Lesson 4: Dynamical extension

- ✓ Dynamical extension of pair correlation functions
- ✓ Intermediate scattering function, dynamical structure function
- ✓ Link to the inelastic scattering
- ✓ Inelastic scattering and density fluctuations dispersion relations
- ✓ Quasiparticles and phonons

Dynamical extension of the structure of liquids

✓ The dynamical extension of the pair correlation function is the space/time density correlation function

$$\rho g(r) = \frac{1}{N}\left\langle \sum_{i \neq j} \delta(r-(r_i - r_j))\right\rangle \rightarrow G(r,t) = \frac{1}{N}\left\langle \sum_{i,j} \delta(r-(r_i(0)-r_j(t)))\right\rangle = \frac{1}{\rho}\left\langle \rho(0,0)\rho(r,t)\right\rangle \xrightarrow{\text{general}} \frac{1}{N}\left\langle \int d\mathbf{r'}\rho(\mathbf{r'},0)\rho(\mathbf{r'}+\mathbf{r},t)\right\rangle$$

where the central form holds also in the quantum, provided the ρ is intended as operator. The very last form holds also for non isotropic systems (not homogeneous single particle densities). G depends on the time difference only, and on the distance of particles only, in the isotropic case.

✓ Note that, at variance with the static version, the sum includes also the "same particles", whose correlations can be followed in time. Therefore G is usually split in a self part including only the diagonal part of the sum, and a different particles part. In the static limit one has
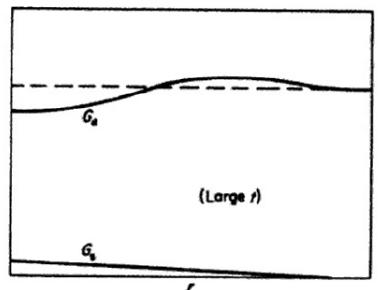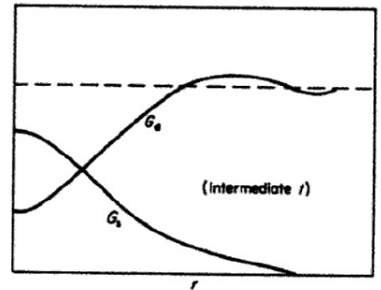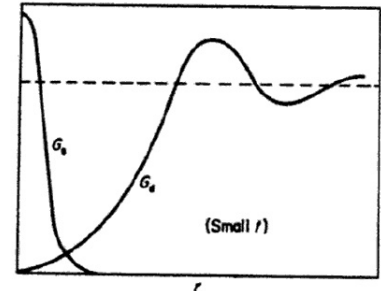
$$G(r,t) = G_s(r,t) + G_d(r,t) \xrightarrow{t=0} G(r,t=0) = \delta(r) + \rho g(r)$$

i.e., the static limit returns a "snapshot" of the space correlation, which is, in fact, measured $S(k)$ and related to $g(r)$

→ it is hard to distinguish a liquid from and amorphous solid from the static S(k)

✓ In the long time limit in liquids, one can assume that time correlations among particles are lost, i.e. the statistical average of the product of the two densities is the product of the statistical averages: $G(r,t) \approx \frac{1}{N}\int d\mathbf{r''}\rho(\mathbf{r}-\mathbf{r''})\rho(\mathbf{r''})$

✓ This implies, in liquids, that $G(r,\infty)\sim G_d(r,\infty)\rightarrow\rho$, while $G_s(r,\infty)\rightarrow 1/V\sim 0$ because the number of couples scales as N^2 and the number of particles as N. Therefore the time self correlation function vanishes in liquids in the long time limit. In solid, conversely, V is the volume in which a single particle is confined, and it is small, thereofore Gs is non null

(Small r)

(intermediate r)

(Large r)

Dynamical extension of the structure of liquids

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where the central form holds also in the quantum, provided the ρ is intended as operator. The very last form holds also for non isotropic systems (not homogeneous single particle densities). G depends on the time difference only, and on the distance of particles only, in the isotropic case.

