# Advanced Topics in Condensed Matter

## Lecture 4: Partially ordered systems

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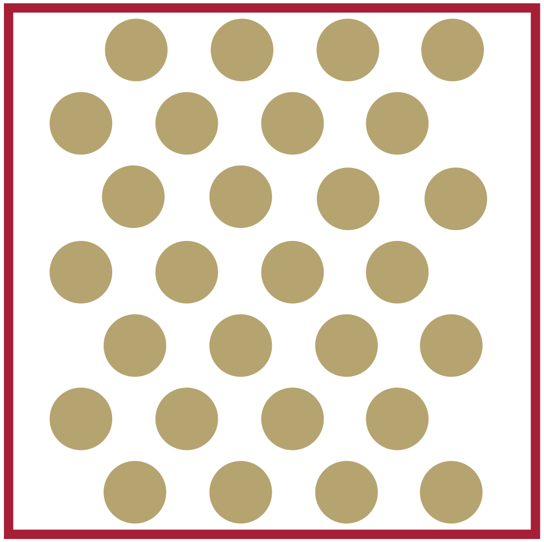
# Ideal liquid and ideal crystal

Crystal lattice is periodic and anisotropic:

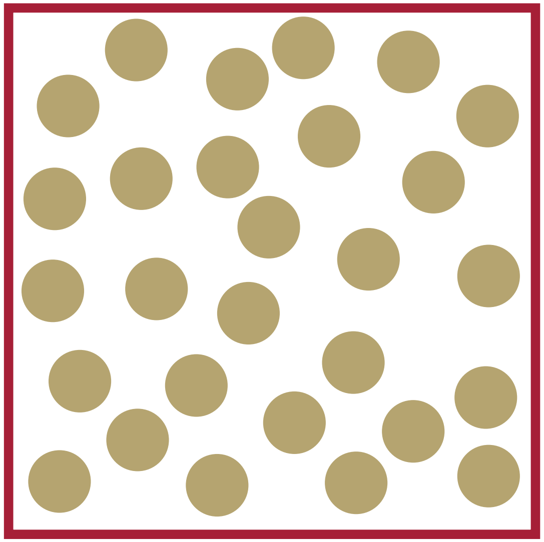
$$\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$



Crystal

Fluids are homogeneous and isotropic:

$$P(\vec{r}) = \text{const}$$

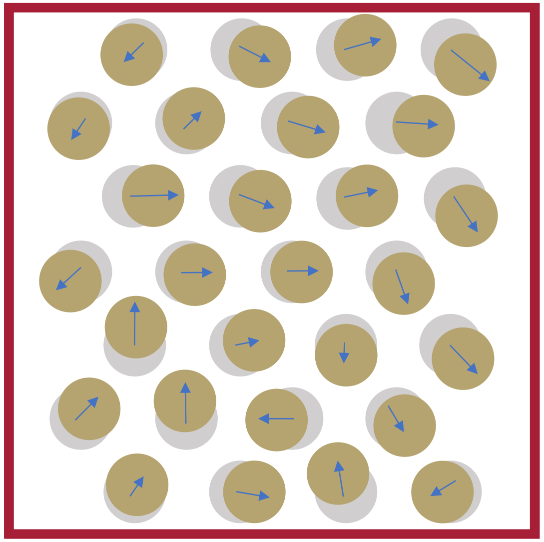


Fluid

# Real liquid and real crystal

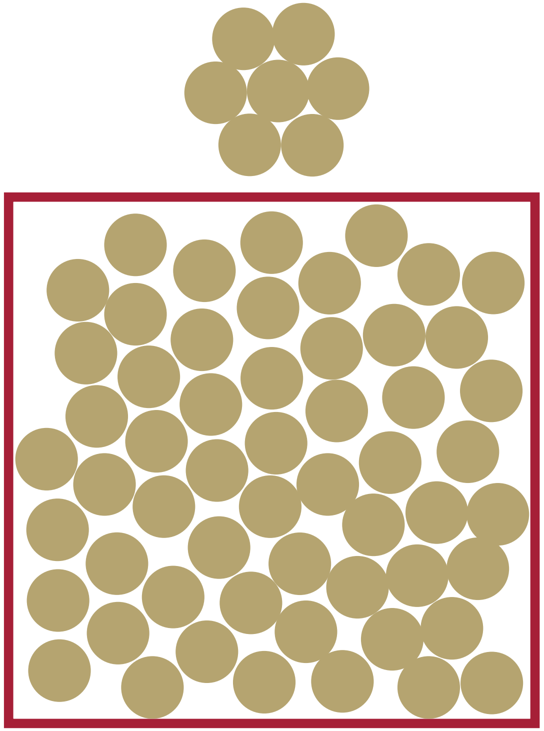
In real crystals atoms might be displaced due to defects:

$$\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 + \vec{u}_n$$



Sparce crystal

Real liquids have local order:

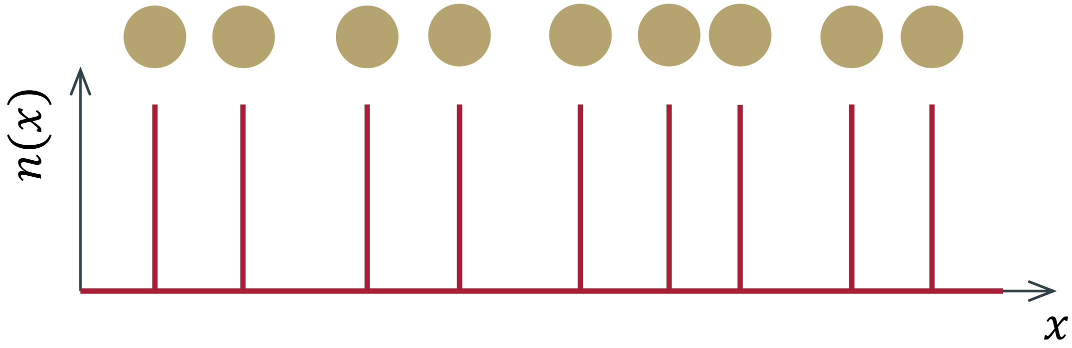


Dense liquid

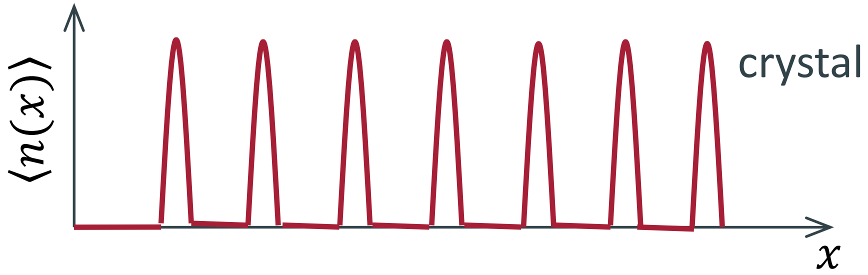
# Correlation function

The structure of the material (positions of each atom) can be described by the number density:

$$n(\vec{r}) = \sum_{\alpha} \delta(\vec{r} - \vec{r}_{\alpha})$$



$\langle n(\vec{r}) \rangle$ is useful in crystals:



$\langle n(\vec{r}) \rangle$ is not very useful in liquids:

Here $\langle \ldots \rangle$ denotes statistical averaging, i.e. time-averaging or ensemble-averaging (ergodicity)

# Correlation function

To get more general and meaningful information, one has to compute density-density correlation function:

$$G(\vec{r}_1,\vec{r}_2) = \frac{1}{N}\langle n(\vec{r}_1)n(\vec{r}_2)\rangle = \frac{1}{N}\left\langle \sum_{\alpha\alpha\prime} \delta(\vec{r}_1-\vec{r}_\alpha)\delta(\vec{r}_2-\vec{r}_{\alpha\prime})\right\rangle$$

Here $\langle\ldots\rangle$ denotes statistical averaging, i.e. time-averaging or ensemble-averaging (ergodicity)

