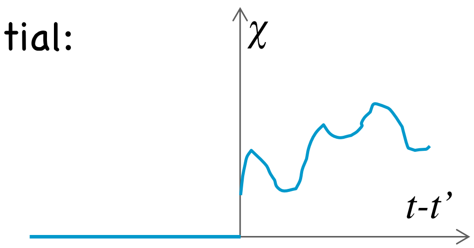
Lesson 6: Fluctuation-Dissipation Theorem, response function and related stuff

- ✓ Deconstruction of Fluctuation-Dissipation theorem
- ✓ Causal response function and consequences
- ✓ Classical limits and limiting behavior
- ✓ Damped harmonic oscillator

Dynamical extension of the structure of liquids

A step backward: deconstructing Fluctuation-Dissipation theorem



- Let's consider the linear space-time response in density to an external potential:

$$\delta\rho(\mathbf{r},t) = \int d\mathbf{r}' \int_{-\infty}^{t} \chi_l(\mathbf{r}-\mathbf{r}', t-t')\, v(\mathbf{r}',t')\, dt = \int d\mathbf{r}' \int_{-\infty}^{+\infty} \chi(\mathbf{r}-\mathbf{r}', t-t')\, v(\mathbf{r}',t')\, dt$$

$$\chi(\mathbf{r}-\mathbf{r}', t-t') = \chi_l(\mathbf{r}-\mathbf{r}', t-t')\,\Theta(t-t')$$

- Note that the first integral is over all the space coordinate, but, due to causality, the integral over time is only between -∞ and t. The space-time symmetry can be restored including the Heaviside step function
- The function χ_l is defined only for positive times, while χ is defined for all times and null for negative
- Passing to the FT both in space and time domain (i.e. trasforming with $\exp[i(\mathbf{kx}-\omega t)]$) one gets

$$\delta\bar{\rho}(\mathbf{k},\omega) = \bar{\chi}(\mathbf{k},\omega)\,\bar{v}(\mathbf{k},\omega)$$

$$\bar{\chi}(\mathbf{k},\omega) = \int d\omega' \bar{\chi}_l(\mathbf{k},\omega-\omega')\bar{\Theta}(\omega') = \int d\omega' \bar{\chi}_l(\mathbf{k},\omega-\omega')\left[\frac{1}{2}\delta(\omega') + \frac{i}{2\pi\omega'}\right] = \frac{1}{2}\left[\bar{\chi}_l(\mathbf{k},\omega) + \int d\omega' \frac{i}{\pi\omega'}\bar{\chi}_l(\mathbf{k},\omega-\omega')\right]$$

- χ_l is real in the positive t domain. In the negative t domain it can assume any value, without loosing generality. Therefore we first assume it symmetric. We then have $\bar{\chi}_l(\mathbf{k},\omega)$ symmetric and real. Therefore

$$\mathrm{Re}\left[\bar{\chi}(\mathbf{k},\omega)\right] = \frac{1}{2}\bar{\chi}_l(\mathbf{k},\omega) \qquad \mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega)\right] = \frac{1}{2}\int d\omega' \frac{\bar{\chi}_l(\mathbf{k},\omega-\omega')}{\pi\omega'} \Rightarrow \boxed{\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega)\right] = \int d\omega' \frac{\mathrm{Re}\left[\bar{\chi}(\mathbf{k},\omega-\omega')\right]}{\pi\omega'}}$$

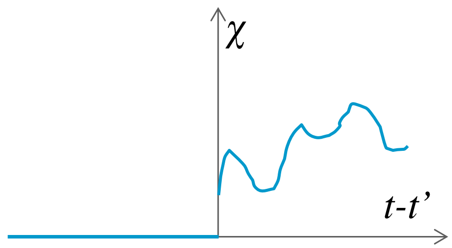
- Assuming now the antisymmetric extension of χ_l, we have that $\bar{\chi}_l(\mathbf{k},\omega)$ is imaginary (and antisimmetric)

$$\mathrm{Re}\left[\bar{\chi}(\mathbf{k},\omega)\right] = -\frac{1}{2}\int d\omega' \frac{\bar{\chi}_l(\mathbf{k},\omega-\omega')}{\pi\omega'} \qquad \mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega)\right] = \frac{1}{2}\bar{\chi}_l(\mathbf{k},\omega) \Rightarrow \boxed{\mathrm{Re}\left[\bar{\chi}(\mathbf{k},\omega)\right] = -\int d\omega' \frac{\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega-\omega')\right]}{\pi\omega'}}$$

