{\vec{k},\alpha}{}' \left(|P_{\vec{k},\alpha}|^2 + \omega_\alpha(\vec{k})\, |Q_{\vec{k},\alpha}|^2 \right)$$

$$\hookrightarrow \propto i\,\omega_\alpha(\vec{k}) \cdot \left(a_{\vec{k},\alpha} - a^{*}_{\vec{k},\alpha}\right)$$

$$\omega_\alpha(\vec{k}) = c \cdot |\vec{k}| = c \cdot k \,, \quad \alpha = 1,2$$

$$\vec{k},\alpha \longrightarrow k_B T \qquad \vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$$

Quantization of Normal Modes and Canonical Partition Function

$$H^{QM} = \sum_{\vec{k},\alpha}' \underbrace{\hbar\omega_\alpha(\vec{k})\left(n_\alpha(\vec{k})+1/2\right)}_{\text{L Ho}}$$

$$Z \overset{PHYS616}{=} \sum_n' e^{-\beta E_n}$$

, PHYS 616 $\rightarrow Z = Z_1^N$

$$= \sum_{\{n_\alpha(\vec{k})\}}' e^{-\beta H^{QM}} = \prod_{\vec{k},\alpha}\left[\sum_{n_\alpha(\vec{k})=0}^{\infty}{}' e^{-\beta\hbar c k\left(n_\alpha(\vec{k})+1/2\right)}\right]$$

$$= \prod_{\vec{k},\alpha} \frac{e^{-\beta\hbar c k/2}}{1-e^{-\beta\hbar c k}}$$

Evaluation of Canonical Partition Function and Thermodynamic Quantities

$$F = -k_B T \ln Z,$$

$$E = -\frac{\partial}{\partial \beta} \ln Z$$

$$p = -\partial F / \partial V = p_0 + \frac{1}{3}\frac{E}{V}$$

$$p_0 \;\Big|\; p_0' \;\Big|\; p_0$$

$$-\ln Z = \sum_{\vec{k},\alpha}{}' \left(\frac{\beta \hbar c k}{2} + \ln\left(1 - e^{-\beta \hbar c k}\right) \right)$$

$$E^*$$

$$E = -\frac{\partial}{\partial \beta} \ln Z = E_0 \cdot V + \sum_{\vec{k},\alpha}{}' \frac{e^{-\beta \hbar c k}}{1 - e^{-\beta \hbar c k}} \cdot \beta \hbar c k = E_0 V + \sum_{\vec{k},\alpha}{}' \frac{\hbar c k}{e^{\beta \hbar c k} - 1}$$

$$\sum_{\vec{k},\alpha}{}' f(\vec{k}) \to \frac{1}{\Delta \vec{k}} \sum{}' f(\vec{k}) \Delta \vec{k} \xrightarrow[\Delta \vec{k} \to 0]{\lim} \frac{L^3}{(2\pi)^3} \int f(\vec{k})\, d^3 \vec{k}$$

$$2\pi / L^3$$

Total Energy Flux Emitted by Cavity and Stefan-Boltzmann Law

$$E^* = 2\frac{V}{(2\pi)^3}\int \frac{\hbar c k}{e^{\beta\hbar c k}-1} d^3\vec{k} = 2\frac{V}{(2\pi)^3}\int \frac{\hbar c k}{e^{\beta\hbar c k}-1} k^2 \sin\theta\, d\theta\, d\varphi$$

$$x = \beta\hbar c k, \quad E^*/V = \frac{\hbar c}{\pi^2}\left(\frac{k_B T}{\hbar c}\right)^4 \int_0^\infty \frac{dx\, x^3}{e^x - 1} \qquad \pi^4/15$$

$$= \frac{\pi^2}{15}\left(\frac{k_B T}{\hbar c}\right)^3 k_B T$$

$$\Phi = \frac{E^*}{V}\cdot\langle c_\perp\rangle = \frac{\pi^2}{60}\frac{k_B^4}{\hbar^3 c^2} T^4 \qquad \text{Stefan-Boltzmann law}$$

$\pi/2$

$$\langle c_\perp\rangle = c/4\pi \int_0 \cos\theta\, 2\pi \sin\theta\, d\theta = c/4$$

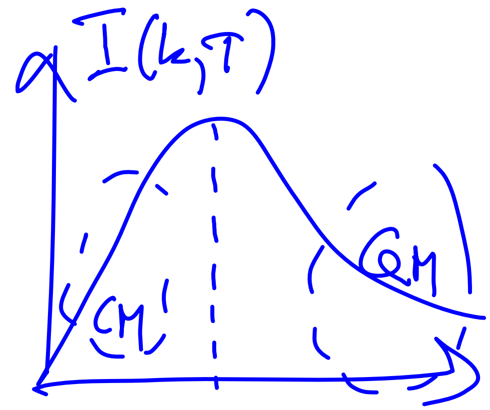
Energy Flux Emitted by Cavity at Each Wavevector (or Wavelength)

$$\frac{E^*(T)}{V} = \int dk\, \mathcal{E}(k,T)$$

$$k^* \approx \frac{k_B T}{\hbar c} \quad \text{QM}$$

$$\mathcal{E}(k,T)\cdot\frac{c}{4} = I(k,T)$$

$$I(k,T)\,dk \rightarrow [k, k+dk]$$



$$\mathcal{E}(k,T) = \frac{\hbar c}{\pi^2}\cdot\frac{k^3}{e^{\beta\hbar c k}-1}$$

$$I(k,T) = \frac{c}{4}$$

$$k^*(T) \approx \frac{k_B T}{\hbar c}$$

$$k \ll k^* \Rightarrow I(k,T) = \frac{c k_B T k^2}{4\pi}\ ; \quad k \gg k^*,\ I(k,T) = \frac{\hbar c^2 k^3 e^{-\beta\hbar c k}}{4\pi^2}$$