If the system is translationally invariant, i.e. the correlation function depends only on $\vec{r}=(\vec{r}_2-\vec{r}_1)$, the correlation function can be simplified:

$$G(\vec{r}) = \frac{1}{N}\langle n(\vec{R})n(\vec{R}+\vec{r})\rangle = \frac{1}{N}\left\langle \sum_{\alpha\alpha\prime} \delta(\vec{R}-\vec{r}_\alpha)\delta(\vec{R}+\vec{r}-\vec{r}_{\alpha\prime})\right\rangle =$$

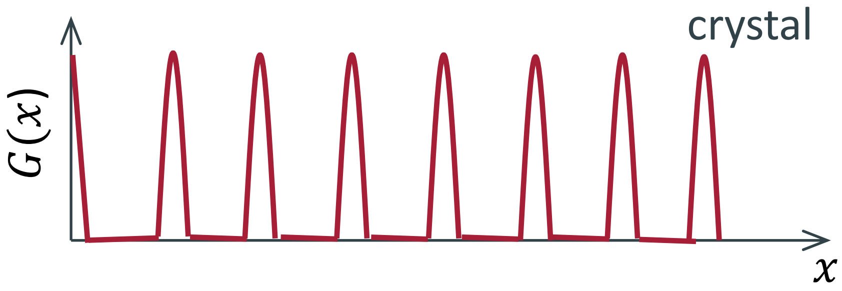
$$= \frac{1}{N}\int \left\langle \sum_{\alpha\alpha\prime} \delta(\vec{R}-\vec{r}_\alpha)\delta(\vec{R}+\vec{r}-\vec{r}_{\alpha\prime})\right\rangle d\vec{R} =$$

$$= \frac{1}{N}\left\langle \sum_{\alpha\alpha\prime} \int \delta(\vec{R}-\vec{r}_\alpha)\delta(\vec{R}+\vec{r}-\vec{r}_{\alpha\prime})d\vec{R}\right\rangle =$$

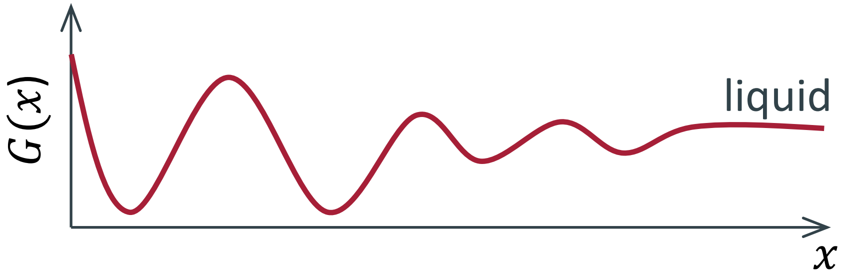
$$= \frac{1}{N}\left\langle \sum_{\alpha\alpha\prime} \delta(\vec{r}-(\vec{r}_{\alpha\prime}-\vec{r}_\alpha))\right\rangle$$

# Correlation function is always useful

$G(\vec{r})$ is useful in crystals:



$G(\vec{r})$ is useful in liquids:



# Structure factor

General equation for the scattered amplitude: $E \propto \sum_i f_i\,(q) \cdot e^{-i\vec{q}\vec{r}_i}$

General equation for the scattered intensity:

$$I \propto |E|^2 \propto \left|\sum_{i=1}^{N} f(q) \cdot e^{-i\vec{q}\vec{r}_i}\right|^2 = |f(q)|^2 \cdot \sum_{i=1}^{N} e^{-i\vec{q}\vec{r}_i} \cdot \sum_{j=1}^{N} e^{+i\vec{q}\vec{r}_j}$$

$$= |f(q)|^2 \sum_{i,j=1}^{N} \exp\left(-i\vec{q}\left(\vec{r}_i - \vec{r}_j\right)\right) = |f(q)|^2 \left[N + \sum_{\substack{i,j=1\\ i\neq j}}^{N} \exp\left(-i\vec{q}\left(\vec{r}_i - \vec{r}_j\right)\right)\right]$$

$$I \propto N \cdot |f(q)|^2 \cdot \underbrace{\left[1 + \frac{1}{N}\left\langle \sum_{\substack{i,j=1\\ i\neq j}}^{N} \exp\left(-i\vec{q}\left(\vec{r}_i - \vec{r}_j\right)\right)\right\rangle\right]}_{\text{structure factor } S(\vec{q})} = N \cdot |f(q)|^2 \cdot S(\vec{q})$$

# Correlation function and scattering

$$S(\vec{q}) = \frac{1}{N}\left\langle \sum_{\alpha\alpha'} e^{-i\vec{q}(\vec{r}_\alpha - \vec{r}_{\alpha'})} \right\rangle = \frac{1}{N}\int e^{-i\vec{q}(\vec{r}_1-\vec{r}_2)} \langle n(\vec{r}_1) n(\vec{r}_2)\rangle d\vec{r}_1\, d\vec{r}_2 = \frac{1}{N}\langle n(\vec{q}) n(-\vec{q})\rangle$$

where

$$n(\vec{q}) = \int e^{-i\vec{q}\vec{r}} n(\vec{r}) d\vec{r} = \sum_{\alpha} e^{-i\vec{q}\vec{r}_\alpha}$$

$$\langle n(\vec{r}_1) n(\vec{r}_2)\rangle = \left\langle \sum_{\alpha\alpha'} \delta(\vec{r}_1 - \vec{r}_\alpha)\delta(\vec{r}_2 - \vec{r}_{\alpha'}) \right\rangle$$

Alternatively,

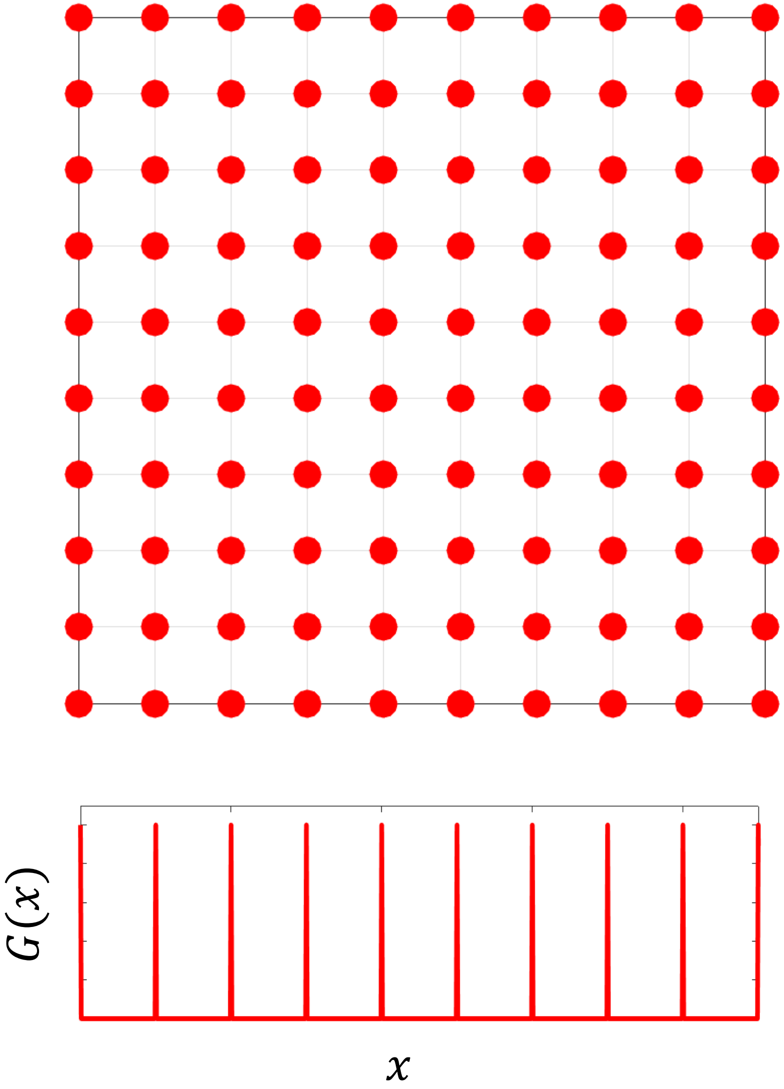
$$S(\vec{q}) = \frac{1}{N}\int e^{-i\vec{q}(\vec{r}_1-\vec{r}_2)} \langle n(\vec{r}_1) n(\vec{r}_2)\rangle d\vec{r}_1\, d\vec{r}_2 = \int e^{-i\vec{q}(\vec{r}_1-\vec{r}_2)} G(\vec{r}_1, \vec{r}_2) d\vec{r}_1\, d\vec{r}_2$$