Dynamical extension of the structure of liquids

A step backward: deconstructing FD theorem

Linear response



$$\delta\rho(\mathbf{r},t) = \int d\mathbf{r}' \int_{-\infty}^{t} \chi_l(\mathbf{r}-\mathbf{r}',t-t')v(\mathbf{r}',t')\,dt = \int d\mathbf{r}' \int_{-\infty}^{+\infty} \chi(\mathbf{r}-\mathbf{r}',t-t')v(\mathbf{r}',t')\,dt$$

$$\chi(\mathbf{r}-\mathbf{r}',t-t') = \chi_l(\mathbf{r}-\mathbf{r}',t-t')\Theta(t-t') \qquad \delta\bar\rho(\mathbf{k},\omega) = \bar\chi(\mathbf{k},\omega)\bar v(\mathbf{k},\omega)$$

$$\mathrm{Re}\left[\bar\chi(\mathbf{k},\omega)\right] = \frac{1}{2}\bar\chi_l(\mathbf{k},\omega) \qquad \mathrm{Im}\left[\bar\chi(\mathbf{k},\omega)\right] = \frac{1}{2}\int d\omega' \frac{\bar\chi_l(\mathbf{k},\omega-\omega')}{\pi\omega'} \Rightarrow \mathrm{Im}\left[\bar\chi(\mathbf{k},\omega)\right] = \int d\omega' \frac{\mathrm{Re}\left[\bar\chi(\mathbf{k},\omega-\omega')\right]}{\pi\omega'}$$

$$\mathrm{Re}\left[\bar\chi(\mathbf{k},\omega)\right] = -\frac{1}{2}\int d\omega' \frac{\bar\chi_l(\mathbf{k},\omega-\omega')}{\pi\omega'} \qquad \mathrm{Im}\left[\bar\chi(\mathbf{k},\omega)\right] = \frac{1}{2}\bar\chi_l(\mathbf{k},\omega) \Rightarrow \mathrm{Re}\left[\bar\chi(\mathbf{k},\omega)\right] = -\int d\omega' \frac{\mathrm{Im}\left[\bar\chi(\mathbf{k},\omega-\omega')\right]}{\pi\omega'}$$

- ✓ χ is real, therefore. $\bar\chi(\mathbf{k},\omega) = \bar\chi^*(\mathbf{k},-\omega)$. With a variable change one has

$$\mathrm{Im}\left[\bar\chi(\mathbf{k},\omega)\right] = -\int d\omega' \frac{\mathrm{Re}\left[\bar\chi(\mathbf{k},\omega')\right]}{\pi(\omega'-\omega)} \qquad \mathrm{Re}\left[\bar\chi(\mathbf{k},\omega)\right] = \int d\omega' \frac{\mathrm{Im}\left[\bar\chi(\mathbf{k},\omega')\right]}{\pi(\omega'-\omega)}$$

namely the Kramers Kronig relations or, recasting it in a general complex form: $\bar\chi(\mathbf{k},\omega) = \int \frac{d\omega'}{i\pi}\frac{\bar\chi(\mathbf{k},\omega')}{(\omega'-\omega)}$

- ✓ The KK relationships depends on causality and consequent indefiniteness of the response function in the “future times”
- ✓ Mathematically, these are related to the convolution with the response function with a Heaviside function and to the possibility of evaluating an integral in the complex space on different paths
- ✓ The FT of χ_l is undefined. Only its Laplace transform is defined, and coincides with the FT of χ
- ✓ The integrals involved in the KK relations is called Hilbert transform:

Real and imaginary part of a causal response function are the Hilbert transform one another;
The total causal response function is the complex Hilbert transform of itself

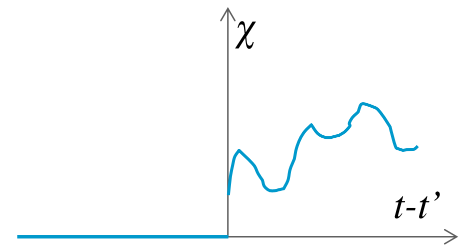
Dynamical extension of the structure of liquids

A step backward: deconstructing FD theorem

Linear response

$$\delta\rho(\mathbf{r},t) = \int d\mathbf{r}' \int_{-\infty}^{t} \chi_l(\mathbf{r}-\mathbf{r}',t-t')v(\mathbf{r}',t')\,dt = \int d\mathbf{r}' \int_{-\infty}^{+\infty} \chi(\mathbf{r}-\mathbf{r}',t-t')v(\mathbf{r}',t')\,dt$$

$$\chi(\mathbf{r}-\mathbf{r}',t-t') = \chi_l(\mathbf{r}-\mathbf{r}',t-t')\Theta(t-t')$$



Causality, KK

$$\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega)\right] = -\int \frac{d\omega'}{\pi}\frac{\mathrm{Re}\left[\bar{\chi}(\mathbf{k},\omega')\right]}{(\omega'-\omega)} \qquad \mathrm{Re}\left[\bar{\chi}(\mathbf{k},\omega)\right] = \int \frac{d\omega'}{\pi}\frac{\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega')\right]}{(\omega'-\omega)} \qquad \bar{\chi}(\mathbf{k},\omega) = \int \frac{d\omega'}{i\pi}\frac{\bar{\chi}(\mathbf{k},\omega')}{(\omega'-\omega)}$$

