# Block I – Bonus Track: Korrelationen G(r,t)

Fahrplan

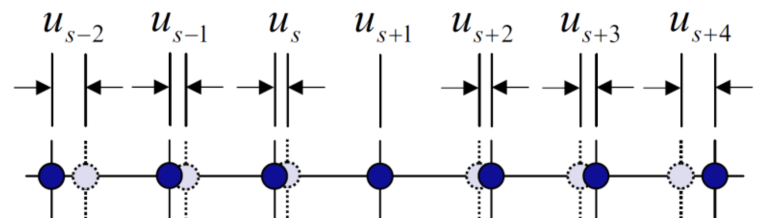
- Korrelationen G(r,t)
- Verallgemeinertes Streusignal $S(q,\omega) \sim FT[G(r,t)]$
- Anwendungen
  - Phononen … 1 diskretes q, 1 diskretes $\hbar\omega$
  - Diffusion … exponentiell zerfallende Korrelationen
  - anomale Diffusion … Abweichungen davon …

- Anregungen
  - Kristalle … „Phononen“
  - Quasi-Kristalle … „Phasonen“
  - Gläser … „Boson-Peak“ etc
  - Flüssigkeiten … „Diffusion“ etc

- weitergehendes: vgl. ATCOMA
- Fragestunde
- Frohe Feiertage!

http://www.soft-matter.uni-tuebingen.de/vorlesung_ws25_condmat.html
Ergänzungen zur Vorlesung
… Zusammenfassung Phononen
… Zusammenfassung Quantenstatistik
… Neutron spectroscopy

# Block I – Bonus Track: Korrelationen G(r,t)




Verständnisfrage:

Warum kann man überhaupt Bragg-Reflexe messen,
obwohl doch die Phononen (Schwingungen mit Auslenkungen)
die Translationsinvarianz des Gitter „zerstören" ?

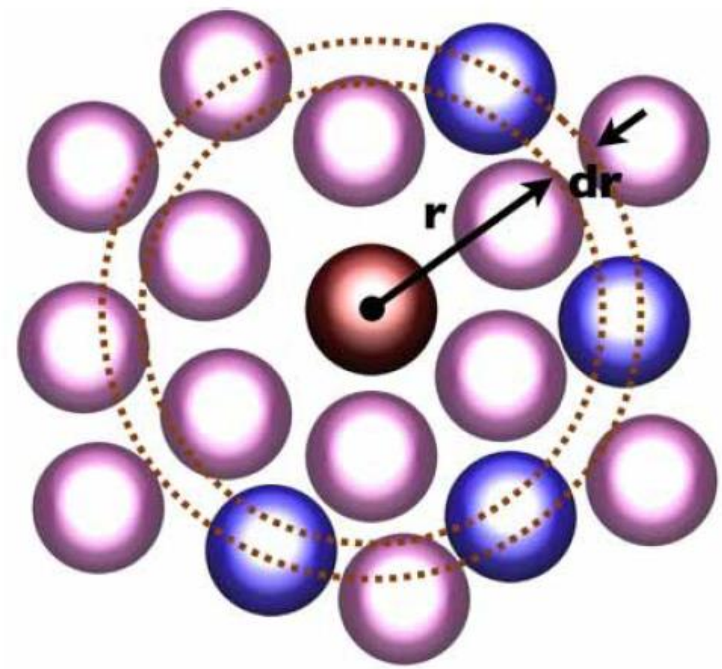
Abschliessende Bemerkungen zu Phononen

Messung entspricht einem Spezialfall von $S(q,\omega) \sim FT[G(r,t)]$
(mit einfach nur einer Frequenz $\omega$ entsprechend einem Phonon)
(berücksichtigt auch Erhaltung von Impuls (q) und Energie ($\hbar\omega$)

Überleitung zu allg. $S(q,\omega) \sim FT[G(r,t)]$
für nichtkristalline Systeme

# Block I – Bonus Track: Korrelationen G(r,t)

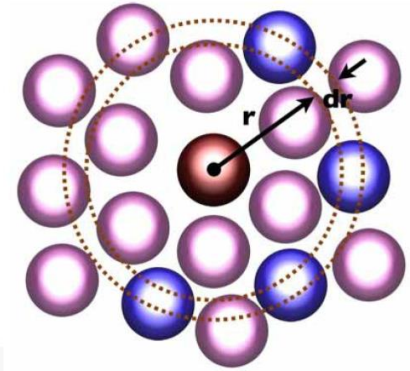
## Paarverteilungsfunktion g(r)




$$\rho g(r) 4\pi r^2 dr$$

= mittl. Teilchenzahl
in Schale [r,r+dr]
wenn ein Teilchen
bei r=0 sitzt

# Block I – Bonus Track: Korrelationen G(r,t)




Formen kondensierter Materie / Wiederholung

Strukturen g(r) im Sinne der zeitlichen Mittelung

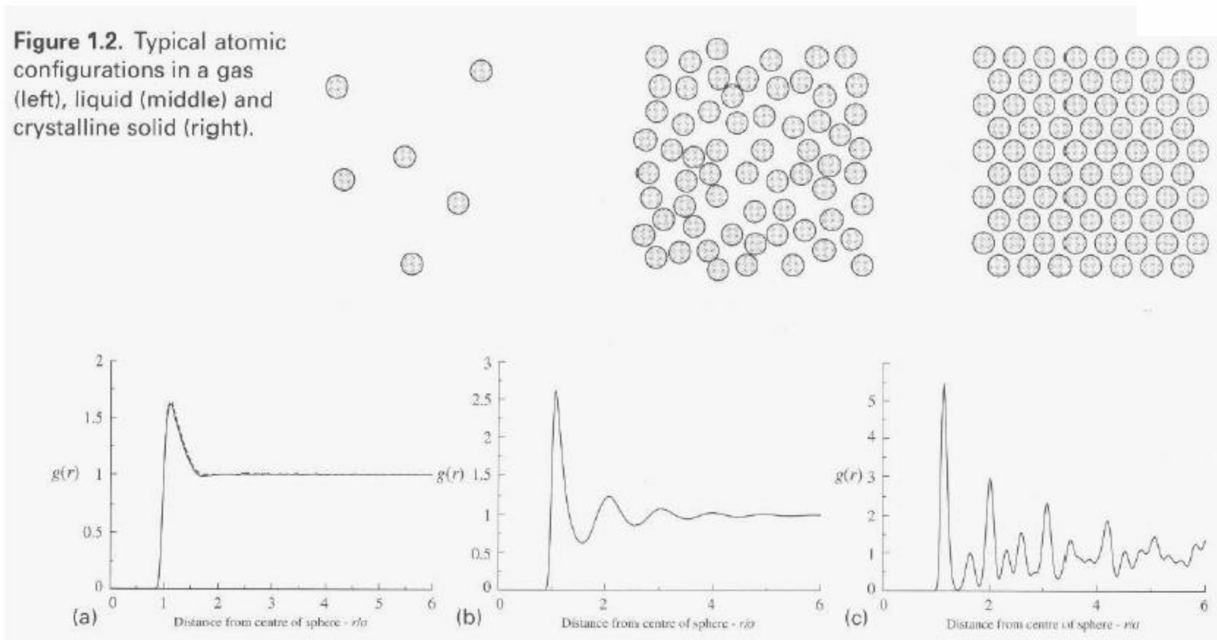



**Figure 1.2.** Typical atomic configurations in a gas (left), liquid (middle) and crystalline solid (right).

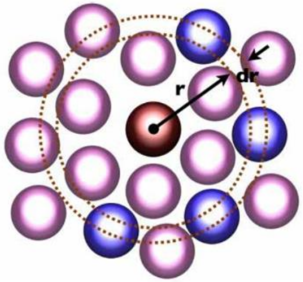
Alle Formen kondensierter Materie haben (natürlich!) auch eine Dynamik.