$$S(\vec{q}) = \frac{1}{N}\int e^{-i\vec{q}\vec{r}} \left\langle n\left(\vec{R}\right) n\left(\vec{R}+\vec{r}\right)\right\rangle d\vec{r}\, d\vec{R} = \int e^{-i\vec{q}\vec{r}} G\left(\vec{r}\right) d\vec{r} \qquad \text{(here } \vec{r} = \vec{r}_1 - \vec{r}_2\text{)}$$

Thus, in scattering, we measure the Fourier transform of the correlation function under the assumptions from lecture #2: a) Single-scattering (kinematical theory, valid for not too perfect crystals)

b) Far-field regime (Fraunhofer diffraction, $L \gg d^2/\lambda$, always valid for x-rays, because $d \sim \lambda \sim 1\text{Å}$)

# Ideal crystal

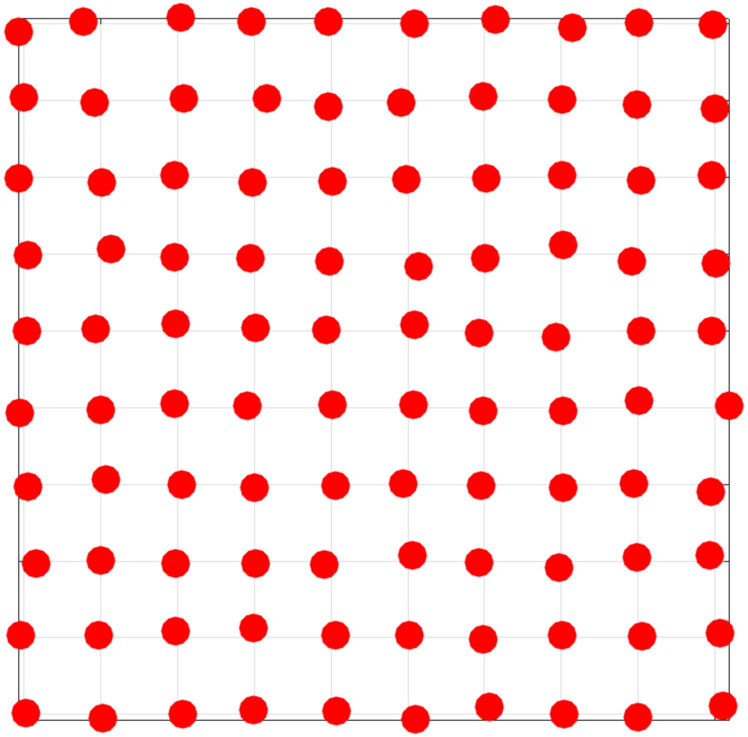


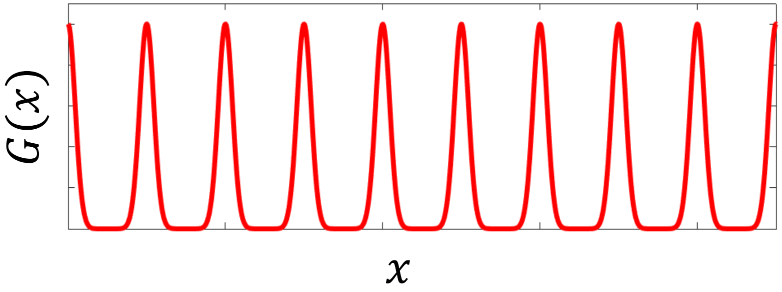
In a crystal, we are sure that we will find an atom at the separation

$$\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

from a given atom, even if $\left|\vec{R}_n\right| \gg a$. This type of order is called long-range order (LRO). In LRO, the correlation function $G(\vec{r})$ is approaching non-zero limit at large distances.

# Ideal crystal + random displacements



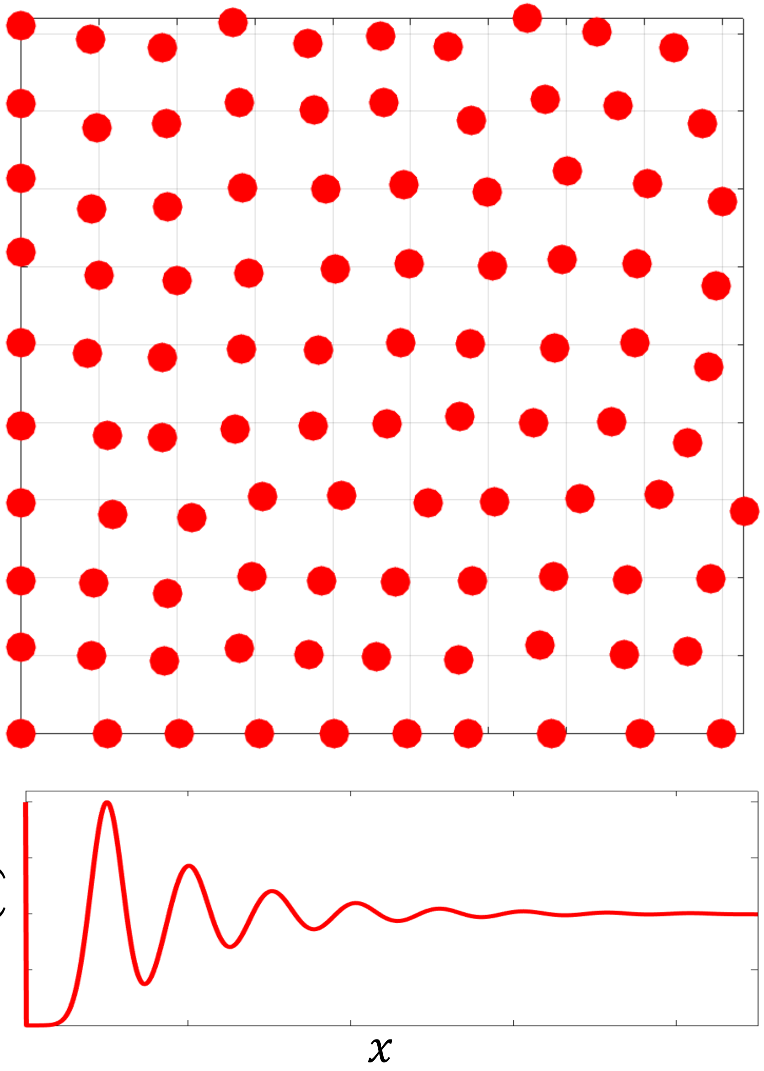


Even if the atoms are randomly displaced from the equilibrium positions, i.e.

$$\vec{r}_n = \vec{R}_n + \vec{u}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 + \vec{u}_n$$

The long-range order is not destroyed. The correlation function $G(\vec{r})$ is approaching non-zero constant value at large distances.

