Correlation Functions & Responses to Disturbances

fluctuation here at $t=0$

anti-correlated fluctuation here at $t=t'$

$$\langle A(0)\cdot B(t')\rangle$$ ← fluctuation correlation also measures:

external push here at $t=0$

response here at $t=t'$ ← This is a measurement

We need to spend a little while on functional or variational derivatives:

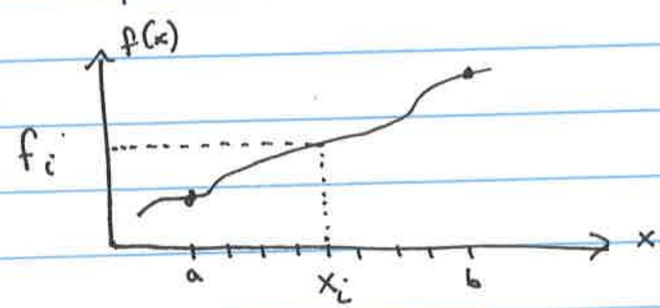
A Functional maps an entire function → number

$$F[f(x)]$$

a functional of $f(x)$

Q is a functional of the Hamiltonian: $Q = \int dr^N \int dp^N e^{-\beta \mathcal{H}}$

Here's one way to think about it:



A function with variable x discretized into a set of points $\{x_i\}$

With the discretization

$$F[f(x)] = F[f_1, f_2, \cdots f_n]$$

with

$$f_i = f(x_i)$$

Suppose we alter one value:

$$f_i \to f_i + \delta f_i$$

The functional would change

$$F \to F + \delta F$$

And the variation could depend on any of the discretized values, so in a Taylor series:

$$\delta F = \sum_{i=1}^{N} \underbrace{\left(\frac{\partial F}{\partial f_i}\right)_0}_{\text{evaluated where } \delta f_i = 0} \delta f_i + \sum_{i,j=1}^{N} \left(\frac{\partial^2 F}{\partial f_i \partial f_j}\right)_0 \delta f_i \delta f_j + \cdots$$

Now suppose the function is continuous instead of discrete:

$$\delta F = \int_a^b dx \underbrace{\left(\frac{\delta F}{\delta f(x)}\right)}_{\text{A functional derivative.}} \delta f(x) + \cdots$$

$\frac{\delta F}{\delta f(x)}$ is a function of x.

Suppose we have an exponential functional:

$$F = \int dx_1 \cdots \int dx_n \, e^{\sum_i f(x_i)}$$

Then

$$\delta F = \int dx_1 \cdots \int dx_n \sum_i \delta f(x_i)\, e^{\sum_j f(x_j)} + \text{H.O.T.}$$

$$\delta F = \int dx_1 \cdots \int dx_n \left(\sum_i \delta(x-x_i)\right) \delta f(x)\, e^{\sum_j f(x_j)} + \ldots$$

And therefore:

$$\frac{\delta F}{\delta f(x)} = \int dx_1 \cdots \int dx_n \left(\sum_i \delta(x-x_i)\right) e^{\sum_j f(x_j)}$$

A functional derivative is essentially a partial derivative for a continuum of variables:

$$\frac{\partial F}{\partial x} \longrightarrow \frac{\delta F}{\delta f(x)}$$

1 variable continuous variables

they have chain rules:

$$\frac{\delta F}{\delta g(x)} = \int \left(\frac{\delta F}{\delta f(x')}\right)\left(\frac{\delta f(x')}{\delta g(x)}\right) dx'$$

and identities:

$$\frac{\delta f(x)}{\delta f(x')} = \delta(x-x')$$

Let $\phi(\vec{r})$ = external potential field at $\vec{r}$

$$\Phi = \sum_{i=1}^{N} \phi(\vec{r}_i) = \int d\vec{r} \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i)\, \phi(\vec{r})$$

particle locations

$$= \int d\vec{r}\; \phi(\vec{r})\, \rho(\vec{r})$$

particle density

At constant N, V, T,

$$A = -k_B T \ln Q$$

contains Φ also

$$e^{-\beta A} = Q = \frac{1}{N!\,\lambda^{3N}} \int d\vec{r}^N \, e^{-\beta U(r^N)}$$

all momentum parts

$$= Q_{ideal} \int \frac{d\vec{r}^N}{V^N} \, e^{-\beta U(r^N)}$$

If there's an external potential, it is built in to U

We can take a functional derivative:

$$\frac{\delta(-\beta A)}{\delta(-\beta \phi(\vec{r}))} = \frac{-\delta \ln Q}{\delta(\beta\phi(\vec{r}))}$$ ← from above

$$= -\frac{1}{Q} \frac{\delta Q}{\delta(\beta\phi(\vec{r})}$$

$$= \frac{(-1/\beta)}{\int dr^N e^{-\beta U}} \int dr^N \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i) \frac{\partial}{\partial\phi(r_i)} e^{-\beta U}$$

Since Φ is built in to U:

$$U = \text{potential} + \sum_{i=1}^{N} \phi(\vec{r}_i) \Rightarrow \frac{\partial \ln e^{-\beta U}}{\partial \phi(\vec{r}_i)} = -\beta$$

$$\therefore \quad \frac{\delta(-\beta A)}{\delta(-\beta\phi(\vec{r}))} = \frac{\int d\vec{r}^N \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i)\, e^{-\beta U}}{\int d\vec{r}^N \, e^{-\beta U}} = \langle \rho(\vec{r}) \rangle$$

$$\therefore \quad \frac{\delta A}{\delta \phi(\vec{r})} = \langle \rho(\vec{r}) \rangle$$

What does this <u>mean</u>?