Diese ist ebenso charakteristisch, und in manchen Formen ist

die Dynamik das wichtige Unterscheidungsmerkmal

(z.B. Flüssigkeit vs. Glas).

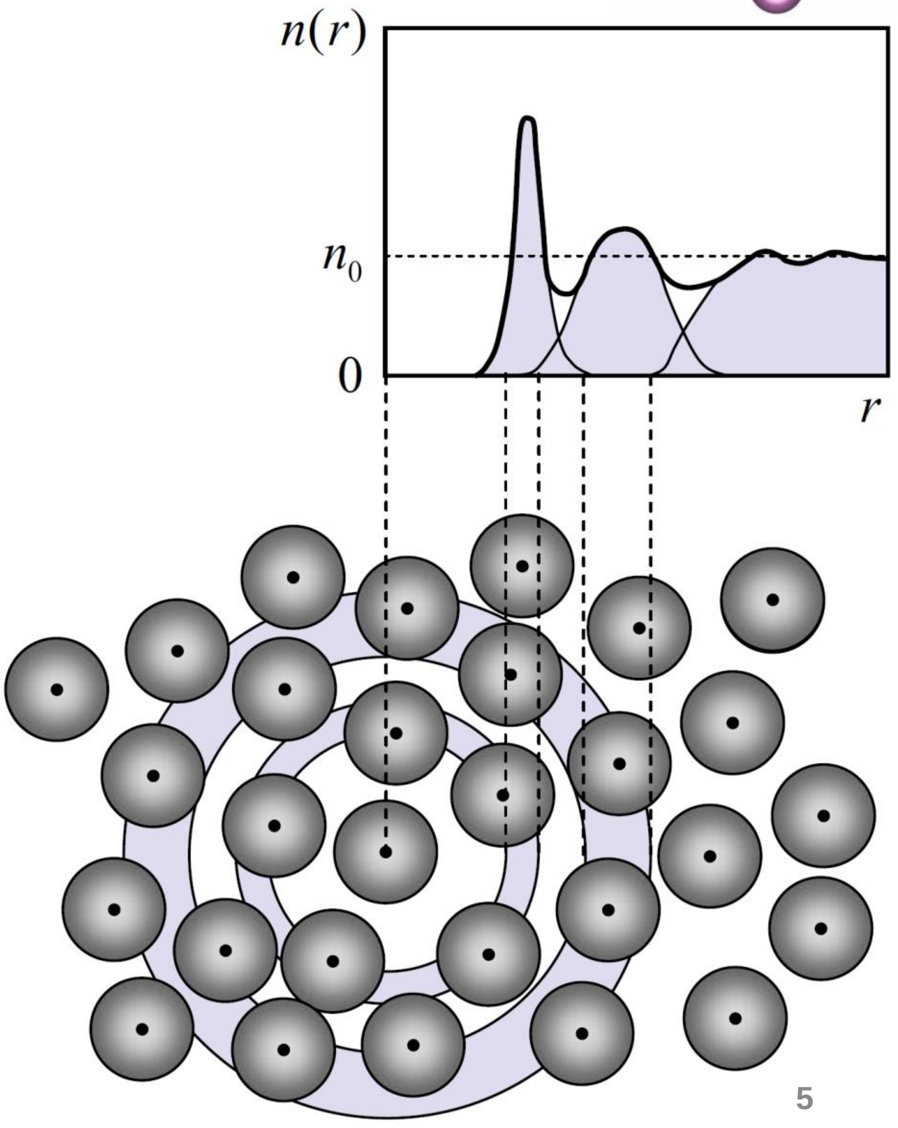
# Block I – Bonus Track: Korrelationen G(r,t)




Flüssigkeiten (vgl. I.4.1)

Was kennzeichnet die Struktur ?

... Strukturfaktor S(q) der Flüssigkeit
mit Nahordnung



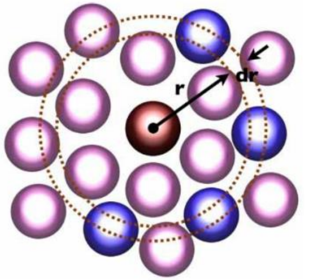

Was kennzeichnet die Dynamik ?

... Diffusion D

... Viskosität $\eta \sim 1/D$

... komplexes Anregungsspektrum
(kollektive Moden; ...)