# Short-range order



In liquids, the correlation function $G(\vec{r})$ decays exponentially at large distances, i.e.

$$G(\vec{r}) \propto \exp\left(-\frac{r}{\xi}\right).$$

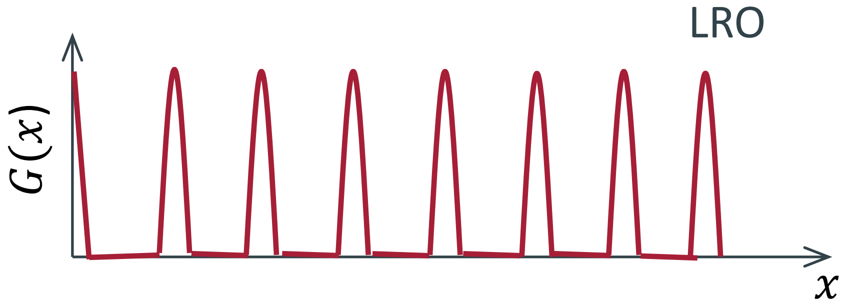
This is considered as a fast decay, which can be described by a correlation length $\xi$. Such an order is called short-range order (SRO)

Short-range order can be observed if atoms have no fixed equilibrium positions, but placed relative to each other at some distance $a$, which can be randomly changed (see example 2):

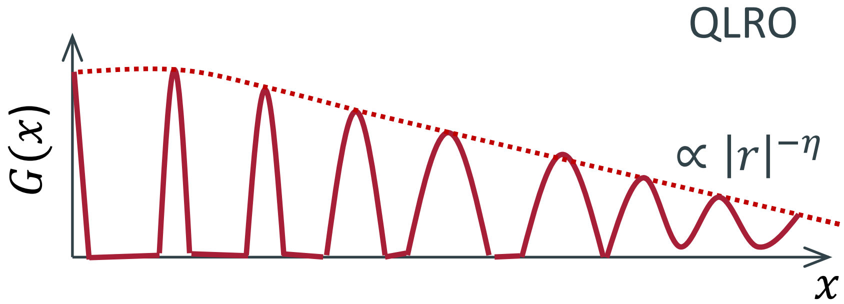
$$\vec{r}_n = \vec{r}_{n-1} + \vec{a} + \vec{u}$$

# Difference between liquids and crystals

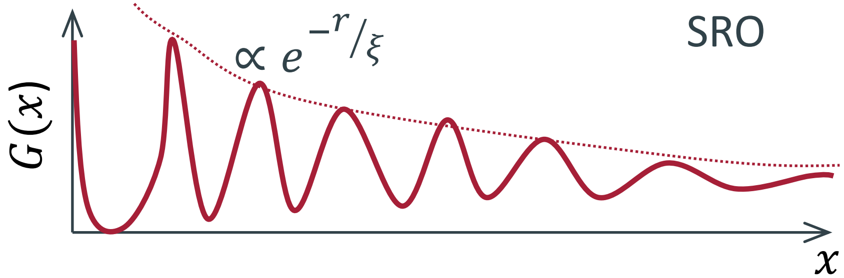
In **a crystal**, we are still sure that we will find an atom at the separation $\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$ from the given one, even if $|\vec{R}_n| \gg a$. This type of order is called long-range order. In LRO, the correlation function $G(\vec{r})$ is approaching non-zero limit at large distances.



In quasi-long-range order (**crystal with certain defects**), it slowly decays (algebraically): $G(r) \propto |r|^{-\eta}$



In short- range order (**a liquid or amorphous solid**), it exponentially decays with a characteristic length $\xi$: $G(r) \propto \exp\left(-{}^{r}/_{\xi}\right)$



Important is, how the correlation function behaves at large distances ($|\vec{r}| \to \infty$)

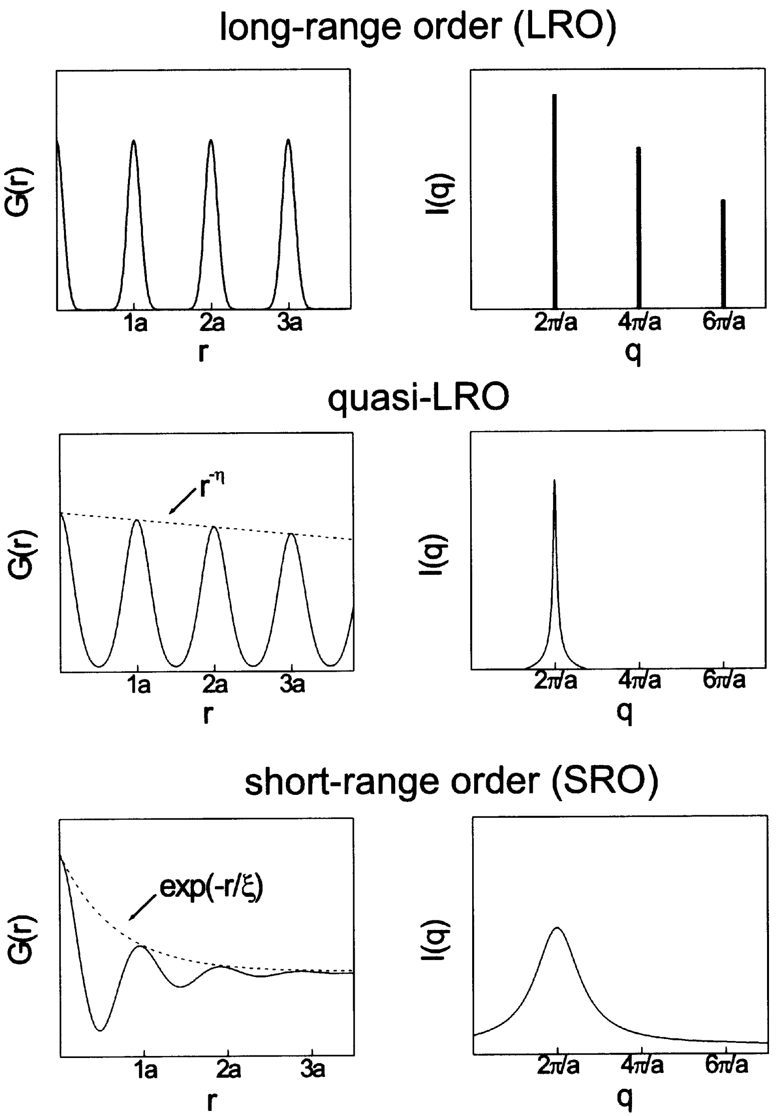
# Difference between liquids and crystals

In **a crystal**, we are still sure that we will find an atom at the separation $\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$ from the given one, even if $|\vec{R}_n| \gg a$. This type of order is called long-range order. In LRO, the correlation function $G(\vec{r})$ is approaching non-zero limit at large distances.

In quasi-long-range order (**crystal with certain defects**), it slowly decays (algebraically): $G(r) \propto |r|^{-\eta}$

In short- range order (**a liquid or amorphous solid**), it exponentially decays with a characteristic length $\xi$: $G(r) \propto \exp\left(-{}^{r}/_{\xi}\right)$

Important is, how the correlation function behaves at large distances ($|\vec{r}| \to \infty$)



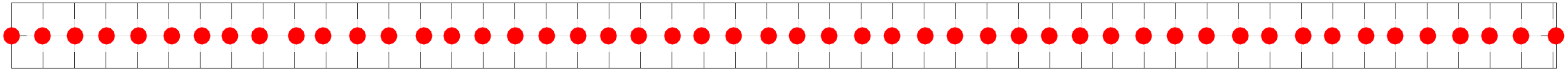
de Jeu et al., Rev. Mod. Phys. **75**, 181 (2003)

# Examples of 1D long- and short-range order

**Example 1**: scattering from a 1D crystal with random displacements.
Consider a 1D crystal, in which positions of atoms are defined as

$$X_n = n \cdot a + u_n,$$

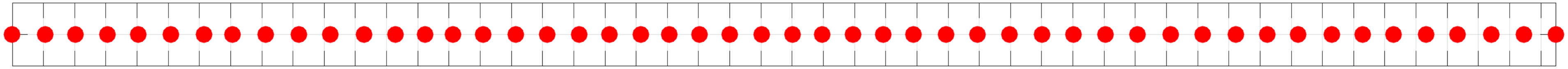
where $a$ is a lattice parameter, $n = 1 \ldots N$ enumerates atoms ($N \gg 1$), and $u_n$ is a displacement of the nth atom from its equilibrium position. Let $u_n$ be a gaussian variable with zero mean and a variance $\langle u_n^2 \rangle = \sigma^2$. Calculate the density-density correlation function $G(x)$ and the structure factor $S(q)$.