$$G(r,t) = G_s(r,t) + G_d(r,t) \xrightarrow{\;t=0\;} G(r,t=0) = \delta(r) + \rho g(r)$$

$$\xrightarrow{t=\infty,\;liquid} G(r,\infty) = \frac{1}{N}\int d\mathbf{r}''\rho(\mathbf{r}-\mathbf{r}'')\rho(\mathbf{r}'') = \begin{cases} G_s = 1/V \sim 0 \\ \qquad + \; G_d = \rho \end{cases}$$

$$\xrightarrow{t=\infty,\;crystal} G(r,\infty) = \frac{1}{N}\int d\mathbf{r}''\rho(\mathbf{r}-\mathbf{r}'')\rho(\mathbf{r}'') = \begin{cases} G_s \sim \rho_{loc}(r) \\ G_d \sim \xrightarrow{FT} \left|\rho(k)\right|^2 \end{cases}$$

(Small r)

(Intermediate r)

(Large r)

In liquids the self correlation function vanishes for long times because the particle move and looses the memory of its starting position. The decay time can be considered a feature of the liquid: if it is short, the system is a real liquid, if it is long, the viscosity is high and the system can be a glass.

In crystals, the self correlation function never completely vanishes, because the particles stays localized: $G_S(r)$ has a range limited in the volume explored by a particle, or little larger.

Analogously, in crystals, the G_d is not uniform, but the different sites particles are sufficiently uncorrelated for the convolution integral approximation to be valid even at relatively short times. This is the approximation leading to the simple form $S(k)\propto|\rho(k)|^2$ for the static structure factor (see first lessons).
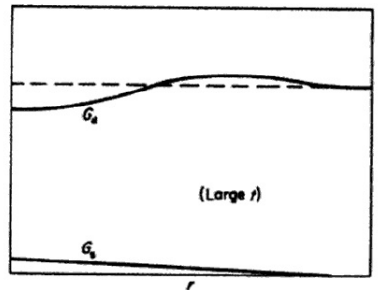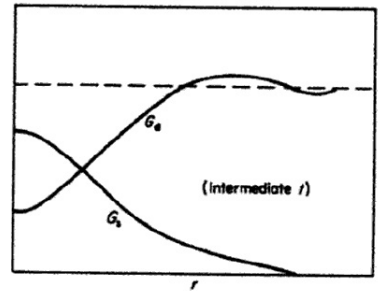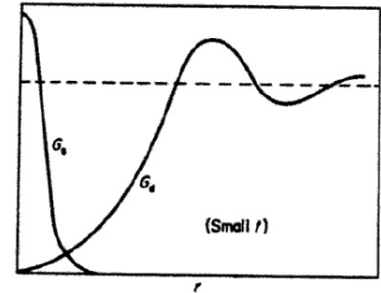
Dynamical extension of the structure of liquids

✓ G is called the Van Hove function, and describe the space and time correlations between density fluctuations.