# Block I – Bonus Track: Korrelationen G(r,t)

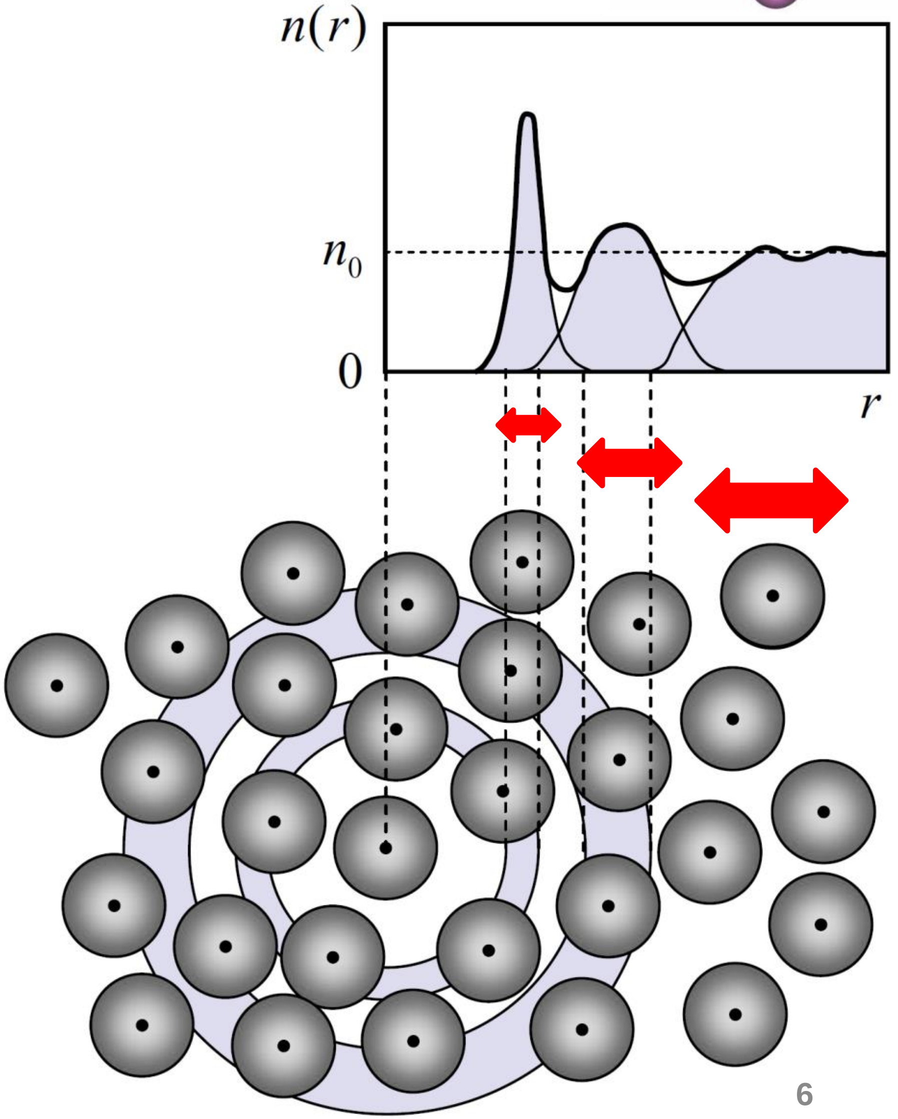



Flüssigkeiten (vgl. I.4.1)

Was kennzeichnet die Struktur ?

... Strukturfaktor S(q) der Flüssigkeit
mit Nahordnung

Dynamik (Diffusion etc.) führt zu
*zeitabhängigen* Korrelationen G(r,*t*).

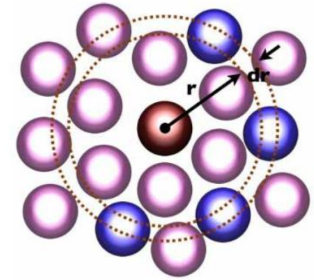



*G*(*r*,*t*) gives the probability of finding
a particle *j* at *r* for time *t*
if particle *i* has been at *r*=0 for *t*=0.



Van Hove, Phys. Rev. 95 (1954) 249

# Block I – Bonus Track: Korrelationen G(r,t)




... illustration of time-dependent correlations G(r,t) for a liquid

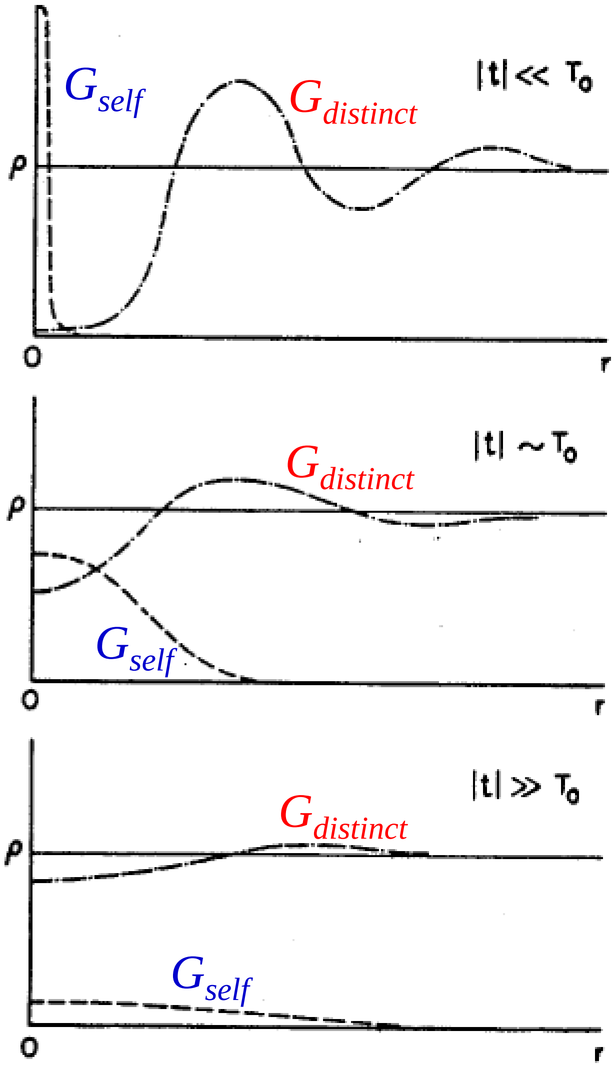



FIG. 1. The dependence of $G_s(r,t)$, (– – – –) and $G_d(r,t)$, (–·–·–) on $r$ for three values of $t$. The solid line corresponds to the average density of the system.

for short times:
essentially "static" structure factor of liquid
(see previous section)

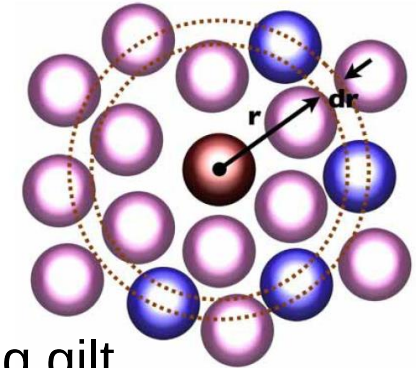
as time goes by ...
(diffusion)

for long times:
structure factor "smears out"
since all particles will have moved
(more than their own diameter after $T_0$)



Van Hove, Phys. Rev. 95 (1954) 249

# Block I – Bonus Track: Korrelationen G(r,t)




Physikalische Intuition:

Wenn für Korrelationen g(r) im Sinne der zeitlichen Mittelung gilt

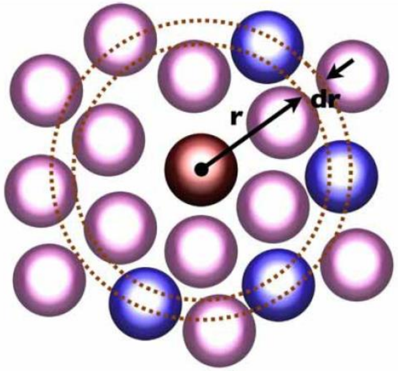
$$\boxed{S(\vec{q}) \sim \int g(\vec{r}) e^{i(\vec{q}\cdot\vec{r})}\, d\vec{r}}$$

dann sollte für die raum-zeitlichen Korrelationen G(r,t) entsprechend die Fourier-Transformation in r und t gelten, d.h.

$$\boxed{S(\vec{q},\omega) \sim \int G(\vec{r},t) e^{i(\vec{q}\cdot\vec{r}-\omega t)}\, d\vec{r} dt}$$

Dies erfordert i.allg. inelastische Streuung mit Energieübertrag $\hbar\omega$.
Daher macht die Herleitung von Energieerhaltung Gebrauch.