**Example 2**: scattering from a 1D liquid with short-range order .
Consider a 1D crystal, in which positions of atoms are defined recurrently as

$$X_n = X_{n-1} + a_n,$$

where $a_n$ is a lattice parameter, $n = -\infty \ldots +\infty$ enumerates atoms. Let $a_n$ be a gaussian variable with the mean $a$ and a variance $\langle (a_n - a)^2 \rangle = \sigma^2$. Calculate the density-density correlation function $G(x)$ and the structure factor $S(q)$.



# Scattering from a 1D crystal

Example #1.

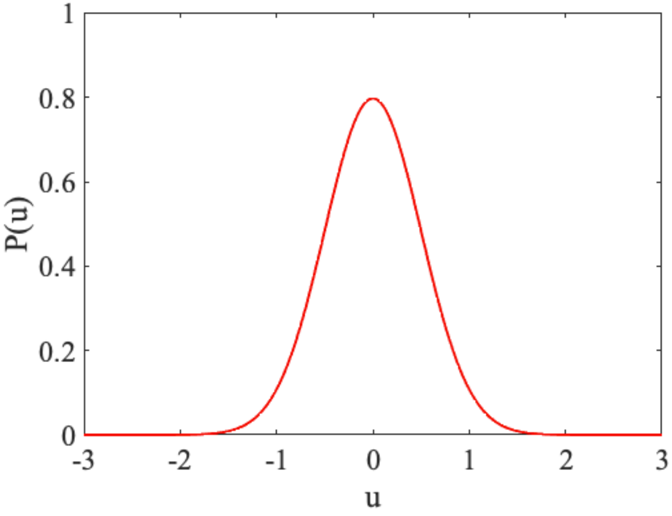
Consider a 1D crystal, in which positions of atoms are defined as

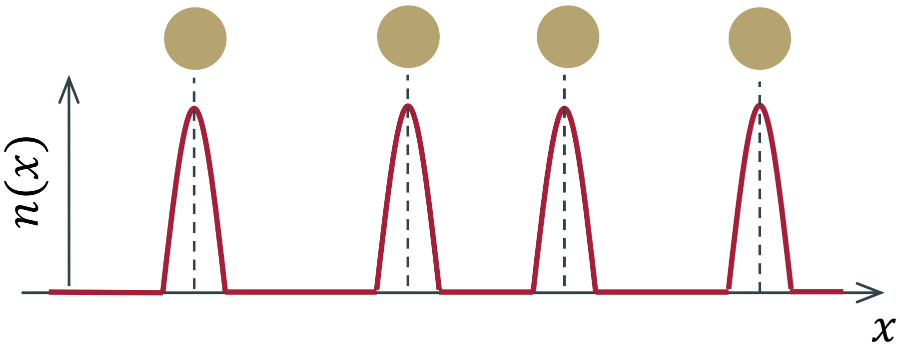
$$X_n = n \cdot a + u_n,$$

where $a$ is a lattice parameter, $n = 1 \dots N$ enumerates atoms ($N \gg 1$), and $u_n$ is a displacement of the nth atom from its equilibrium position. Let $u_n$ be a gaussian variable with zero mean and a variance $\langle u_n^2 \rangle = \sigma^2$.

1. Calculate the density-density correlation function $G(x)$
2. Calculate the structure factor $S(q)$

$$P(u) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{u^2}{2\sigma^2}}$$





# Solution #1

For an ideal crystal:

$$S(q) = \frac{1}{N}\sum_{n,m}^{N} e^{-iq(x_n - x_m)} = \frac{1}{N}\sum_{n,m}^{N} e^{-iqa(n-m)} \xrightarrow[N\gg 1]{} N\sum_h \delta\left(q - \frac{2\pi}{a}h\right)$$

For a crystal with displacements:

$$S(q) = \frac{1}{N}\left\langle \sum_{n,m}^{N} e^{-iq(x_n + u_n - x_m - u_m)} \right\rangle = \frac{1}{N}\sum_{n,m}^{N} e^{-iq(x_n - x_m)} \left\langle e^{-iq(u_n - u_m)} \right\rangle$$

$$\xrightarrow[N\gg 1]{} Ne^{-q^2\sigma^2}\sum_h \delta\left(q - \frac{2\pi}{a}h\right)$$

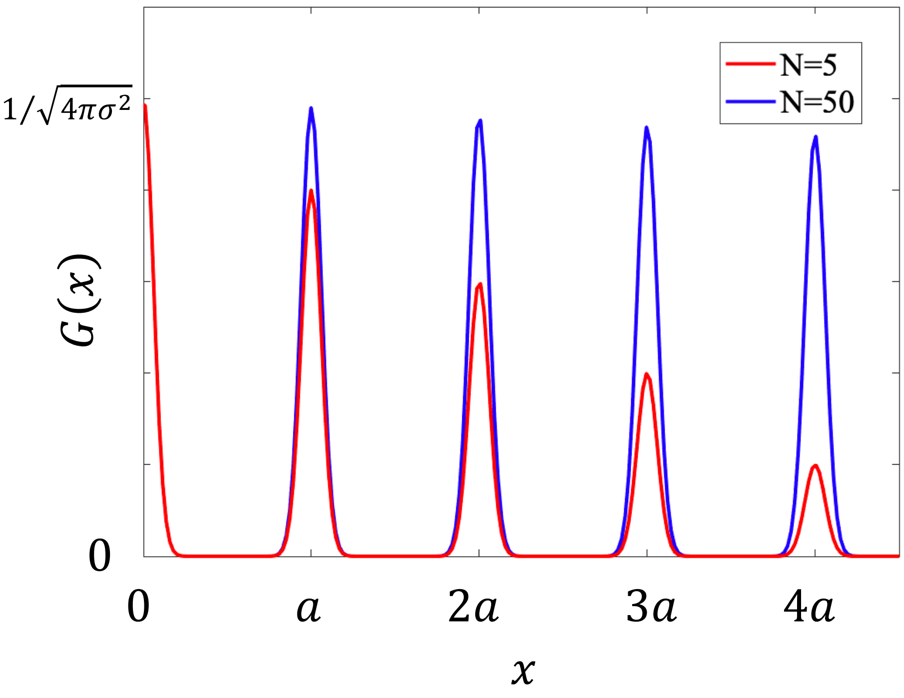
$$\left\langle e^{-iq(u_n - u_m)} \right\rangle = \int_{-\infty}^{+\infty} e^{-iq(u_n - u_m)} \cdot P(u_n - u_m) d(u_n - u_m)$$