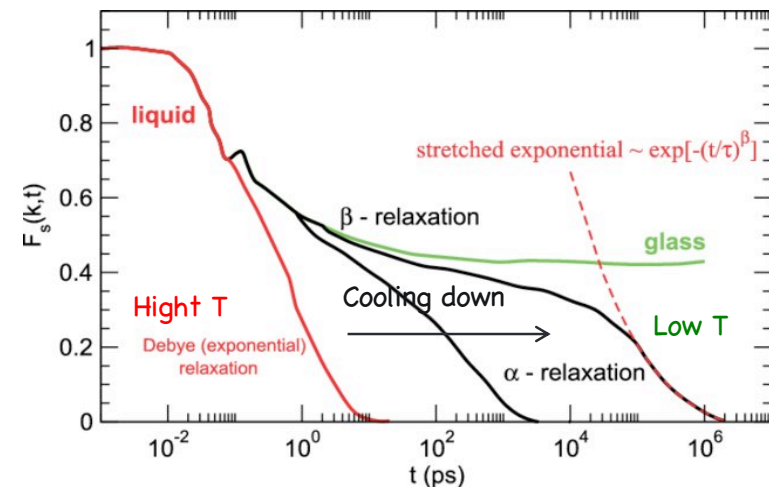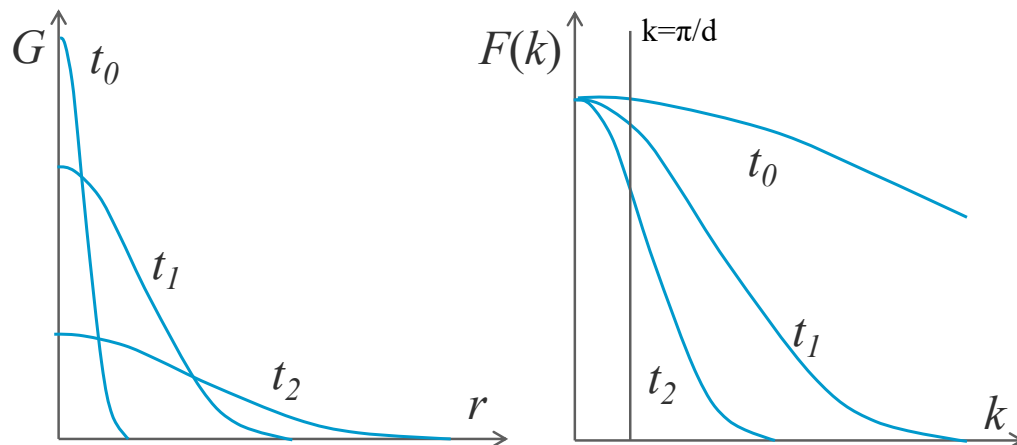✓ The space FT of the Van Hove function is called the Intermediate scattering function

$$F(k,t) = \int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} G(r,t) = \frac{1}{\rho}\int d(\mathbf{r}-\mathbf{r}')e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\langle\rho(\mathbf{r}',0)\rho(r,t)\rangle = \frac{1}{N}\langle\overline{\rho}(-k,0)\overline{\rho}(k,t)\rangle$$

That is: the intermediate scattering function measures the time correlation of density fluctuation with a given wave number k, or the probability that a density fluctuation with k generated at time 0 is still there at time t, i.e. the time persistence of a k- wave density fluctuation

✓ As G, F can be separated in self and different particles parts

$$F(\mathbf{k},t) = F_s(\mathbf{k},t) + F_d(\mathbf{k},t) = \frac{1}{N}\left\langle\sum_i \exp(i\mathbf{k}(\mathbf{r}_i(t)-\mathbf{r}_i(0)))\right\rangle + \frac{1}{N}\left\langle\sum_{i\neq j}\exp(i\mathbf{k}(\mathbf{r}_i(t)-\mathbf{r}_j(0)))\right\rangle$$

✓ While G_s delocalizes with time, the self intermediate scattering function $F_s(\mathbf{k},t)$ decays with time, therefore its value at a fixed wavenumber (usually k=π/d, interparticle distance) has a characteristic behavior as a function of time
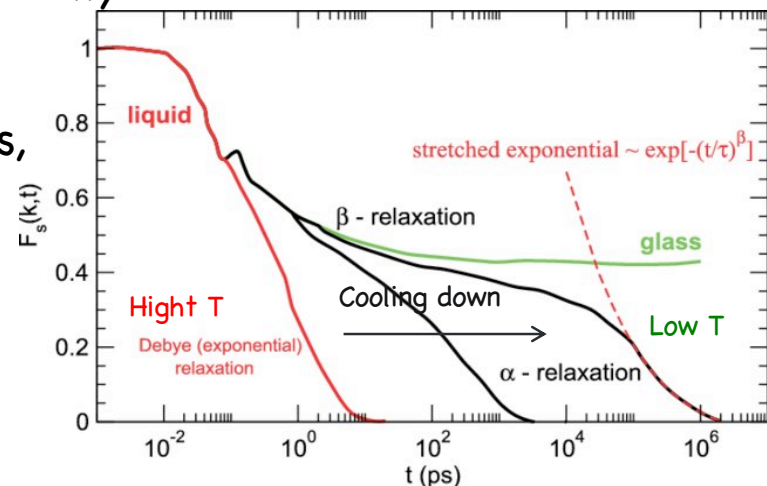
Dynamical extension of the structure of liquids