Effect of the external perturbation (static)

- ✓ We now evaluate the system reaction to an external perturbation to the Hamiltonian within the perturbation theory. We first consider the static case: a system is subject to an external field constant in time, and is in steady state. Therefore the static susceptibility comes into play.
- ✓ Because of the invariance by inversion, $\chi_s(\mathbf{r})$ is symmetric (and real). Therefore its space FT $\chi_s(\mathbf{k})$ is symmetric and real

$$\delta\rho(\mathbf{r}) = \int d\mathbf{r}'\chi_s(\mathbf{r}-\mathbf{r}')v(\mathbf{r}')$$

$$\delta\bar{\rho}(\mathbf{k}) = \bar{\chi}_s(\mathbf{k})\bar{v}(\mathbf{k})$$

$$\chi_s(\mathbf{r}-\mathbf{r}') = \int \chi(\mathbf{r}-\mathbf{r}',t)\,dt$$

- ✓ We now assume that the Hamiltonian of the system is $H = H_0 - \int d\mathbf{r}' v(\mathbf{r}')\delta\hat{\rho}(\mathbf{r}')$ $\qquad \hat{\rho}(\mathbf{r}) = \sum \delta(\mathbf{r}-\mathbf{r}_i)$

(the minus sign indicates that the density variation induced by an external field decreases the total energy)

- ✓ Assuming the classical Boltzmann distribution at equilibrium and small perturbations one gets

$$\delta\rho(\mathbf{r}) = \left\langle \delta\hat{\rho}(\mathbf{r})\right\rangle = \frac{1}{Z}\int \delta\hat{\rho}(\mathbf{r})\exp(-\beta H) \approx \frac{1}{Z}\int \delta\hat{\rho}(\mathbf{r})\exp(-\beta H_0)[1+\beta\int d\mathbf{r}'\,v(\mathbf{r}')\delta\hat{\rho}(\mathbf{r}')] = \beta\int d\mathbf{r}'\,v(\mathbf{r}')\left\langle \delta\hat{\rho}(\mathbf{r})\delta\hat{\rho}(\mathbf{r}')\right\rangle_0$$

(the last equality descends from the definition of χ_s)

The thermal fluctuation correlations in absence of external fields are related to the linear response function

$$\Rightarrow \chi_s(\mathbf{r}-\mathbf{r}') = \frac{1}{kT}\left\langle \delta\hat{\rho}(\mathbf{r})\delta\hat{\rho}(\mathbf{r}')\right\rangle_0$$

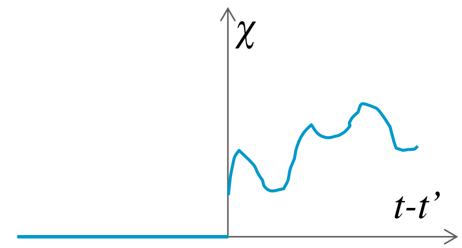
Dynamical extension of the structure of liquids

A step backward: deconstructing FD theorem

Linear response

$$\delta\rho(\mathbf{r},t)=\int d\mathbf{r}'\int_{-\infty}^{t}\chi_l(\mathbf{r}-\mathbf{r}',t-t')v(\mathbf{r}',t')\,dt=\int d\mathbf{r}'\int_{-\infty}^{+\infty}\chi(\mathbf{r}-\mathbf{r}',t-t')v(\mathbf{r}',t')\,dt$$

$$\chi(\mathbf{r}-\mathbf{r}',t-t')=\chi_l(\mathbf{r}-\mathbf{r}',t-t')\Theta(t-t')$$



Causality, KK

$$\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega)\right]=-\int\frac{d\omega'}{\pi}\frac{\mathrm{Re}\left[\bar{\chi}(\mathbf{k},\omega')\right]}{(\omega'-\omega)}\qquad \mathrm{Re}\left[\bar{\chi}(\mathbf{k},\omega)\right]=\int\frac{d\omega'}{\pi}\frac{\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega')\right]}{(\omega'-\omega)}\qquad \bar{\chi}(\mathbf{k},\omega)=\int\frac{d\omega'}{i\pi}\frac{\bar{\chi}(\mathbf{k},\omega')}{(\omega'-\omega)}$$

Effect of the external perturbation (static)

$$\delta\rho(\mathbf{r})=\int d\mathbf{r}'\chi_s(\mathbf{r}-\mathbf{r}')v(\mathbf{r}')\qquad \delta\bar{\rho}(\mathbf{k})=\bar{\chi}_s(\mathbf{k})\bar{v}(\mathbf{k})\qquad \left\langle\delta\hat{\rho}(\mathbf{r})\delta\hat{\rho}(\mathbf{r}')\right\rangle=kT\chi_s(\mathbf{r}-\mathbf{r}')$$