# Block I – Bonus Track: Korrelationen G(r,t)




Rechnungen zur Herleitung an der Tafel

$$\boxed{S(\vec{q},\omega) \sim \int G(\vec{r},t)e^{i(\vec{q}\cdot\vec{r}-\omega t)}\, d\vec{r}dt}$$

# Rechnung nach van Hove

## 1. Schritt

$$\delta(E_f - E_i + \hbar\omega) = \frac{1}{2\pi\hbar}\int dt\, e^{-it[E_f - E_i + \hbar\omega]/\hbar}$$

$$\Rightarrow S(q,\omega) \sim \Big\langle \frac{1}{2\pi\hbar}\int dt\, e^{-i\omega t}\, e^{-it[E_f - E_i]/\hbar} \sum_{m,n} b_m b_n e^{iq(R_m - R_n)}$$

## 2. Schritt

Schreibe quantenmechanisch ... und R's

$$S(q,\omega) \sim \sum_{\Psi_i,\Psi_f} \int dt\, e^{-i\omega t}\, e^{-it(E_f - E_i)/\hbar} \langle \Psi_i | e^{-iqR_m} | \Psi_f \rangle \langle \Psi_f | e^{iqR_n} | \Psi_i \rangle$$

ist im Typ ... $e^{-it\hat{H}/\hbar}\, A\, e^{it\hat{H}/\hbar}$ usw.

$\to e^{-iqR_m(t)}$

$\to e^{iqR_n(0)}$

## 3. Schritt

Übergang zu Heisenberg-Bild

$$A(t) = e^{i\hat{H}t/\hbar}\, A(0)\, e^{-i\hat{H}t/\hbar}$$

mit hier

$$A(t) = e^{-iqR_m(t)}$$

d.h. $R_m = R_m(t)$ zeitabhängig

Schritt 1-3 führt zu:

$$S(q,\omega) \sim \int dt\, e^{-i\omega t} \sum_{m,n} \langle b_m b_n \rangle\, e^{iq(R_m(t) - R_n(0))}$$

↳ spiegelt wider die raum-zeitliche Korrelation $R_m(t) - R_n(0)$

$\to r(t)$

## Konsequenzen und Spezialfälle

1) nur elastische Streuung messen, d.h. nur $\hbar\omega = 0$

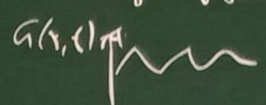
↳ liefert $\int G(r,t)\, dt$

d.h. Langzeitmittel $\to g(r)$

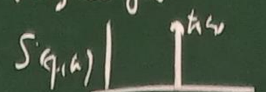
→ Bragg-Peaks

2) Phononen

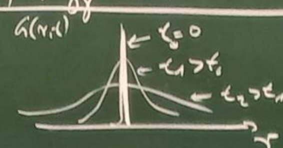
↳ energieaufgelöste Streuung liefert



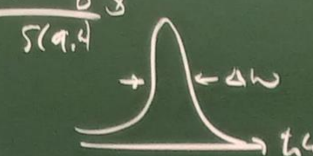

⇒




3) Diffusion (Brown'sche Bewegung)




⇒

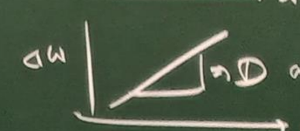



analog random walk

$(\Delta x)^2 \sim t$

$(\Delta r)^2 \sim (\text{Zeit})$

⇒



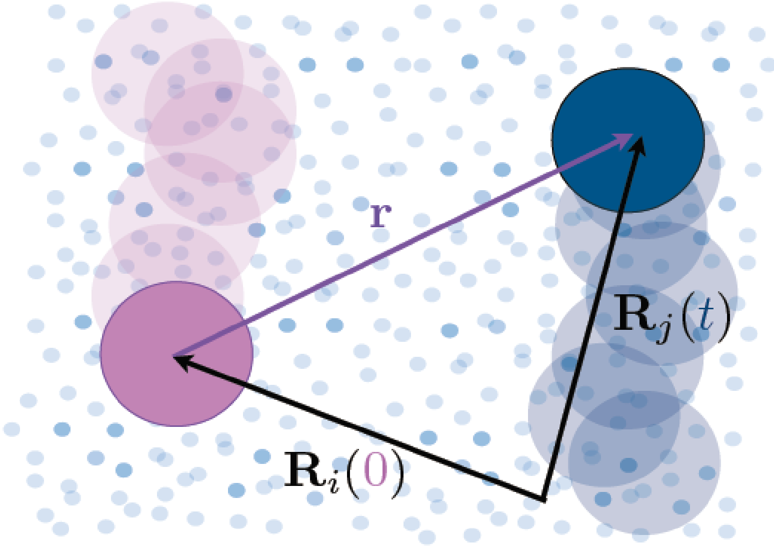

$\sim D$ aus $\Delta\omega = Dq^2$

Frequenz $\sim (q)^2$

4) nicht-Brown'sche Diffusion

Abweichung von $\Delta\omega \sim q^2$

# Correlations in space *and* time

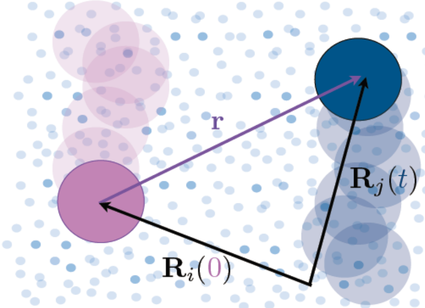



Note:

This is of general relevance for scattering, not only for neutrons;

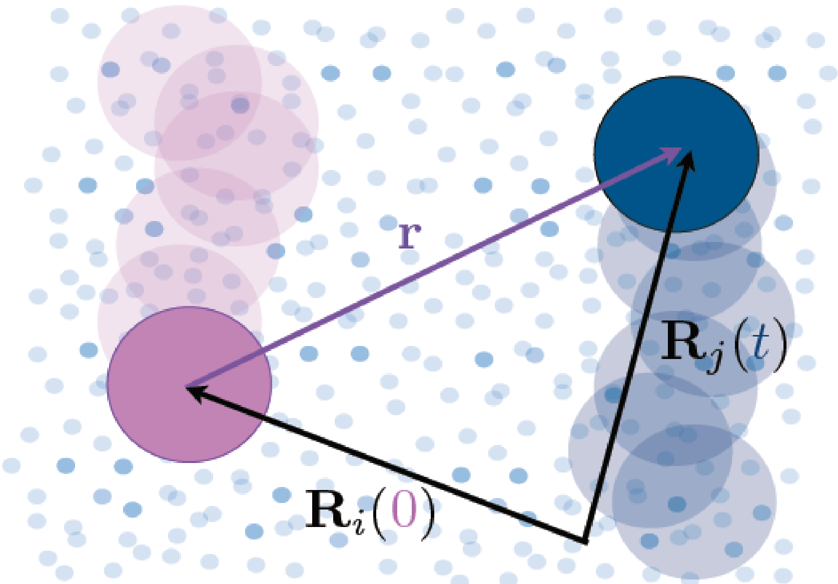
see, e.g., dynamics probed with X-rays using XPCS