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$$F(\mathbf{k},t) = F_S(\mathbf{k},t)+F_d(\mathbf{k},t) = \frac{1}{N}\left\langle \sum_i \exp(i\mathbf{k}(\mathbf{r}_i(t)-\mathbf{r}_i(0)))\right\rangle + \frac{1}{N}\left\langle \sum_{i\neq j} \exp(i\mathbf{k}(\mathbf{r}_i(t)-\mathbf{r}_j(0)))\right\rangle$$

✓ In the short time range, the particles are free to move basically until they find another particle (ballistic regime, short plateau)

✓ At high T, however, the particle soon experiences viscosity due to interactions with others and an exponential relaxation region is clearly visible ("Debye")

✓ As the system is cooled down, viscosity increases, and the mobility decreases. Relaxation is increasingly slow and a plateau typical of glasses is appears.

✓ Both liquid and glasses, the behavior is usually dominated by viscosity, however they can be distinguished based on the different relaxation times. The appearance of very long relaxation times is a signature of the glass transition, and is usually revealed by the appearance of plateaus, double or multiple exponentials or other complex behaviors

✓ In crystals, particles oscillate around their positions, G_s does not delocalize, and has a space extension corresponding to the inter-particle distance. F does not decay in first approximation (harmonic), but oscillates according to the excited modes

✓ However relaxation can be present and due to the interaction between phonons

Dynamical extension of the structure of liquids

✓ The space FT of the Van Hove function is called the Intermediate scattering function

$$F(k,t) = \int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} G(r,t) = \frac{1}{\rho}\int d(\mathbf{r}-\mathbf{r}')e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\left\langle\rho(\mathbf{r}',0)\rho(r,t)\right\rangle = \frac{1}{N}\left\langle\bar{\rho}(-k,0)\bar{\rho}(k,t)\right\rangle$$

$$F(\mathbf{k},t) = F_s(\mathbf{k},t) + F_d(\mathbf{k},t) = \frac{1}{N}\left\langle\sum_i \exp(i\mathbf{k}(\mathbf{r}_i(t)-\mathbf{r}_i(0)))\right\rangle + \frac{1}{N}\left\langle\sum_{i\neq j}\exp(i\mathbf{k}(\mathbf{r}_i(t)-\mathbf{r}_j(0)))\right\rangle$$

✓ Clearly, F is somehow related to phonons in crystals. However, this is also true in general: Because density is the average of the particle position, density fluctuations are related to variations in the particle positions. Therefore, the $\rho(k,t)$ describes the time variation of "wavelike" density fluctuations with a given wavelength, corresponding to a phonon in a crystal. Collective coherent vibrations of density fluctuations in a fluid are the generalization of phonons to fluids, and $\rho(k,t)$ can be used as collective variables of the eigenmodes. If such modes are present, they are expected to vary in time with a given frequency, as $\exp(i\omega_k\cdot t)$.