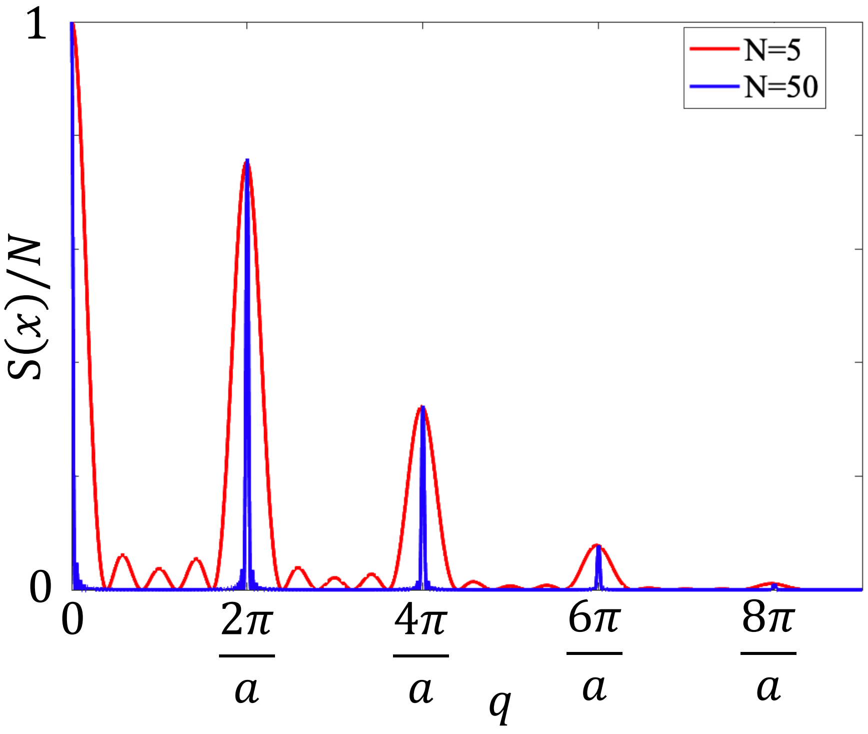
$$P(u_n - u_m) = \frac{1}{\sqrt{4\pi\sigma^2}} \exp\left[-\frac{|u_n - u_m|^2}{4\sigma^2}\right]$$

$$\left\langle e^{-iq(u_n - u_m)} \right\rangle = \int_{-\infty}^{+\infty} e^{-iqz} \cdot \frac{1}{\sqrt{4\pi\sigma^2}} \exp\left[-\frac{z^2}{4\sigma^2}\right] dz \;= e^{-q^2\sigma^2}$$

# Solution #1

- Deviations of the atoms from the crystal sites do not destroy the long-range order.
- We see sharp Bragg peaks at $q = \frac{2\pi}{a}n$ with a full width at half maxima (FWHM) of $\approx \frac{2\pi}{aN}$ and magnitude of $\approx e^{-q^2\sigma^2}N$.





# Scattering from a 1D liquid

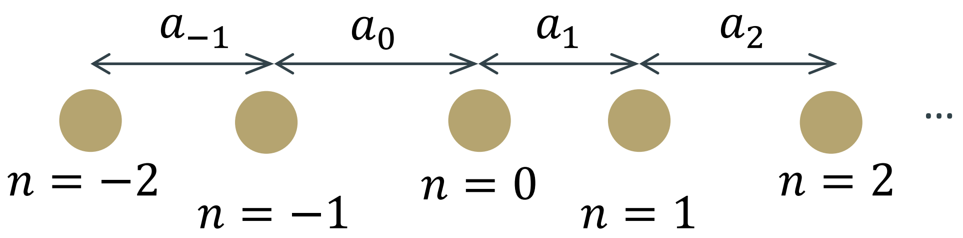
Example #2.

Consider a 1D liquid, in which positions of atoms are defined as

$$X_0 = 0,$$
$$X_1 = X_o + a_1,$$
$$\dots$$
$$X_n = X_{n-1} + a_n,$$

where $a_n$ is a lattice parameter, $n = -\infty \dots + \infty$ enumerates atoms. Let $a_n$ be a gaussian variable with the mean $a$ and a variance $\langle (a_n - a)^2 \rangle = \sigma^2$.

1. Calculate the density-density correlation function $G(x)$
2. Calculate the structure factor $S(q)$



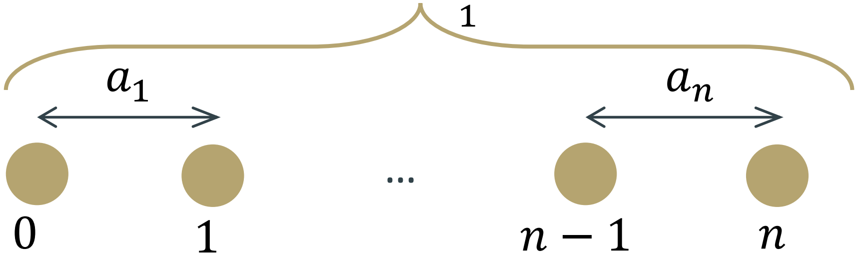
# Solution #2

We will do the same type of calculations

$$G(x) = \frac{1}{N}\left\langle \sum_{n_1 n_2} \delta\left(x - \left(X_{n_2} - X_{n_1}\right)\right)\right\rangle = \frac{1}{N}\left\langle \sum_{n_2}\sum_{n_1} \delta\left(x - \left(X_{n_2} - X_{n_1}\right)\right)\right\rangle$$

$$= \frac{1}{N}\left\langle N\sum_{n_2} \delta\left(x - \left(X_{n_2} - X_0\right)\right)\right\rangle = \left\langle \sum_{n} \delta(x - X_n)\right\rangle$$

$$X_n = \sum_{1}^{n} a_i$$



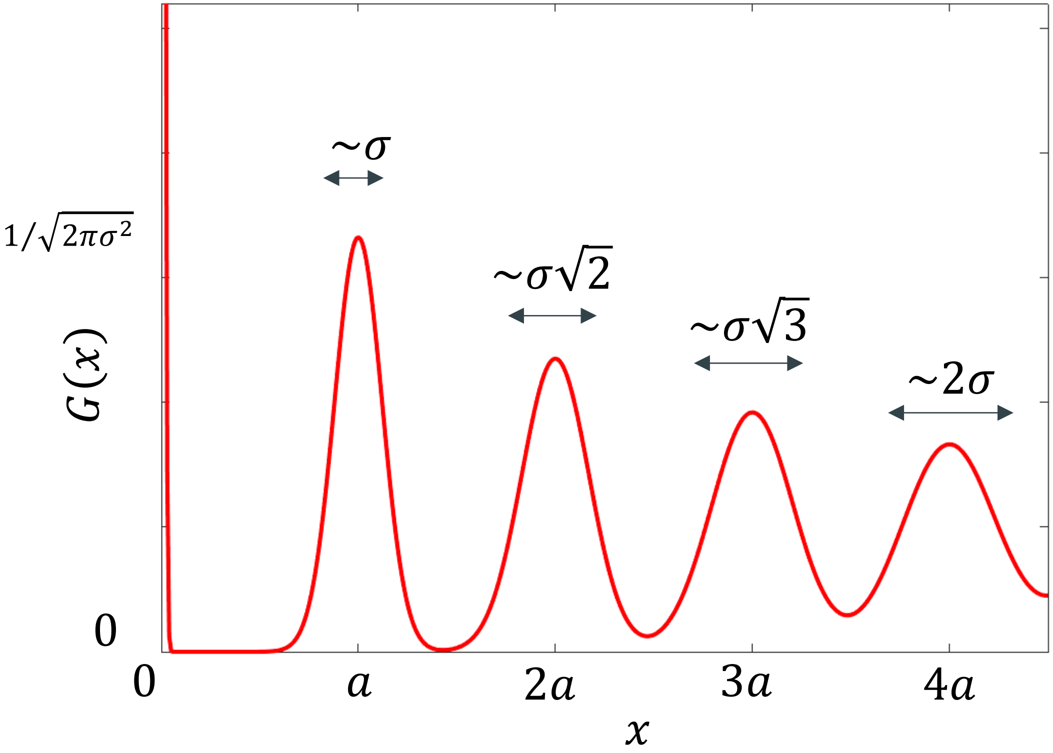
The separation $X_n$ between two atoms is a random variable, which is equal to the sum of $|n|$ Gaussian variables.