- ✓ The space correlations of thermal fluctuations in absence of the external filed are are related to the linear response to the external field
- ✓ Using the definition of the static structure factor S(k) and its relation to S(k,ω), and its dependence only on r–r′, one can write the following relationships in the Fourier space

$$\frac{1}{kT}\left\langle\rho(\mathbf{k})\rho(\mathbf{k}')\right\rangle=\chi_s(\mathbf{k})\delta(\mathbf{k}+\mathbf{k}')=\mathrm{Re}[\chi_s(\mathbf{k})]\delta(\mathbf{k}+\mathbf{k}')=\mathrm{Re}[\bar{\chi}(\mathbf{k},0)]$$

$$\frac{1}{kT}\left\langle\left|\rho(\mathbf{k})\right|^2\right\rangle=\frac{S(k)}{\rho kT}=\mathrm{Re}[\bar{\chi}(\mathbf{k},0)]=\int\frac{d\omega'}{\pi}\frac{\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega')\right]}{\omega'}=\int d\omega'\frac{S(k,\omega')}{\rho kT}$$

The FT of the squared density fluctuations at equilibrium (i.e. the static structure factor) is related to the real part of the FT of the total response function evaluated at ω=0. Due to KK relations, this involves an integral of the imaginary part. The last equality derives from the integral relationship between static and dynamic structure factor

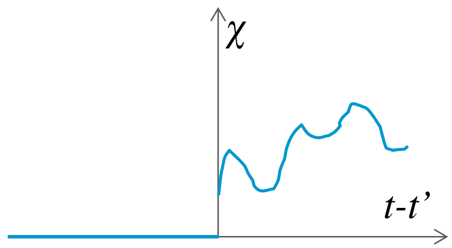
Dynamical extension of the structure of liquids

A step backward: deconstructing FD theorem

Linear response

$$\delta\rho(\mathbf{r},t) = \int d\mathbf{r}' \int_{-\infty}^{t} \chi_l(\mathbf{r}-\mathbf{r}',t-t')v(\mathbf{r}',t')\,dt = \int d\mathbf{r}' \int_{-\infty}^{+\infty} \chi(\mathbf{r}-\mathbf{r}',t-t')v(\mathbf{r}',t')\,dt$$

$$\chi(\mathbf{r}-\mathbf{r}',t-t') = \chi_l(\mathbf{r}-\mathbf{r}',t-t')\Theta(t-t')$$



Causality, KK

$$\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega)\right] = -\int \frac{d\omega'}{\pi}\frac{\mathrm{Re}\left[\bar{\chi}(\mathbf{k},\omega')\right]}{(\omega'-\omega)} \qquad \mathrm{Re}\left[\bar{\chi}(\mathbf{k},\omega)\right] = \int \frac{d\omega'}{\pi}\frac{\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega')\right]}{(\omega'-\omega)} \qquad \bar{\chi}(\mathbf{k},\omega) = \int \frac{d\omega'}{i\pi}\frac{\bar{\chi}(\mathbf{k},\omega')}{(\omega'-\omega)}$$

Effect of the external perturbation (static)

$$\delta\rho(\mathbf{r}) = \int d\mathbf{r}'\chi_s(\mathbf{r}-\mathbf{r}')v(\mathbf{r}') \qquad \delta\bar{\rho}(\mathbf{k}) = \bar{\chi}_s(\mathbf{k})\bar{v}(\mathbf{k})$$

$$\frac{1}{kT}\left\langle\left|\rho(\mathbf{k})\right|^2\right\rangle = \mathrm{Re}[\bar{\chi}(\mathbf{k},0)]$$

$$\int \frac{d\omega'}{\pi}\frac{\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega')\right]}{\omega'} = \int d\omega' \frac{S(k,\omega')}{\rho kT}$$

- ✓ Although an integral equality does not automatically imply the equality of the integrands, the second equation indicates a direct relationship between the dynamic structure factor and the imaginary part of the response function.
- ✓ The imaginary part of the response function bears the dissipation, the dynamics structure factor bears the fluctuations, therefore this relation is clearly related to fluctuation/dissipation theorem
- ✓ We want to show that this relationship is true also for any ω (i.e. for the integrand)

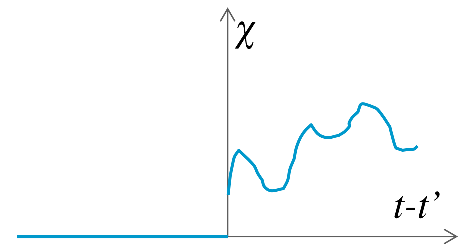
Dynamical extension of the structure of liquids