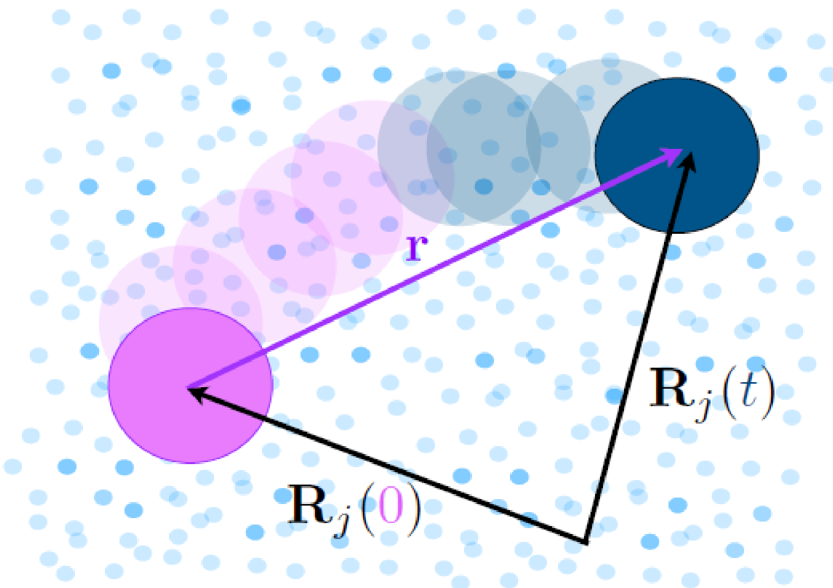
# Correlations in space and time




distinguish correlations "distinct" ($i \neq j$) and "self" ($i=j$)

$$I(\vec{q},\omega) \sim [\sigma_{coh} S_{coh}(\vec{q},\omega) + \sigma_{inc} S_{inc}(\vec{q},\omega)]$$

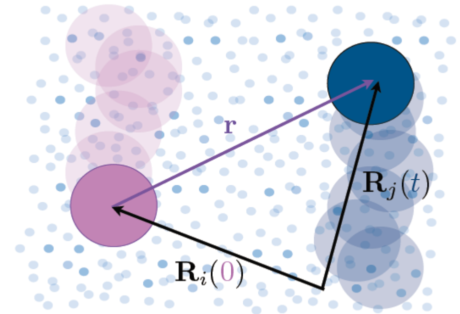




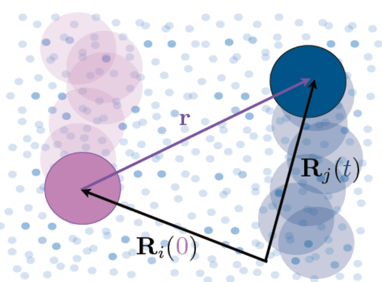

Van Hove, Phys. Rev. 95 (1954) 249

# Correlations in space and time

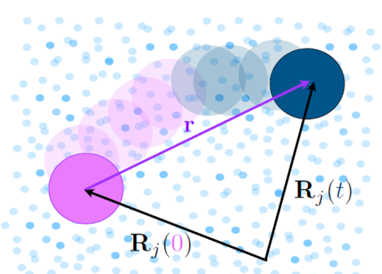



distinguish correlations “distinct“ ($i \neq j$) and “self“ ($i=j$)

$$I(\vec{q},\omega) \sim [\sigma_{coh} S_{coh}(\vec{q},\omega) + \sigma_{inc} S_{inc}(\vec{q},\omega)]$$




$$\boxed{\begin{aligned} S_{coh}(\vec{q},\omega) &= \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} dt\, e^{i\omega t} \sum_{m,n} \left\langle e^{i\vec{q}\left(\vec{R}_m(0)-\vec{R}_n(t)\right)} \right\rangle \\ &= \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} dt \int d\vec{r}\, e^{-i(\vec{q}\cdot\vec{r}-\omega t)} G_d(\vec{r},t) \end{aligned}}$$




$$\boxed{\begin{aligned} S_{inc}(\vec{q},\omega) &= \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} dt\, e^{i\omega t} \sum_{n} \left\langle e^{i\vec{q}\left(\vec{R}_n(0)-\vec{R}_n(t)\right)} \right\rangle \\ &= \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} dt \int d\vec{r}\, e^{-i(\vec{q}\cdot\vec{r}-\omega t)} G_s(\vec{r},t) \end{aligned}}$$

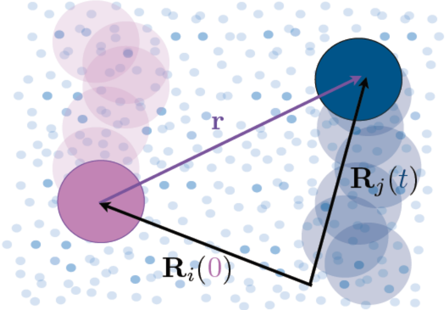
note that also $\sigma_{inc}$ carries information: “self“-correlations



Van Hove, Phys. Rev. 95 (1954) 249

# Correlations in space and time

... distinguish "self" and "distinct" correlations




$$S_{coh}(\vec{q},\omega) = \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} dt \int d\vec{r}\, e^{-i(\vec{q}\cdot\vec{r}-\omega t)} G_d(\vec{r},t)$$

$$\boxed{G_d(\vec{r},t) = \frac{1}{N}\sum_{m,n}\int d\vec{r}'\left\langle \delta(\vec{r}'-\vec{R}_n(0))\delta(\vec{r}'+\vec{r}-\vec{R}_m(t))\right\rangle_T}$$

Correlation "distinct" (with another particle)

$$S_{inc}(\vec{q},\omega) = \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} dt \int d\vec{r}\, e^{-i(\vec{q}\cdot\vec{r}-\omega t)} G_s(\vec{r},t)$$

$$\boxed{G_s(\vec{r},t) = \frac{1}{N}\sum_{n}\int d\vec{r}'\left\langle \delta(\vec{r}'-\vec{R}_n(0))\delta(\vec{r}'+\vec{r}-\vec{R}_n(t))\right\rangle_T}$$

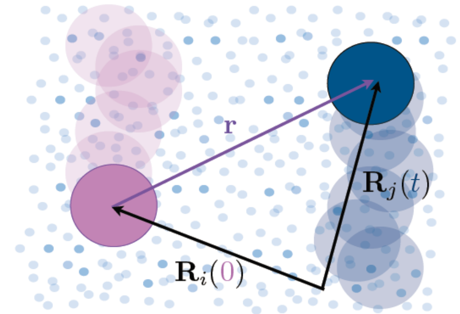
Correlation "self" (particle with itself)



