Part I: Phase Transitions

Part II: Dynamics and Correlation Functions

II.1 Linear Response Theory

<u>configuration space</u> $\Gamma = \{\vec{R}_i\}_{i=1..N}$

for N particles or

<u>phase space</u> $\Gamma = \{\vec{R}_i, \vec{P}_i\}_{i=1..N}$

as equivalent of sample space in probability theory, an event is denoted

$\omega = (\vec{R}_i, \vec{P}_i)_{i=1..N} \in \Gamma$

<u>canonical probability density</u> $\rho: \Gamma \to [0, \infty[$

$$\rho(\omega) = \frac{1}{Z} \exp\{-\beta \mathcal{H}(\omega)\}$$

Hamiltonian $\mathcal{H}: \Gamma \to \mathbb{R}$

partition sum $Z = \int \underbrace{d\Gamma(\omega)}_{\text{phase space element}} \exp\{-\beta \mathcal{H}(\omega)\} < \infty$

probability measure $\mathbb{P}: \mathcal{F}(\text{Borel sets of } \Gamma) \to [0,1]$

$$\mathbb{P}[F] = \int_F \rho(\omega)\, d\Gamma(\omega)$$

and $\mathbb{P}[\Gamma] = 1$ by construction

<u>random variables</u> $X: \Gamma \to \mathbb{R}$ phase space function

↳ observable of theory

canonical expectation

$$\mathbb{E}[X] = \langle X \rangle := \mathrm{Tr}(X\varrho) := \int d\Gamma(\omega)\, X(\omega)\, \varrho(\omega)$$

square-integrable complex random variable

$$X \in L^2(\Gamma, \mathbb{P}) \text{ if } \mathbb{E}[|X|^2] < \infty$$

$L^2(\Gamma, \mathbb{P})$ is a vector space

- $X \in L^2,\ \lambda \in \mathbb{C} \Rightarrow \lambda X \in L^2$ ✓
- $X, Y \in L^2 \Rightarrow |X+Y|^2 \leq |X| + |Y|)^2$
  $\leq 2^2 \max(|X|, |Y|) \leq 4 (|X|^2 + |Y|^2)$
  $\Rightarrow \mathbb{E}[|X+Y|^2] \leq 4(\mathbb{E}(|X|^2) + \mathbb{E}(|Y|^2)) < \infty$ ✓

If $X, Y \in L^2 \Rightarrow \mathbb{E}[X^* Y] < \infty$

$$|X^* Y| \leq |X||Y| = \frac{1}{2}(|X| + |Y|)^2 - \frac{1}{2}|X|^2 - \frac{1}{2}|Y|^2$$

$$\Rightarrow |\mathbb{E}[X^* Y]| \leq \frac{1}{2}\mathbb{E}[(|X| + |Y|)^2] < \infty \checkmark$$

Definition Inner Product

$$\langle X | Y \rangle := \mathbb{E}[X^* Y] = \langle X^* Y \rangle$$

overlap of fluctuating variables

Definition equivalance

$$X \sim Y \text{ if } \mathbb{P}[\{\omega \in \Gamma : X(\omega) \neq Y(\omega)\}] = 0$$

i.e. random variables differ only on sets of measure zero

Theorem: $L^2(\Gamma, \mathbb{P})$ is a Hilbert space with $\langle \cdot | \cdot \rangle$ as its scalar product

Proof: functional analysis

- inner product linear
$$\langle X | a_1 Y_1 + a_2 Y_2 \rangle = \ldots = a_1 \langle X|Y_1\rangle + a_2 \langle X|Y_2\rangle$$
- hermitian
$$\langle X|Y\rangle^* = \mathbb{E}[X^* Y]^* = \mathbb{E}[Y^* X] = \langle Y|X\rangle$$
- positive
$$\langle X|X\rangle = \mathbb{E}[|X|^2] \geq 0 \quad \text{and "=" only if } |X|^2 = 0$$

Static correlation functions are overlap matrix elements in Hilbert space. $\langle \cdot | \cdot \rangle$ is called Vubo product.

II. 1.A Fluctuation Response Theorem

reference system 0

$$\rho_0 = \frac{1}{Z_0} \exp\{-\beta \mathcal{H}_0\}$$

canonical averages

$$\langle X \rangle_0 = \mathrm{Tr}(X \rho_0) = \int d\Gamma(\omega)\, X(\omega) \rho(\omega)$$
$$= \int dP(\omega)\, X(\omega)$$

perturbation

$$\mathcal{H} = \mathcal{H}_0 - \alpha^i Y_i^* \quad , \text{Einstein convention}$$