✓ Therefore, collective vibrational modes will appear as sharp peaks (= resonances) in the FT of F(k,t). We define the "power spectrum" of fluctuations the function

$$S(k,\omega) = \int dt\, F(k,t)e^{-i\omega t} = \int dt \int d\mathbf{r}\, e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}G(r,t) \;=\; \frac{1}{N}\int dt\left\langle\bar{\rho}(-k,0)\bar{\rho}(k,t)\right\rangle e^{-i\omega t}$$

also called the dynamic structure factor

✓ Clearly by definition one has $\displaystyle\int\frac{d\omega}{2\pi}S(k,\omega) = F(k,0) = S(k)$

✓ Therefore, S(k,ω) must some extension of the elastic neutron scattering function S(k)
✓ Extension to what? ℏω is an energy, therefore S(k,ω) allows process which exchange also energy, not only the momentum k, i.e. inelastic scattering!
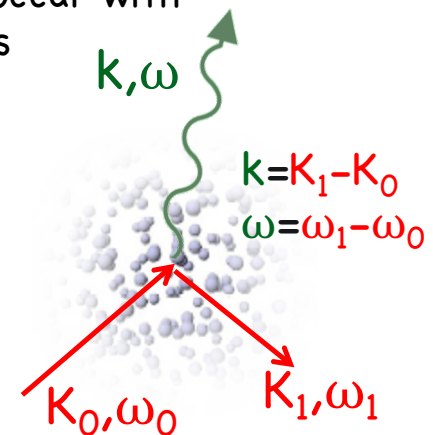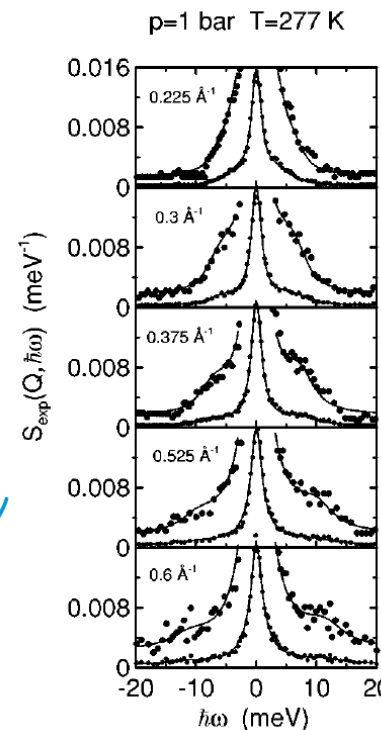
Dynamical extension of the structure of liquids

✓ Precisely, the dynamics structure factor defined as

$$S(k,\omega) = \int dt F(k,t) e^{-i\omega t} = \int dt \int d\mathbf{r} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} G(r,t) = \frac{1}{N}\int dt \langle \bar{\rho}(-k,0)\bar{\rho}(k,t)\rangle e^{-i\omega t}$$

is proportional to the inelastic scattering cross-section, e.g. from neutron scattering on a liquid. The demonstration involves the second order perturbation theory:

- As the probe with (k_0,ω_0) incident momentum/energy hits the system, it acts as a time dependent perturbation. The second order perturbation theory gives the interaction probability as a function of the incident frequency, predicting maximum absorption when ω_0 is in resonance with some internal energy level difference (March–Tosi, Capter 3)
- If the probe interact with the collective vibrations of the system, the resonances occur with energies of the phonons. Therefore the interaction will release some energy (besides momentum) to a phonon (inelastic scattering)

✓ The $S(k,\omega)$ (or equivalently, the scattering cross section) display peaks (resonances) at those frequencies where the collective variables $\rho_k(t)$ vibrates coherently. Therefore it identifies the dispersion relation $\omega(k)$ of the collective vibration (= phonons, in crystals), where k, and ω are the amount of momentum and energy released by the radiation during interaction, i.e energy and momentum variations

✓ Therefore the maxima of the S in the (q,ω) plane identify the relationship between momentum and energy exchanged with the system. If this relationship is well defined, it identify a "quasiparticle" associated to the collective density fluctuations modes in the system, i.e. the phonon.