A step backward: deconstructing FD theorem

Linear response

$$\delta\rho(\mathbf{r},t) = \int d\mathbf{r}' \int_{-\infty}^{t} \chi_l(\mathbf{r}-\mathbf{r}', t-t')v(\mathbf{r}',t')\,dt = \int d\mathbf{r}' \int_{-\infty}^{+\infty} \chi(\mathbf{r}-\mathbf{r}', t-t')v(\mathbf{r}',t')\,dt$$

$$\chi(\mathbf{r}-\mathbf{r}', t-t') = \chi_l(\mathbf{r}-\mathbf{r}', t-t')\Theta(t-t')$$



Causality, KK

$$\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega)\right] = -\int \frac{d\omega'}{\pi} \frac{\mathrm{Re}\left[\bar{\chi}(\mathbf{k},\omega')\right]}{(\omega'-\omega)} \qquad \mathrm{Re}\left[\bar{\chi}(\mathbf{k},\omega)\right] = \int \frac{d\omega'}{\pi} \frac{\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega')\right]}{(\omega'-\omega)} \qquad \bar{\chi}(\mathbf{k},\omega) = \int \frac{d\omega'}{i\pi} \frac{\bar{\chi}(\mathbf{k},\omega')}{(\omega'-\omega)}$$

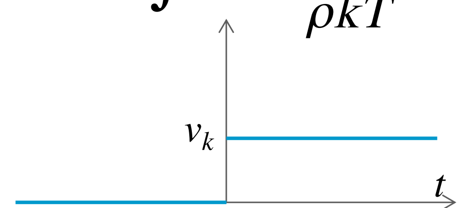
$$\delta\rho(\mathbf{r}) = \int d\mathbf{r}' \chi_s(\mathbf{r}-\mathbf{r}')v(\mathbf{r}') \qquad \delta\bar{\rho}(\mathbf{k}) = \bar{\chi}_s(\mathbf{k})\bar{v}(\mathbf{k})$$

$$\frac{1}{kT}\left\langle \left|\rho(\mathbf{k})\right|^2 \right\rangle = \mathrm{Re}[\bar{\chi}(\mathbf{k},0)]$$

$$\int \frac{d\omega'}{\pi} \frac{\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega')\right]}{\omega'} = \int d\omega' \frac{S(k,\omega')}{\rho kT}$$

Effect of the external perturbation (time dependent)

✓ We now consider a time dependent perturbation v_k switched on at a time t_0. We evaluate the average value of the fluctuation at time t_0+t (using the classical transition probability)



$$\delta\rho_{\mathbf{k}}(t) = \left\langle \delta\hat{\rho}_k \right\rangle_t = \frac{1}{Z}\int \delta\hat{\rho}_k \exp(-\beta H) = \frac{1}{Z}\int \delta\hat{\rho}_k \exp(-\beta H_0)[1+\beta v_k(t)\delta\hat{\rho}_{-k}(t)]$$

$$\delta\rho_{\mathbf{k}}(t) = \beta v_k(t)\left\langle \delta\hat{\rho}_k(t_0)\delta\hat{\rho}_{-k}(t_0+t) \right\rangle_0 = \int_{-\infty}^{+\infty} \chi_k(t-t')v_k\Theta(-t)dt'$$

Note: the proof is formally similar to the static case, with differences due to the fact that the dependence on time and space of probability distribution are different.

and passing to the FT, using the fact that $\delta\rho_k(t)$ is real and symmetric, and therefore its FT is real and symmetric, one gets

$$\frac{1}{kT}\left\langle \rho_k(\omega)\rho_{-k}(-\omega) \right\rangle = \frac{2}{\omega}\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega)\right]$$

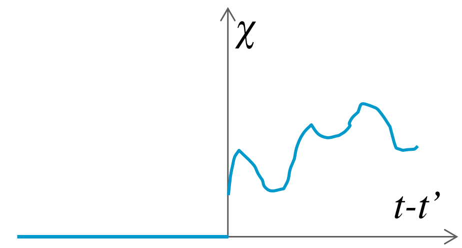
Dynamical extension of the structure of liquids

A step backward: deconstructing FD theorem

Linear response

$$\delta\rho(\mathbf{r},t) = \int d\mathbf{r}' \int_{-\infty}^{t} \chi_l(\mathbf{r}-\mathbf{r}',t-t')v(\mathbf{r}',t')\,dt = \int d\mathbf{r}' \int_{-\infty}^{+\infty} \chi(\mathbf{r}-\mathbf{r}',t-t')v(\mathbf{r}',t')\,dt$$

$$\chi(\mathbf{r}-\mathbf{r}',t-t') = \chi_l(\mathbf{r}-\mathbf{r}',t-t')\Theta(t-t')$$