Reversible work to change the potential <u>field</u> at point $\vec{r}$ is proportional to the probability of finding a particle at $\vec{r}$.

One more functional derivative:

$$\frac{\delta \langle \rho(\vec{r}) \rangle}{\delta(-\beta\phi(\vec{r}\,'))} = \frac{\delta^2(-\beta A)}{\delta(-\beta\phi(\vec{r}))\,\delta(-\beta\phi(\vec{r}\,'))}$$

$$= \frac{\delta}{\delta(-\beta\phi(\vec{r}\,'))}\left[\frac{1}{\int dr^N e^{-\beta U}} \int dr^N \rho(\vec{r}) e^{-\beta U}\right]$$

Eg. A "partial" with $\rho(\vec{r})$ held fixed.

Again, since

$$U = U_0 + \int d\vec{r}\, \rho(\vec{r})\phi(\vec{r})$$

$$\frac{\delta\langle \rho(\vec{r})\rangle}{\delta(-\beta\phi(\vec{r}\,'))} = \frac{-1}{(\int dr^N e^{-\beta U})^2}\left[\int dr^N \rho(\vec{r}) e^{-\beta U}\right]\left[\int dr^N \rho(\vec{r}\,') e^{-\beta U}\right]$$

$$+ \frac{1}{(\int dr^N e^{-\beta U})} \int dr^N \rho(\vec{r})\rho(\vec{r}\,') e^{-\beta U}$$

$$= \langle \rho(\vec{r})\rho(\vec{r}\,')\rangle - \langle\rho(\vec{r})\rangle\langle\rho(\vec{r}\,')\rangle$$

That is:

$$\frac{\delta \langle \rho(\vec{r}) \rangle}{\delta \phi(\vec{r}\,')} = -\beta \langle \delta\rho(\vec{r}) \cdot \delta\rho(\vec{r}\,') \rangle$$

$$\equiv -\beta \chi(\vec{r}, \vec{r}\,')$$

with $\delta\rho(\vec{r}) = \rho(\vec{r}) - \langle \rho(\vec{r}) \rangle$

In English, the response of density at $\vec{r}$ to a disturbance at $\vec{r}\,'$ is proportional to spontaneous density fluctuations at the two points

This is a <u>very</u> important result!

Linear & Self-consistent models of correlation functions

Results to date:

$$\frac{\delta A}{\delta \phi(\vec{r})} = \langle \rho(\vec{r}) \rangle$$

$$\frac{\delta \langle \rho(\vec{r}) \rangle}{\delta \phi(\vec{r}\,')} = -\beta \langle \delta\rho(\vec{r}) \cdot \delta\rho(\vec{r}\,') \rangle$$

The idea is to take these results and treat a single particle as responsible for $\phi(\vec{r})$

test particle at origin

If $\phi(\vec{r})$ = effect of test particle at origin $= 0$
then particle has been removed.

If $\phi(\vec{r}) = u(r) =$ pair potential, particle is back.

$$0 \xrightarrow{\phi(\vec{r})} u(r) \qquad \leftarrow \text{effect on potential}$$

$$\rho \xrightarrow{\langle \rho(\vec{r}) \rangle} \rho g(r) \qquad \leftarrow \text{effect on density}$$

Bulk density (nothing special about origin)

there's a particle known to be at the origin!

How can we connect $g(r)$ (a bulk property) to $u(r)$ (a microscopic property)?

A functional Taylor series:

$$\langle \rho(\vec{r}) \rangle = \rho + \int d\vec{r}\,' \left(\frac{\delta \langle \rho(\vec{r}) \rangle}{\delta \phi(\vec{r}\,')} \right)_0 \phi(\vec{r}\,')$$

$$+ \frac{1}{2} \int d\vec{r}\,' \int d\vec{r}\,'' \left(\frac{\delta^2 \langle \rho(\vec{r}) \rangle}{\delta \phi(\vec{r}\,') \, \delta \phi(\vec{r}\,'')} \right)_0 \phi(\vec{r}\,') \, \phi(\vec{r}\,'')$$

$$+ \ldots$$

We neglect beyond <u>linear</u> order:

$$\rho g(r) = \rho + \int d\vec{r}\,' \chi(\vec{r}, \vec{r}\,') \left[-\beta u(\vec{r}\,') \right]$$

For a uniform system we can recall the definition of $g(r)$:

$$\chi(\vec{r}, \vec{r}\,') = \rho \, \delta(\vec{r} - \vec{r}\,') + \rho^2 \left[g(|\vec{r} - \vec{r}\,'|) - 1 \right]$$

$\therefore$

$$\rho g(r) = \rho + \int d\vec{r}\,' \left[\rho \, \delta(\vec{r} - \vec{r}\,') + \rho^2 \left[g(|\vec{r} - \vec{r}\,'|) - 1 \right] \right] (-\beta u(\vec{r}\,'))$$

$h(r) \equiv g(r) - 1$, so

$$\boxed{h(r) = -\beta u(r) + \rho \int d\vec{r}\,' \left[-\beta u(\vec{r}\,') \right] h(|\vec{r} - \vec{r}\,'|)}$$

This self-consistent linear equation is also known as the Debye-Hückel equation.