Van Hove, Phys. Rev. 95 (1954) 249

# Correlations in space and time

... what we observe depends on how we integrate

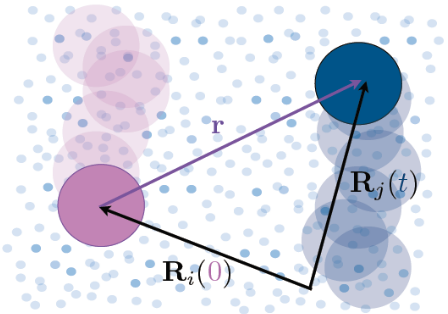



| Correlation function | Scattering function | |
|---|---|---|
| $G(\vec{r},t)$ | $S(\vec{q},\omega)$ | |
| $G(\vec{r},t=0)$ | $\int S(\vec{q},\omega)\,d\omega$ | |
| $G(\vec{r}=0,t)$ | $\int S(\vec{q},\omega)\,d\vec{q}$ | |
| $G(\vec{r}=0,t=0)$ | $\int S(\vec{q},\omega)\,d\vec{q}d\omega$ | |
| $\int G(\vec{r},t)\,dt$ | $S(\vec{q},\omega=0)$ | elastic scattering |
| $\int G(\vec{r},t)\,d\vec{r}$ | $S(\vec{q}=0,\omega)$ | |



Van Hove, Phys. Rev. 95 (1954) 249

# Correlations in space and time




## Remark on elastic scattering

In the case of $\hbar\omega = 0$

$$S(\vec{q}, \omega = 0) = \frac{1}{2\pi} \int e^{i(\vec{q}\cdot\vec{r} - 0t)} G(\vec{r}, t)\, d\vec{r} dt$$

$$= \frac{1}{2\pi} \int e^{i\vec{q}\cdot\vec{r}} \underbrace{\left[ \int G(\vec{r}, t)\, dt \right]}_{\text{“Long-term exposure”}} d\vec{r}$$

→ Elastic scattering is the spatial Fourier transform of the time-averaged correlation function!

*This makes Bragg peaks observable despite lattice dynamics !*



Van Hove, Phys. Rev. 95 (1954) 249

# Correlations in space and time

Example:

Phonons

… one phonon with wavevector k and frequency $\omega$ corresponds to exactly these correlations of the type $\sim \sin((2\pi/\lambda)r - \omega t)$

… thus, the Fourier transform

$$\boxed{S(\vec{q},\omega) \sim \int G(\vec{r},t)e^{i(\vec{q}\cdot\vec{r}-\omega t)}\, d\vec{r}dt}$$

… delivers these parameters,

i.e. one discrete q and one diskrete $\omega$

… as expected from phonon spectroscopy experiments

… using inelastic neutron scattering

# Correlations in space and time

Example:

Diffusion (Brownian motion)

… the smoking gun is the simple Lorentzian for $S(q,\omega)$

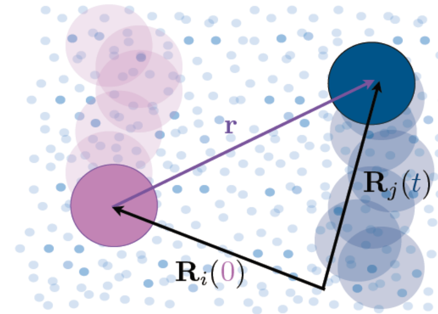
with

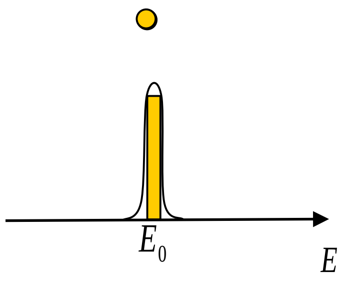
“ width $\Delta\omega \sim q^2$ “

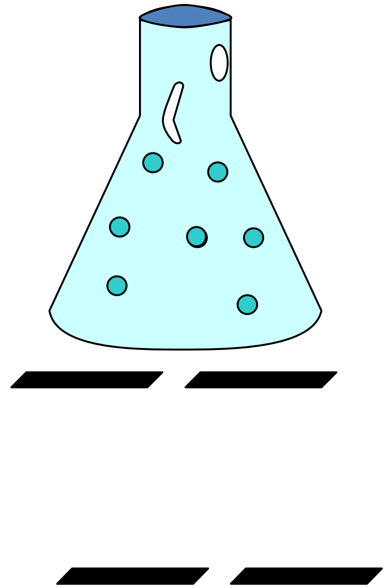
which is connected to

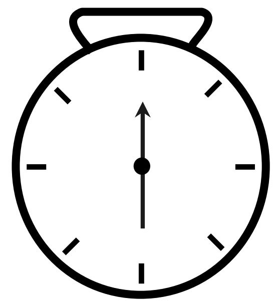
“ correlations $G(r,t) \sim \exp(- C\, r^2 / t)$ “

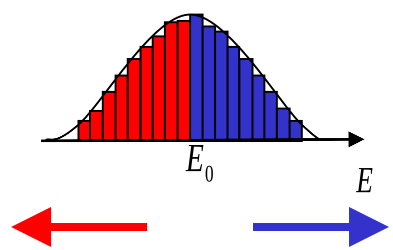
# Correlations in space and time





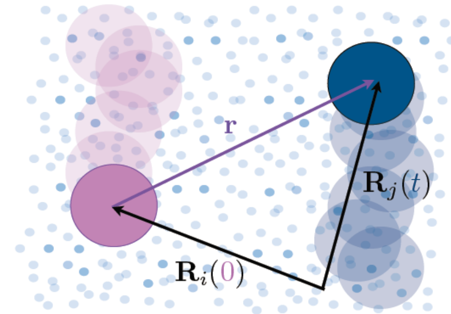



red-shifted neutrons
("energy loss")

blue-shifted neutrons
("energy gain")

→ Broadening of $E = \hbar\omega$ contains information on dynamics in sample!

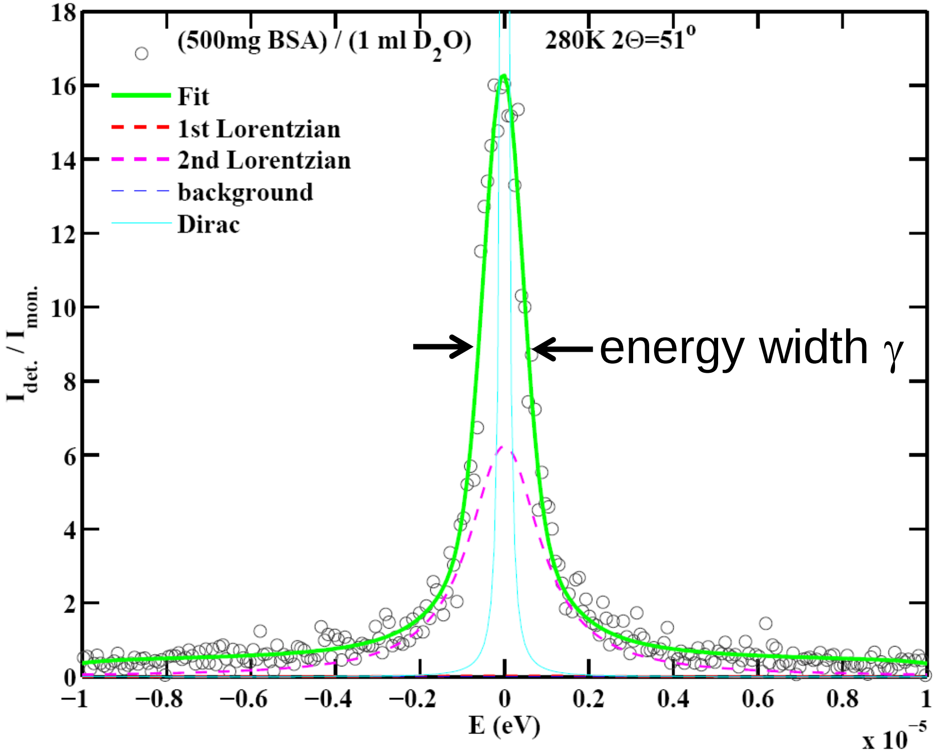
# Correlations in space and time




Example: Diffusion and quasi-elastic neutron scattering

$$G(\vec{r},t) = \frac{1}{N}\sum_{k,j}^{N}\langle\delta\{\vec{r}+\vec{r}_k(0)-\vec{r}_j(t)\}\rangle$$