From statistics it is known, that $X_n$ is also a Gaussian variable with the mean $an$ and variance $\langle (X_n - an)^2\rangle = |n|\sigma^2$

# Solution #2

$$G(x) = \left\langle \sum_n \delta(x - X_n) \right\rangle = \sum_n \langle \delta(x - X_n) \rangle = \sum_n \int \delta(x - X_n) \frac{1}{\sqrt{2\pi n \sigma^2}} e^{-\frac{(X_n - an)^2}{2|n|\sigma^2}} dX_n$$

$$= \sum_n \frac{1}{\sqrt{2\pi n \sigma^2}} e^{-\frac{(x - an)^2}{2|n|\sigma^2}}$$



# Solution #2

$$S(q) = \int e^{-iqx} G(x)dx = \sum_n \frac{1}{\sqrt{2\pi n\sigma^2}} \int e^{-iqx} e^{-\frac{(x-an)^2}{2|n|\sigma^2}} dx$$

$$\int_{-\infty}^{+\infty} e^{-iqx} e^{-\frac{(x-an)^2}{2|n|\sigma^2}} dx = e^{-iqan} \int_{-\infty}^{+\infty} e^{-iqz} e^{-\frac{z^2}{2|n|\sigma^2}} dz \quad = e^{-iqan} \int_{-\infty}^{+\infty} \cos qz \, e^{-\frac{z^2}{2|n|\sigma^2}} dz$$

Change of variable: $x - an = z; dx = dz$

$$= e^{-iqan} \sqrt{2\pi n\sigma^2} e^{-\frac{q^2\sigma^2|n|}{4}}$$

Hint: $\displaystyle\int_{-\infty}^{+\infty} \cos bx \, e^{-\beta x^2} dx = \sqrt{\frac{\pi}{\beta}} e^{-\frac{b^2}{4\beta}}$

$$S(q) = \sum_n \frac{1}{\sqrt{2\pi n\sigma^2}} e^{-iqan} \sqrt{2\pi n\sigma^2} e^{-\frac{q^2\sigma^2|n|}{4}} = \sum_{-\infty}^{+\infty} \exp\left[-iqan - \frac{q^2\sigma^2|n|}{4}\right]$$

# Solution #2

$$S(q) = \sum_{-\infty}^{+\infty} \exp\left[-iqan - \frac{q^2\sigma^2|n|}{4}\right] = \sum_{n=-\infty}^{n=0} e^{-iqan-\frac{q^2\sigma^2|n|}{4}} + \sum_{n=0}^{n=+\infty} e^{-iqan-\frac{q^2\sigma^2|n|}{4}} - 1$$

$$= \sum_{n=0}^{n=\infty} e^{iqan-\frac{q^2\sigma^2 n}{4}} + \sum_{n=0}^{n=+\infty} e^{-iqan-\frac{q^2\sigma^2 n}{4}} - 1$$

$$= \sum_{n=0}^{n=\infty} \left[e^{iqa-\frac{q^2\sigma^2}{4}}\right]^n + \sum_{n=0}^{n=+\infty} \left[e^{-iqa-\frac{q^2\sigma^2}{4}}\right]^n - 1$$

$$\sum_{n=0}^{n=\infty} \left[e^{iqa-\frac{q^2\sigma^2}{4}}\right]^n = \frac{1}{1 - e^{iqa-\frac{q^2\sigma^2}{4}}}$$

$$\sum_{n=0}^{n=\infty} \left[e^{-iqa-\frac{q^2\sigma^2}{4}}\right]^n = \frac{1}{1 - e^{-iqa-\frac{q^2\sigma^2}{4}}}$$

# Solution #2

$$S(q)=\frac{1}{1-e^{iqa-\frac{q^2\sigma^2}{4}}}+\frac{1}{1-e^{-iqa-\frac{q^2\sigma^2}{4}}}-1=$$

$$=\frac{1-e^{-iqa-\frac{q^2\sigma^2}{4}}+1-e^{iqa-\frac{q^2\sigma^2}{4}}-\left(1-e^{iqa-\frac{q^2\sigma^2}{4}}\right)\left(1-e^{-iqa-\frac{q^2\sigma^2}{4}}\right)}{\left(1-e^{iqa-\frac{q^2\sigma^2}{4}}\right)\left(1-e^{-iqa-\frac{q^2\sigma^2}{4}}\right)}=$$

$$=\frac{1-e^{-iqa-\frac{q^2\sigma^2}{4}}+1-e^{iqa-\frac{q^2\sigma^2}{4}}-1+e^{-iqa-\frac{q^2\sigma^2}{4}}+e^{-iqa-\frac{q^2\sigma^2}{4}}-e^{-\frac{q^2\sigma^2}{2}}}{1-e^{-iqa-\frac{q^2\sigma^2}{4}}-e^{-iqa-\frac{q^2\sigma^2}{4}}+e^{-\frac{q^2\sigma^2}{2}}}=$$

$$=\frac{1-e^{-\frac{q^2\sigma^2}{2}}}{1-e^{-\frac{q^2\sigma^2}{4}}\left(e^{-iqa}+e^{iqa}\right)+e^{-\frac{q^2\sigma^2}{2}}}=$$

$$=\frac{1-e^{-\frac{q^2\sigma^2}{2}}}{1-2e^{-\frac{q^2\sigma^2}{4}}\cos qa+e^{-\frac{q^2\sigma^2}{2}}}$$

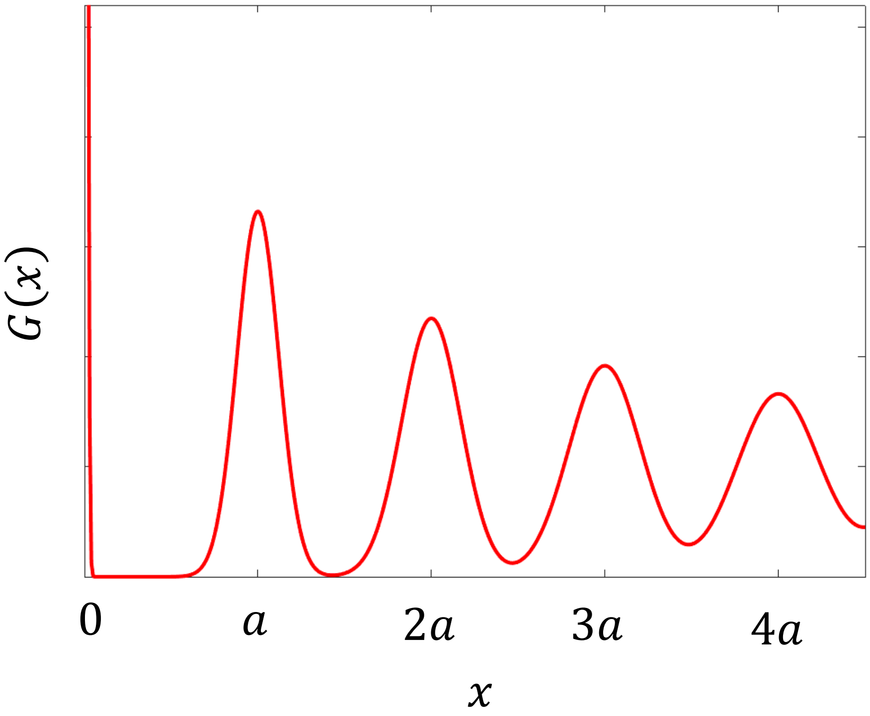
# Solution #2

$$S(q) = \frac{1 - e^{-\frac{q^2\sigma^2}{2}}}{1 - 2e^{-\frac{q^2\sigma^2}{4}} \cos qa + e^{-\frac{q^2\sigma^2}{2}}}$$