k,ω

$k=K_1-K_0$
$\omega=\omega_1-\omega_0$

K_0,ω_0 K_1,ω_1

Example: inelastic (Brillouin) neutron scattering of water at different wave numbers. The central dominant peak is the elastic component; inelastic components are visible especially on the right as shoulders
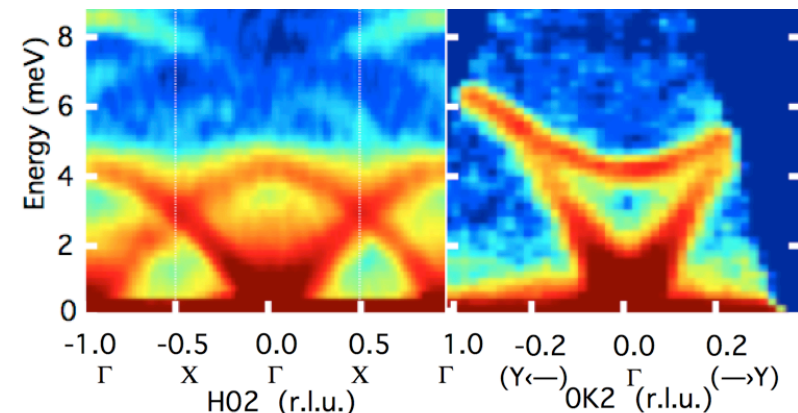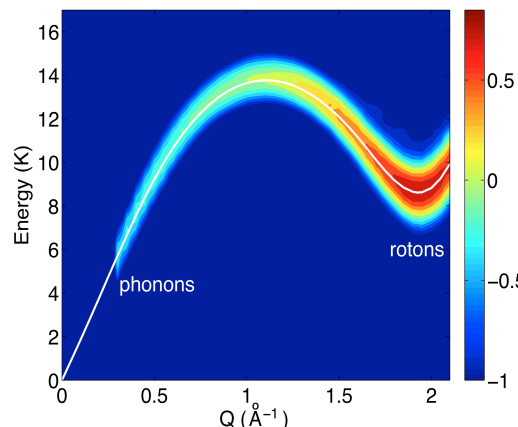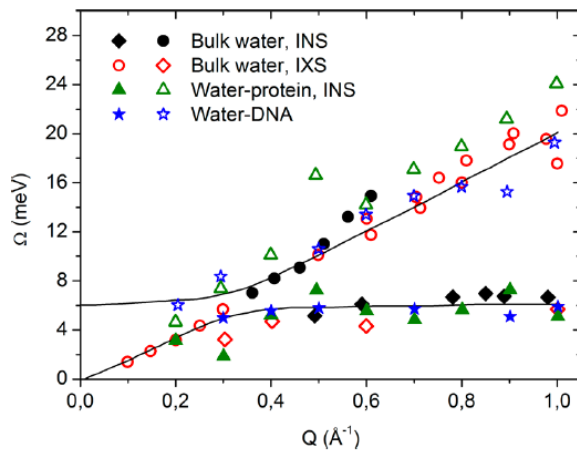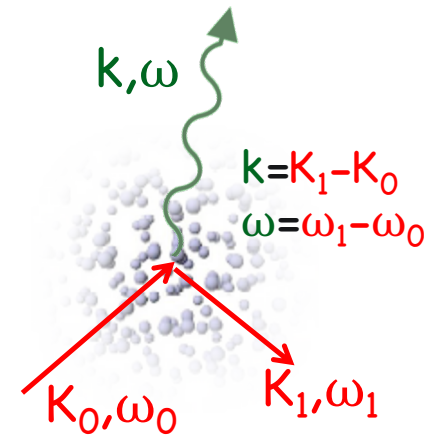
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$$S(k,\omega) = \int dt F(k,t)e^{-i\omega t} = \int dt \int d\mathbf{r} e^{i(\mathbf{k\cdot r}-\omega t)}G(r,t) = \frac{1}{N}\int dt \langle \bar{\rho}(-k,0)\bar{\rho}(k,t)\rangle e^{-i\omega t}$$

is proportional to the inelastic coherent scattering cross-section, e.g. from neutron scattering on a liquid.