$$S(\vec{q},\omega) \sim \int G(\vec{r},t)e^{i(\vec{q}\cdot\vec{r}-\omega t)}\,d\vec{r}dt$$




For diffusive systems

$$D\nabla^2 G_s(\vec{r},t) = \frac{\partial}{\partial t}G_s(\vec{r},t)$$

$$\boxed{G_s(\vec{r},t) = (4\pi D|t|)^{-\frac{3}{2}}\exp\left(-\frac{r^2}{4D|t|}\right)} \xrightarrow{\text{FT}} \boxed{S(q,\omega) = \frac{1}{\pi}\frac{Dq^2}{(Dq^2)^2+\omega^2}}$$

Exponential decay ($r$,$t$)

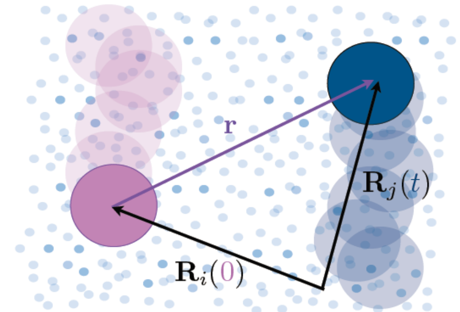
Lorentzian ($q$,$\omega$)



Roosen-Runge et al., PNAS 108 (2011) 11815

Vineyard, Phys. Rev. 110 (1958) 999

# Correlations in space and time




Example: Diffusion and quasi-elastic neutron scattering

$$G(\vec{r},t) = \frac{1}{N}\sum_{k,j}^{N}\langle\delta\{\vec{r}+\vec{r}_k(0)-\vec{r}_j(t)\}\rangle$$

$$S(\vec{q},\omega) \sim \int G(\vec{r},t)e^{i(\vec{q}\cdot\vec{r}-\omega t)}\,d\vec{r}dt$$

For diffusive systems

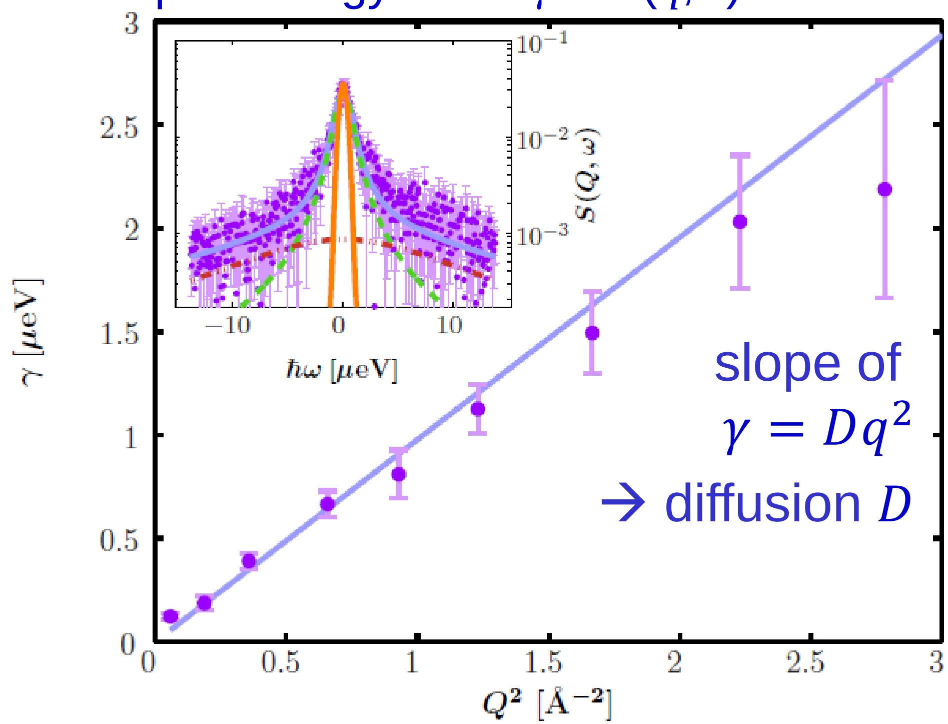
$$D\nabla^2 G_s(\vec{r},t) = \frac{\partial}{\partial t}G_s(\vec{r},t)$$

$$\boxed{G_s(\vec{r},t) = (4\pi D|t|)^{-\frac{3}{2}}\exp\left(-\frac{r^2}{4D|t|}\right)}$$

Exponential decay ($r$,$t$)

FT

plot energy width $\gamma$ of $S(q,\omega)$




slope of $\gamma = Dq^2$

→ diffusion $D$

$$\boxed{S(q,\omega) = \frac{1}{\pi}\frac{Dq^2}{(Dq^2)^2+\omega^2}}$$

Lorentzian ($q$,$\omega$)



Roosen-Runge et al., PNAS 108 (2011) 11815

Vineyard, Phys. Rev. 110 (1958) 999

# Correlations in space and time

Example:

Jump diffusion

… problem as homework

# Correlations in space and time

Unconventional dynamics (non-Brownian)

… the smoking gun is the deviation from the simple Lorentzian for $S(q,\omega)$, i.e.