$\alpha^i \in \mathbb{C}$, Y_i^* observables

$\mathcal{H} = \mathcal{H}^*$ real $\to$ only pairs of complex variables admissable fluctuation around expectation

$$\delta X_i = X_i - \langle X_i \rangle_0$$

perturbed partition sum

$$Z = \mathrm{Tr}(-\beta \mathcal{H}) = \mathrm{Tr}\, e^{-\beta \mathcal{H}_0} e^{\beta \alpha^i \langle Y_i^* \rangle_0} [1 + \beta \alpha^j Y_j^* + O(\alpha^2)] =$$

$$= Z_0 e^{\beta \alpha^i \langle Y_i^* \rangle} \langle 1 + \beta \alpha^j \delta Y_j^* + O(\alpha^2) \rangle$$

$$\langle \delta Y_j^* \rangle = 0$$

$$\boxed{Z = Z_0 e^{\beta \alpha^i \langle Y_i^* \rangle} [1 + O(\alpha^2)]}$$

perturbed probability measure $\rho = \rho_0 + \delta\rho$

with $\delta\rho = \frac{1}{Z_0} e^{-\beta \mathcal{H}_0} [\beta \alpha^j \delta Y_j^* + O(\alpha^2)]$ yields

$$\boxed{\delta\rho = \rho_0 \beta \alpha^j \delta Y_j^* + O(\alpha^2)}$$

observable X in perturbed ensemble

$$\langle X_i \rangle = \mathrm{Tr}(\rho X_i) = \mathrm{Tr}((\rho_0 + \delta\rho) X_i) =$$

$$= \langle X_i \rangle_0 + \mathrm{Tr}(\delta\rho X_i)$$

$$\langle \delta X_i \rangle = \beta \alpha^j \langle \delta Y_j^* X_i \rangle_0 = \beta \alpha^j \langle \delta Y_j^* \delta X_i \rangle_0$$

<u>Fluctuation Response Theorem</u>

$$\boxed{\langle \delta X_i \rangle = \beta \alpha^j \langle \delta Y_j \,|\, \delta X_i \rangle_0 + O(\alpha^2)}$$

<u>susceptibility</u>

$$\boxed{\chi_{XY} := \partial_\alpha \langle X \rangle = \beta \langle \delta Y | \delta X \rangle_0}$$

- fluctuations in equilibrium determine response to external perturbations
- thermal energy β connects response (macroscopic) to fluctuations (microscopic)

- specific heat

$$\beta_0 \mathcal{H} \to \beta\mathcal{H} \sim \beta_0\left(\mathcal{H} - \frac{\delta T}{T}\mathcal{H}\right)$$

$$c_V = \partial_T \langle \mathcal{H}\rangle = \beta \frac{1}{T}\langle(\delta\mathcal{H})^2\rangle_0$$

- fluctuating energy $e(\vec r)$ and particle $\rho(\vec r)$ density, local change in T and μ

$$\beta\mathcal{H} = \int_V d^3\vec r\ \beta e(\vec r) \to \int d^3\vec r\ \frac{e(\vec r)}{k_B T(\vec r)} - \beta\int_V d^3\vec r\ \delta\mu(\vec r)\rho(\vec r)$$

$$= \beta\mathcal{H} - \beta\frac{1}{T}\int_V e(\vec r)\,\delta T(\vec r) - \beta\int_V \delta\mu(\vec r)\rho(\vec r)\,d^3\vec r$$

with Fourier trafo $\delta T_{\vec q} = \int_V d^3\vec r\ e^{i\vec q\vec r}\delta T(\vec r)$

$$\delta T(\vec r) = \frac{1}{V}\sum_{\vec q} e^{-i\vec q\vec r}\delta T_{\vec q}$$

$$\to \beta\mathcal{H} - \frac{\beta}{VT}\sum_{\vec q}\delta T_{\vec q}\, e(\vec q)^* - \frac{\beta}{V}\sum_{\vec q}\delta\mu_{\vec q}\,\rho_{\vec q}^*$$

translational invariance: different wave vectors do not couple

$$\boxed{\begin{aligned}\delta X_{\vec q} &= \frac{\beta}{V}\langle \delta e_{\vec q} | \delta X_{\vec q}\rangle_0 \frac{\delta T_{\vec q}}{T} \\ &+ \frac{\beta}{V}\langle \delta\rho_{\vec q} | \delta X_{\vec q}\rangle_0\, \delta\mu_{\vec q}\end{aligned}}$$

changes in density define

S_q, static structure factor of a fluid

$$\langle \delta \rho_{\vec q} \rangle = \beta/V \langle \delta e_{\vec q} | \delta \rho_{\vec q} \rangle_0 \, \delta T_{\vec q}/T$$
$$+ \beta/V \langle | \delta \rho_{\vec q} |^2 \rangle \, \delta \mu_{\vec q}$$

$$\boxed{S(\vec q) := \frac{1}{N} \langle | \delta \rho_{\vec q} |^2 \rangle_0}$$

wave-number-dependent compressibility

$$\kappa_T(\vec q) = \frac{1}{\rho^2} \frac{\partial \langle \rho_{\vec q} \rangle}{\partial \mu_{\vec q}} \Big|_T = \beta/\rho \; S(\vec q)$$

$$\lim_{q \to 0} S(\vec q) = \rho/\beta \; \kappa_T = k_B T \, \partial_p \rho \big|_T$$

S_q measured in typical scattering experiment,
light, neutrons, ...