✓ By collecting maxima of $S(q,\omega)$ one can get the dispersion curves of phonons

✓ In normal liquids, the elastic peak masks the low wevenumber parts of the spectrum, making measurements at small wavenumbers very difficult

✓ In crystals, or in strongly correlated fluids the measurements are less noisy

✓ In crystals it is possible to see the periodicity in the wavenumber

Dynamical extension of the structure of liquids

✓ The theories to evaluate S(k,ω) are much more complex than those for static version

$$S(k,\omega) = \int dt F(k,t) e^{-i\omega t} = \int dt \int d\mathbf{r} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} G(r,t) = \frac{1}{N} \int dt \langle \bar{\rho}(-k,0)\bar{\rho}(k,t)\rangle e^{-i\omega t}$$

however some interesting properties can be outlined

✓ Short time behavior: the static structure functions are recovered

$$G(r,t) = G_s(r,t) + G_d(r,t) \xrightarrow{t=0} G(r,t=0) = \delta(r) + \rho g(r)$$

$$\int \frac{d\omega}{2\pi} S(k,\omega) = F(k,0) = S(k)$$

✓ Long time behavior: it is assumed that the correlation is totally lost in the liquid as an effect of diffusion; this implies that the self part vanishes as the inverse of the delocalization volume of a particle

$$\xrightarrow{t=\infty,\ liquid} G(r,\infty) = \frac{1}{N} \int d\mathbf{r}'' \rho(\mathbf{r}-\mathbf{r}'')\rho(\mathbf{r}'') = \begin{cases} G_s = 1/V \sim 0 \\ + \ G_d = \rho \end{cases}$$

✓ In crystals, diffusion is not active, however, the low correlation approximation is good for the different-particle part, because different sites can be considered uncorrelated. The self part, conversely, do not vanish because the particle is localized, and is related to the single site one-particle density.

$$\xrightarrow{t=\infty,crystal} G(r,\infty) = \frac{1}{N} \int d\mathbf{r}'' \rho(\mathbf{r}-\mathbf{r}'')\rho(\mathbf{r}'') = \begin{cases} G_s \sim \rho_{loc}(r) \\ G_d \xrightarrow{FT} |\rho(\bar{k})|^2 \end{cases}$$

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✓ The theories to evaluate $S(k,\omega)$ are much more complex than those for static version

$$S(k,\omega) = \int dt F(k,t)e^{-i\omega t} = \int dt \int d\mathbf{r}\, e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} G(r,t) = \frac{1}{N}\int dt \left\langle \bar\rho(-k,0)\bar\rho(k,t)\right\rangle e^{-i\omega t} =$$

$$\int \frac{d\omega}{2\pi} S(k,\omega) = F(k,0) = S(k)$$

$$= \left\langle \bar\rho(-k,-\omega)\bar\rho(k,\omega)\right\rangle$$
FT of density fluctuations

✓ Convolution approximation: let's rewrite the F separating the self and different particle part

$$F(\mathbf{k},t) = F_s(\mathbf{k},t) + \frac{1}{N}\sum_{i\neq j}\left\langle \exp(i\mathbf{k}(\mathbf{r}_i(t)-\mathbf{r}_j(0)))\right\rangle = F_s(\mathbf{k},t) + \frac{1}{N}\sum_{i\neq j}\left\langle \exp(i\mathbf{k}(\mathbf{r}_i(0)-\mathbf{r}_j(0)))\exp(i\mathbf{k}(\mathbf{r}_i(t)-\mathbf{r}_i(0)))\right\rangle$$