It has the form of a <u>convolution</u> integral

$$f(x) = \int a(x) \, b(x+y) \, dy$$

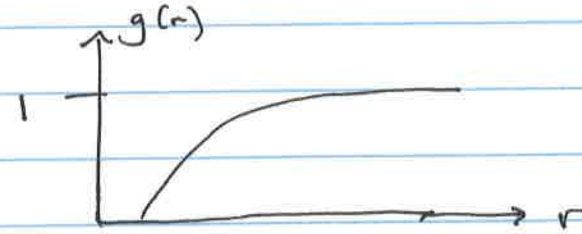
It can even be solved analytically for some pair potentials.

If we know $u(r) \xrightarrow{FT} \hat{u}(k) \rightarrow \hat{h}(k) \xrightarrow{IFT} h(r) \rightarrow g(r)$

If $u(r) = \dfrac{Z^2}{r}$ with Z = charge

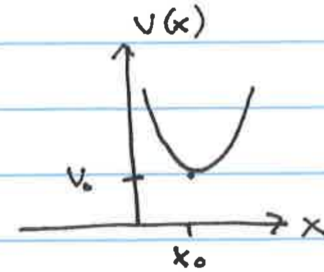
$$h(r) = -\left(\frac{Z^2}{r k_B T}\right) e^{-\kappa r} \qquad \text{with } \kappa = \sqrt{\frac{4\pi Z^2}{\rho k_B T}}$$

$$g(r) = 1 - \frac{Z^2}{r k_B T} e^{-\kappa r}$$



← g(r) for electron gas

Linear Models & Harmonic Oscillators



Consider: $$V(x) = V_0 + \frac{1}{2\alpha}(x-x_0)^2$$

$$P(x) \propto e^{-\beta V(x)} = e^{-\beta V_0} \, e^{-\beta(x-x_0)^2/2\alpha}$$

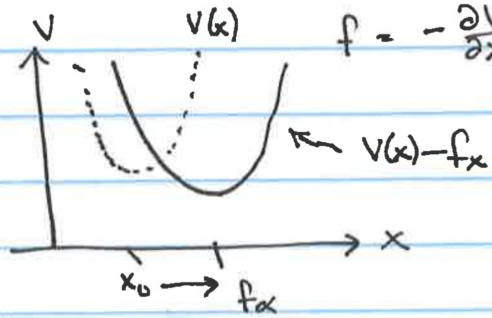
Gaussian!

second moment

$$\langle x \rangle = x_0$$
$$\langle (\delta x)^2 \rangle = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 = \frac{\alpha}{\beta}$$

Suppose we apply an external disturbance with force f.

$$V \rightarrow V(x) - fx$$



$$f = -\frac{\partial V}{\partial x} \Rightarrow V_{applied} = -fx$$

The average position is now:

$$\langle x \rangle_f = x_0 + f\alpha = x_0 + f\beta\langle(\delta x)^2\rangle$$

$$\therefore \frac{\partial \langle x \rangle_f}{\partial f} = \beta\langle(\delta x)^2\rangle \quad \text{i.e. linear response!}$$

response to perturbations

equilibrium fluctuations

We can also do this for multi-dimensional Harmonic Oscillators:

$$V(\vec{x}) = \frac{1}{2}\vec{x}^T \cdot \underline{\underline{K}} \cdot \vec{x} \quad - \vec{f}^T \cdot \vec{x}$$

Here $\vec{x} = (x_1, \ldots x_N)$ and

$$\vec{x}^T \cdot \underline{\underline{K}} \cdot \vec{x} = \sum_i \sum_j x_i x_j K_{ij}$$

← Hessian or force constant matrix

$$\vec{f}^T \cdot \vec{x} = \sum_i f_i x_i$$

One of the things we won't prove, but will use:

$$(K^{-1})_{ij} = \beta \langle \delta x_i \, \delta x_j \rangle \quad \text{in the absence of } \vec{f}$$

With non-zero $\vec{f}$, $V_{min} = \langle \vec{x} \rangle_f$

and

$$\langle x_i \rangle_f = \left(\vec{f}^T \cdot K^{-1} \right)_i = \sum_j f_j \, \beta \langle \delta x_i \, \delta x_j \rangle$$

or:

$$\frac{\partial \langle x_i \rangle_f}{\partial f_j} = \beta \langle \delta x_i \, \delta x_j \rangle$$

response of coordinate i to force on j.

cross correlation between coordinates i & j (at equilibrium)