Causality, KK

$$\mathrm{Im}\left[\overline{\chi}(\mathbf{k},\omega)\right] = -\int \frac{d\omega'}{\pi}\frac{\mathrm{Re}\left[\overline{\chi}(\mathbf{k},\omega')\right]}{(\omega'-\omega)} \qquad \mathrm{Re}\left[\overline{\chi}(\mathbf{k},\omega)\right] = \int \frac{d\omega'}{\pi}\frac{\mathrm{Im}\left[\overline{\chi}(\mathbf{k},\omega')\right]}{(\omega'-\omega)} \qquad \overline{\chi}(\mathbf{k},\omega) = \int \frac{d\omega'}{i\pi}\frac{\overline{\chi}(\mathbf{k},\omega')}{(\omega'-\omega)}$$

Effect of the external perturbation (time dependent)

$$\frac{1}{kT}\left\langle \rho_k(\omega)\rho_{-k}(-\omega)\right\rangle = \frac{2}{\omega}\mathrm{Im}\left[\overline{\chi}(\mathbf{k},\omega)\right]$$

$$\frac{1}{kT}\left\langle \left|\rho(\mathbf{k})\right|^2\right\rangle = \mathrm{Re}[\overline{\chi}(\mathbf{k},0)]$$

$$\int \frac{d\omega'}{\pi}\frac{\mathrm{Im}\left[\overline{\chi}(\mathbf{k},\omega')\right]}{\omega'} = \int d\omega'\frac{S(k,\omega')}{\rho kT}$$

The FT of time correlation fluctuations without external field is linearly related to the imaginary part of the response function. This is in turn related to the dissipated energy under an external field

The static form is obtained integrating over ω and using the KK relationships.
The final result is that the space correlations of density fluctuations are related to the real part of the static response function (i.e. to steady-state external fields); the time correlations are related to the imaginary part of the time dependent response function. This asymmetry in the space/time variable is due to causality, which formally imposes restrains in the time/frequency domain on the response function, specifically relationships between the real and imaginary parts

Dynamical extension of the structure of liquids

A step backward: deconstructing FD theorem

Linear response

$$\delta\rho(\mathbf{r},t) = \int d\mathbf{r}' \int_{-\infty}^{t} \chi_l(\mathbf{r}-\mathbf{r}',t-t')v(\mathbf{r}',t')\,dt = \int d\mathbf{r}' \int_{-\infty}^{+\infty} \chi(\mathbf{r}-\mathbf{r}',t-t')v(\mathbf{r}',t')\,dt$$

$$\chi(\mathbf{r}-\mathbf{r}',t-t') = \chi_l(\mathbf{r}-\mathbf{r}',t-t')\Theta(t-t')$$

Causality, KK

$$\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega)\right] = -\int \frac{d\omega'}{\pi}\frac{\mathrm{Re}\left[\bar{\chi}(\mathbf{k},\omega')\right]}{(\omega'-\omega)} \qquad \mathrm{Re}\left[\bar{\chi}(\mathbf{k},\omega)\right] = \int \frac{d\omega'}{\pi}\frac{\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega')\right]}{(\omega'-\omega)} \qquad \bar{\chi}(\mathbf{k},\omega) = \int \frac{d\omega'}{i\pi}\frac{\bar{\chi}(\mathbf{k},\omega')}{(\omega'-\omega)}$$

Fluctuation-dissipation theorem (classic)

$$\frac{1}{kT}\left\langle \rho_k(\omega)\rho_{-k}(-\omega)\right\rangle = \frac{2}{\omega}\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega)\right]$$

$$\frac{1}{kT}\left\langle \left|\rho(\mathbf{k})\right|^2\right\rangle = \mathrm{Re}[\bar{\chi}(\mathbf{k},0)]$$

$$\int \frac{d\omega'}{\pi}\frac{\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega')\right]}{\omega'} = \int d\omega' \frac{S(k,\omega')}{\rho kT}$$

Genearal form for density fluctuations

$$\left\langle \rho_k(\omega)\rho_{-k}(-\omega)\right\rangle = \mathrm{Im}\,\bar{\chi}(\mathbf{k},\omega)\frac{2\hbar}{[1-e^{-\hbar\omega/kT}]} = \begin{cases} \xrightarrow{\text{classic limit, kT>>}\hbar\omega} \mathrm{Im}\,\bar{\chi}(\mathbf{k},\omega)\dfrac{2kT}{\omega} \\ \xrightarrow{\text{static, classic}} kT\,\mathrm{Re}\,\bar{\chi}(\mathbf{k},0) \\ \xrightarrow{\text{quantum T=0}} \mathrm{Im}\,\bar{\chi}(\mathbf{k},\omega)2\hbar \end{cases}$$

$$= S(\mathbf{k},\omega) \xrightarrow{\int d\omega;\,k\to 0} S(\mathbf{k}\to 0) = \rho kT\kappa_T$$