*not* " width $\Delta\omega \sim q^2$ "

which implies

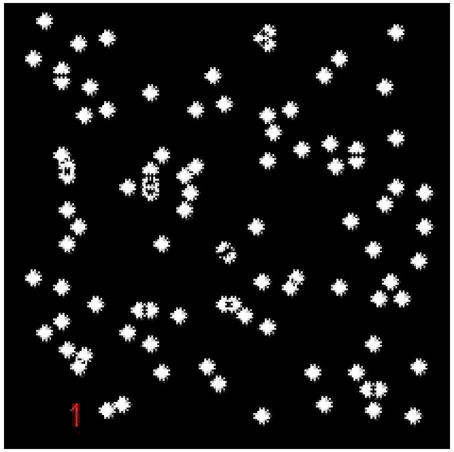
*deviation* from " correlations $G(r,t) \sim \exp(- r^2 / 4Dt)$ "

Examples are anomalous diffusion (subdiffusion; superdiffusion etc)

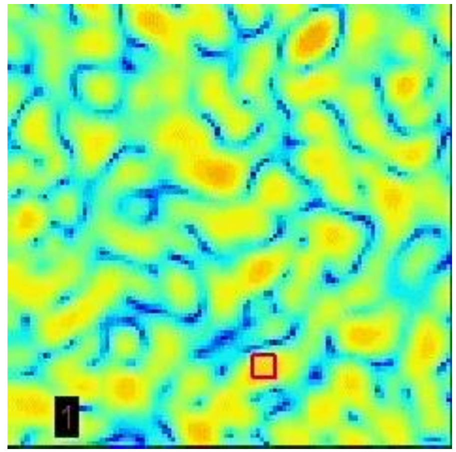
# Correlations in space and time

X-ray photon correlation spectroscopy XPCS

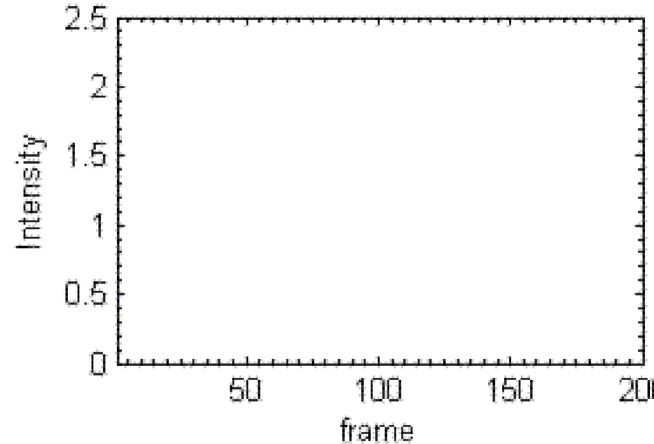
Brownian motion of 100 particles

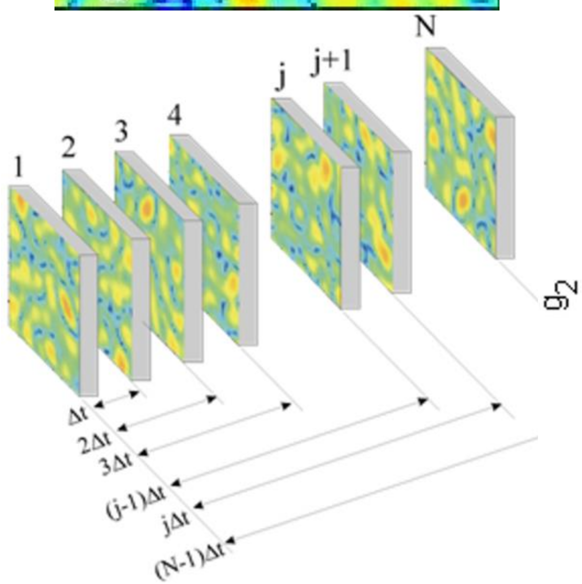


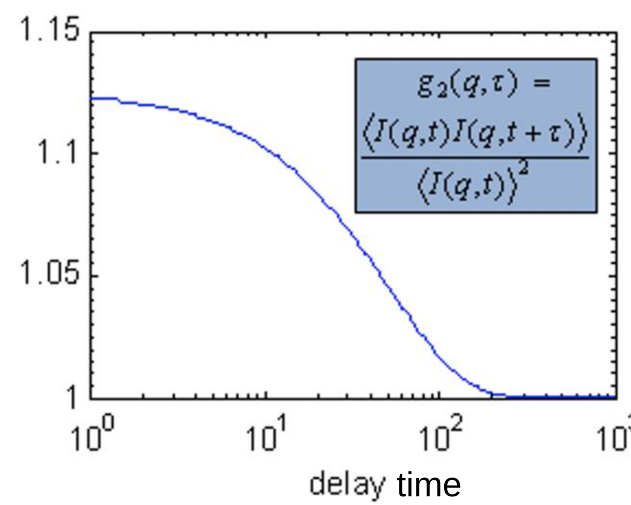

Diffraction pattern with speckles




Fluctuations of intensity




Further correlations, e.g. $Corr(\vec{q}, t_1, t_2) = \frac{\langle I(\vec{q}, t_1) I(\vec{q}, t_2)\rangle}{\langle I(\vec{q}, t_1)\rangle \langle I(\vec{q}, t_2)\rangle}$

https://sinhagroup.ucsd.edu/Research_XPCS.htm

# Correlations in space and time

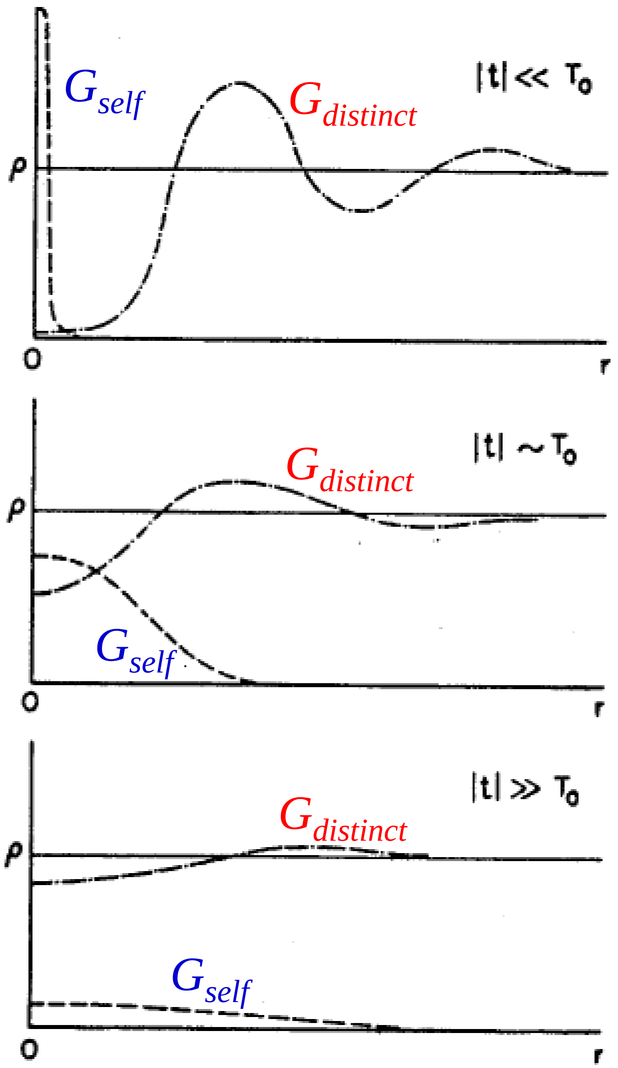



FIG. 1. The dependence of $G_s(r,t)$, (– – – –) and $G_d(r,t)$, (–·–·–) on $r$ for three values of $t$. The solid line corresponds to the average density of the system.

$$\boxed{S(\vec{q},\omega) \sim \int G(\vec{r},t)e^{i(\vec{q}\cdot\vec{r}-\omega t)}\,d\vec{r}dt}$$