Assume that the average of product is the product of averages

$$\approx F_s(\mathbf{k},t) + \frac{1}{N}\sum_i \left\langle \exp(i\mathbf{k}(\mathbf{r}_i(t)-\mathbf{r}_i(0)))\right\rangle\left[\sum_i\left\langle \exp(i\mathbf{k}(\mathbf{r}_i(0)-\mathbf{r}_j(0)))\right\rangle - 1\right] = F_s(\mathbf{k},t)F(\mathbf{k},0)$$

This approximation is equivalent to "separate" space and time correlations, an assume that the time correlation part of the entire function behave as the self-part only, or in other words, that once set at t=0 a set of space correlations is propagated in time only as a consequence of the particle motion itself, without any intrinsic modification. As a consequence

$$F(k,t) = S(k)F_s(k,t) \qquad G(r,t) = G_s(r,t) + \rho\int d\mathbf{r}'g(r')G_s\left(\left|\mathbf{r}-\mathbf{r}'\right|,t\right) \qquad S(k,\omega) = S(k)S_s(k,\omega)$$

This approximation has several problems
1. Does not work well over long times, and in hydrodynamic regime
2. Do not satisfy exactly the total momentum conservation sum rule
3. However it has the advantage of including naturally the evaluation of S(k) and all the approximations usable for it

Dynamical extension of the structure of liquids
Links with the response theory

- ✓ **Fluctuations** can be induced in the fluid by means of an external potential. In the linear response theory these are proportional to the response function χ

$$\delta\rho(\mathbf{r},t) = \int d\mathbf{r}' \int_{-\infty}^{t} \chi(\mathbf{r}-\mathbf{r}',t-t')v(\mathbf{r}',t')dt \xrightarrow{\text{steady state limit}} \delta\rho(\mathbf{r}) = \int d\mathbf{r}'\chi_S(\mathbf{r}-\mathbf{r}')v(\mathbf{r}) \quad \text{susceptibility} \quad \chi_S(\mathbf{r}-\mathbf{r}') = \int \chi(\mathbf{r}-\mathbf{r}',t-t')dt$$

- ✓ Both χ and S are related to the response in density of the system to an external perturbation. In fact, both can be evaluated by means of the perturbation theory
- ✓ The direct calculation (next lesson) gives the following exact relation (quantum calculation at T=0)

$$\overline{\chi}(\mathbf{k},\omega) = \overline{\chi}'(\mathbf{k},\omega) + i\overline{\chi}''(\mathbf{k},\omega) \qquad \overline{\chi}''(\mathbf{k},\omega) = \frac{\rho}{2\hbar}[S(k,\omega) - S(-k,-\omega)]$$

  which is one form of the fluctuation dissipation theorem: the imaginary part of the response function is proportional to the dissipated energy when the system responds to an external (small) stimulus; the dynamic structure factor describe the time correlation spectrum of fluctuations at equilibrium in absence of an external stimulus

- ✓ The fluctuation dissipation theorem is very general: whenever a system responds linearly to an external perturbation, the imaginary part of the response function is related to the correlation function of thermal fluctuations in absence of perturbation
- ✓ The above form is derived based on the quantum form of the response function. Using the thermal distribution of fluctuations one has

$$\overline{\chi}''(\mathbf{k},\omega) = \frac{\rho}{2\hbar}S(k,\omega)[1 - e^{-\hbar\omega/kT}] \xrightarrow{\text{classical limit}} \overline{\chi}''(\mathbf{k},\omega) = \frac{\rho\omega}{2kT}S(k,\omega) \propto \left\langle \left|\rho_k(\omega)\right|^2 \right\rangle$$

- ✓ The causality principle implies that the response function satisfy some exact sum rules and real and imaginary part of the response functions are related by KK relationships; This also implies that

$$\overline{\chi}'(\mathbf{k},\omega) = \frac{1}{\pi}\int d\omega' \frac{\overline{\chi}''(\mathbf{k},\omega)}{\omega'-\omega-i\eta} \Rightarrow S(k) = \frac{kT}{\rho}\overline{\chi}(\mathbf{k},0)$$

Generalization of Ornstein Zernike relationship!