Dynamical extension of the structure of liquids

A step backward: deconstructing FD theorem

Genearal form, response to any field f_i associated to an internal variable x_i

$$\langle x_i x_j \rangle_\omega = \mathrm{Im}\chi_{ij}(\omega)\frac{2\hbar}{1-e^{-\hbar\omega/kT}} \qquad \delta H = -\sum_i f_i x_i \qquad \chi_{ij} = \frac{x_i}{f_j}$$

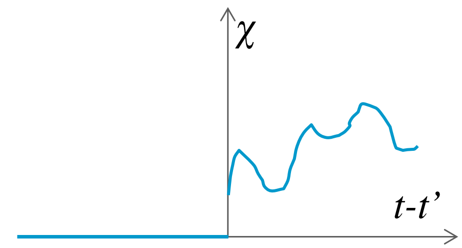
$$\langle f_i f_j \rangle_\omega = (\chi^{-1}\chi^{*-1})_{ij}\mathrm{Im}\chi_{ij}\frac{2\hbar}{1-e^{-\hbar\omega/kT}}$$

Form for the fluctuations of the fields

- ✓ $x_i = \rho_k$ and $f_i = v_k$ → response in density, S(k,ω), Ornstein Zernike etc
- ✓ $x_i = U$ (internal energy) and $f_i = T,\ \chi = C_v \xrightarrow{\text{classical,static}} \langle \Delta U^2 \rangle = kT^2 C_v$
- ✓ $x_i = Q$ and $f_i = -V \xrightarrow{\text{using e.g. a RCL circuit, classical}} \langle V^2 \rangle_\nu = 4kTR\Delta\nu$ Nyquist
- ✓ $x_i =$ coordinates and $f_i =$ forces $\xrightarrow{\text{forced damped classical oscillator}} \langle f^2 \rangle_\omega = mkT\gamma$ Langevin
- ✓ $x_i = p$ electrict dipole $f_i = E$ (EM field). Use Abrham-Lorentz law and get the Plank result for $\langle E^2 \rangle$ (homework).

Dynamical extension of the structure of liquids

A step backward: deconstructing FD theorem



Linear response

$$\delta\rho(\mathbf{r},t)=\int d\mathbf{r}'\int_{-\infty}^{t}\chi_l(\mathbf{r}-\mathbf{r}',t-t')v(\mathbf{r}',t')\,dt=\int d\mathbf{r}'\int_{-\infty}^{+\infty}\chi(\mathbf{r}-\mathbf{r}',t-t')v(\mathbf{r}',t')\,dt$$

$$\chi(\mathbf{r}-\mathbf{r}',t-t')=\chi_l(\mathbf{r}-\mathbf{r}',t-t')\Theta(t-t')$$

Causality, KK

$$\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega)\right]=-\int\frac{d\omega'}{\pi}\frac{\mathrm{Re}\left[\bar{\chi}(\mathbf{k},\omega')\right]}{(\omega'-\omega)}\qquad \mathrm{Re}\left[\bar{\chi}(\mathbf{k},\omega)\right]=\int\frac{d\omega'}{\pi}\frac{\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega')\right]}{(\omega'-\omega)}\qquad \bar{\chi}(\mathbf{k},\omega)=\int\frac{d\omega'}{i\pi}\frac{\bar{\chi}(\mathbf{k},\omega')}{(\omega'-\omega)}$$

General form of fluctuation-dissipation theorem - classical

$$\delta\rho(\mathbf{r})=\int d\mathbf{r}'\chi_s(\mathbf{r}-\mathbf{r}')v(\mathbf{r}')\qquad \delta\bar{\rho}(\mathbf{k})=\bar{\chi}_s(\mathbf{k})\bar{v}(\mathbf{k})\qquad \left\langle\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')\right\rangle=\left\langle\delta\rho(\mathbf{r},t)\delta\rho(\mathbf{r}',t'=t)\right\rangle$$

$$\frac{1}{kT}\left\langle\rho_k(\omega)\rho_{-k}(-\omega)\right\rangle=\frac{2}{\omega}\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega)\right]\xrightarrow{static}\frac{1}{kT}\left\langle\rho(\mathbf{k})\rho(-\mathbf{k})\right\rangle=\int\frac{d\omega'}{\pi}\frac{\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega')\right]}{\omega'}=\mathrm{Re}[\bar{\chi}(\mathbf{k},0)]$$

FD theorem quantum low T limit

$$\left\langle\rho_k(\omega)\rho_{-k}(-\omega)\right\rangle=\frac{2\hbar}{1-\exp(-\hbar\omega/kT)}\mathrm{Im}\left[\bar{\chi}(\mathbf{k},\omega)\right]$$

An example: the damped harmonic oscillator

$$\ddot{x}+\gamma\dot{x}+\omega_0^2x=f(t)$$

✓ Thermal equilibrium $\left\langle x^2\right\rangle=\dfrac{kT}{\omega_0^2}=kT\,\mathrm{Re}[\chi(0)]\quad\rightarrow\quad\mathrm{Re}[\chi(0)]=\dfrac{1}{\omega_0^2}$

✓ In time dependent steady state conditions

$$\bar{x}(\omega)[-\omega^2-i\omega\gamma+\omega_0^2]=\bar{f}(\omega)\ \Rightarrow\ \bar{\chi}(\omega)=\frac{1}{\omega_0^2-\omega^2-i\omega\gamma}=\frac{\omega_0^2-\omega^2+i\omega\gamma}{[\omega_0^2-\omega^2]^2+\omega^2\gamma^2}$$

$$\mathrm{Re}[\bar{\chi}(\omega)]=\frac{\omega_0^2-\omega^2}{[\omega_0^2-\omega^2]^2+\omega^2\gamma^2}\qquad \mathrm{Im}[\bar{\chi}(\omega)]=\frac{\omega\gamma}{[\omega_0^2-\omega^2]^2+\omega^2\gamma^2}$$

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An example: the damped harmonic oscillator

$$\bar{x}(\omega)[-\omega^2 - i\omega\gamma + \omega_0^2] = \bar{f}(\omega) \quad \Rightarrow \quad \bar{\chi}(\omega) = \frac{1}{\omega_0^2 - \omega^2 - i\omega\gamma} = \frac{\omega_0^2 - \omega^2 + i\omega\gamma}{[\omega_0^2 - \omega^2]^2 + \omega^2\gamma^2}$$

$$\mathrm{Re}[\bar{\chi}(\omega)] = \frac{\omega_0^2 - \omega^2}{[\omega_0^2 - \omega^2]^2 + \omega^2\gamma^2}$$

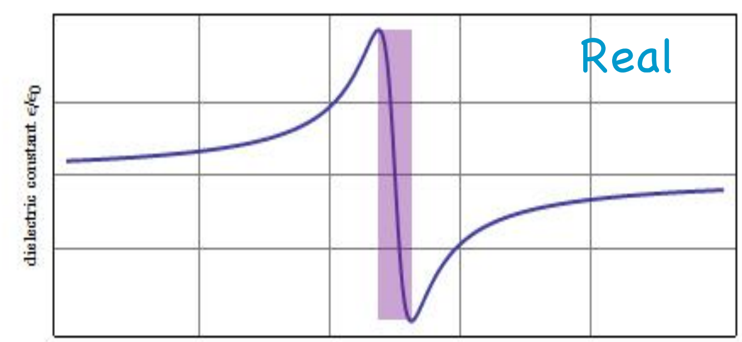
Symmetric, with a quasi divergence in $\omega=\omega_0$, real for $\gamma=0$

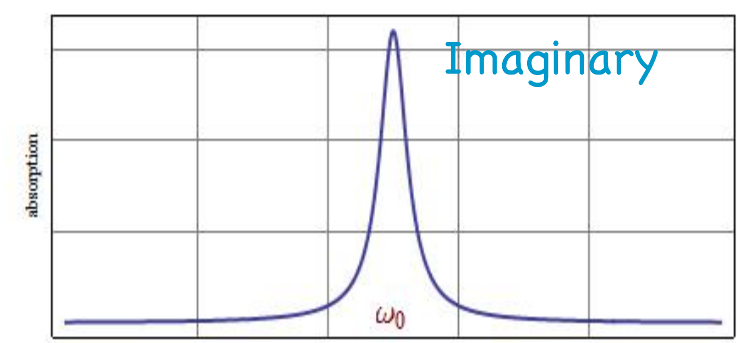
$$\mathrm{Im}[\bar{\chi}(\omega)] = \frac{\omega\gamma}{[\omega_0^2 - \omega^2]^2 + \omega^2\gamma^2}$$

Anti-symmetric, null if with $\gamma=0$, maximum for $\omega=\omega_0$. It measures the dissipation and adsorption ($S(k,\omega)$) and is maximum on a resonance!

In general

- ✓ The response function has poles in correspondence of the characteristic frequencies of the system (resonances)
- ✓ Both real an imaginary part of the response function include all information on the system
- ✓ The response function is related to fluctuations
- ✓ The static part of the response function is real and related to space fluctuations in absence of perturbation
- ✓ The imaginary part of the response function is related to different time fluctuations in absence of the perturbation
- ✓ The imaginary part of the response function is related to dissipation and energy adsorption, which is maximum in the presence of resonances (collective excitations of the system)





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