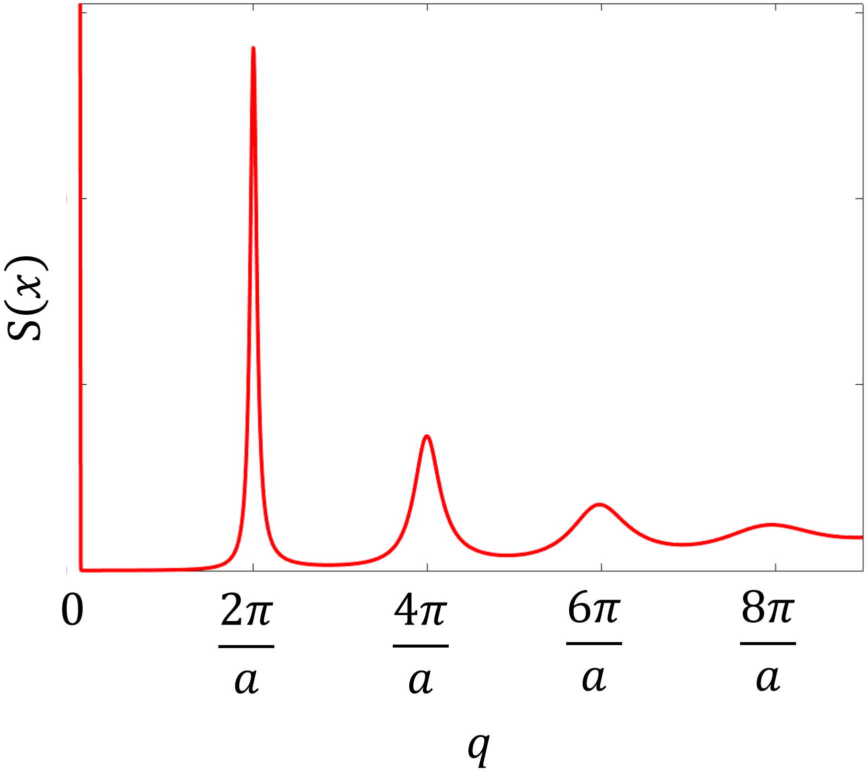
- Peaks at $\cos qa = 1$, i.e. $q_n = \frac{2\pi}{a} n$
- $S(q_n) = \frac{1-e^{-\frac{q^2\sigma^2}{2}}}{1-2e^{-\frac{q^2\sigma^2}{4}}+e^{-\frac{q^2\sigma^2}{2}}} = \frac{1-e^{-\frac{q^2\sigma^2}{2}}}{\left(1-e^{-\frac{q^2\sigma^2}{4}}\right)^2} = \frac{1+e^{-\frac{q^2\sigma^2}{4}}}{1-e^{-\frac{q^2\sigma^2}{4}}} = \coth\left(\frac{q_n^2\sigma^2}{8}\right)$
- In the vicinity of peaks, $S(q_n) \propto \frac{1}{\gamma_n^2+(q-q_n)^2}$ - Lorentzian profile with $\gamma_n = \frac{a}{q_n^2\sigma^2}$

# Solution #2

$$G(x) = \sum_n \frac{1}{\sqrt{2\pi n\sigma^2}} e^{-\frac{(x-an)^2}{2|n|\sigma^2}}$$



$$S(q) = \frac{1 - e^{-\frac{q^2\sigma^2}{2}}}{1 - 2e^{-\frac{q^2\sigma^2}{4}} \cos qa + e^{-\frac{q^2\sigma^2}{2}}}$$

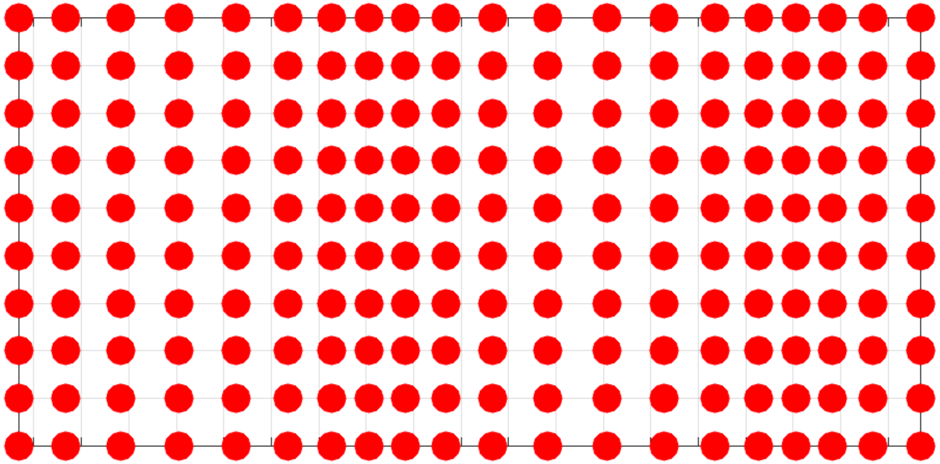


# Diffuse scattering

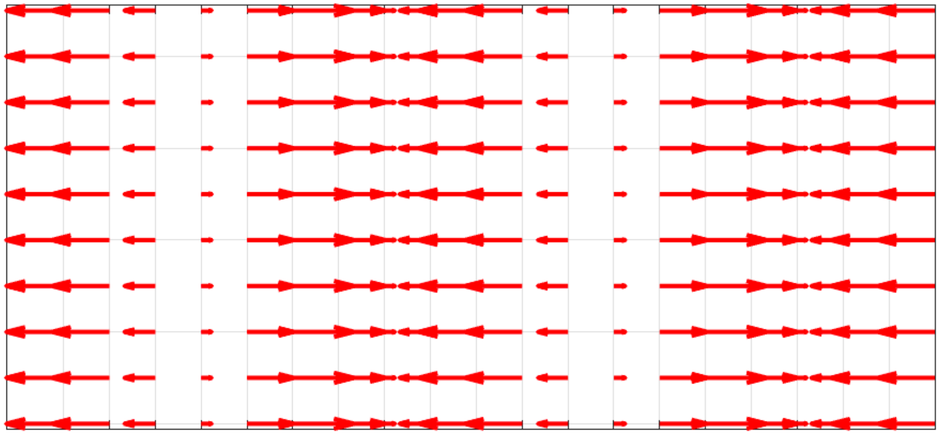
In a more general case, the displacements can be different for different atoms (for example, in the case of phonons):

$$\vec{r}_n = \vec{R}_n + \vec{u}(\vec{r}_n) = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 + \vec{u}(\vec{r}_n).$$

Longitudinal phonon in a crystal



Corresponding displacement



# Diffuse scattering

$$S(\boldsymbol{q}) = \frac{1}{N}\left\langle \sum_{n,m}^{N} e^{-i\boldsymbol{q}(\boldsymbol{x}_n+\boldsymbol{u}_n-\boldsymbol{x}_m-\boldsymbol{u}_m)} \right\rangle = \frac{1}{N}\sum_{n,m}^{N} e^{-i\boldsymbol{q}(\boldsymbol{x}_n-\boldsymbol{x}_m)} \left\langle e^{-i\boldsymbol{q}(\boldsymbol{u}_n-\boldsymbol{u}_m)} \right\rangle$$

$\left\langle e^{-iz} \right\rangle \xrightarrow[z\approx 0]{} e^{-\frac{1}{2}\langle z^2 \rangle}$ (the Baker-Hausdorff theorem)

$$\left\langle e^{-i\boldsymbol{q}(\boldsymbol{u}_n-\boldsymbol{u}_m)} \right\rangle \approx e^{-\frac{1}{2}\langle (\boldsymbol{q}\boldsymbol{u}_n)^2 \rangle} e^{-\frac{1}{2}\langle (\boldsymbol{q}\boldsymbol{u}_m)^2 \rangle} e^{\langle (\boldsymbol{q}\boldsymbol{u}_n)(\boldsymbol{q}\boldsymbol{u}_m) \rangle} \approx e^{-2W_q}\underbrace{(1 +}_{0^{\text{th}}\text{ order}} \underbrace{\langle (\boldsymbol{q}\boldsymbol{u}_n)(\boldsymbol{q}\boldsymbol{u}_m) \rangle}_{1^{\text{st}}\text{ order}})$$

# Diffuse scattering

$$S(\boldsymbol{q}) = \left\langle \frac{1}{N} \sum_{n,m} e^{-i\boldsymbol{q}(r_n-\boldsymbol{r}_m)} \right\rangle = S_0(\boldsymbol{q}) + S_1(\boldsymbol{q}) + \cdots$$

0th-order elastic scattering

$$S_0(\boldsymbol{q}) = e^{-2W_q} \frac{1}{N} \sum_{n,m} e^{-i\boldsymbol{q}(\boldsymbol{r}_n-\boldsymbol{r}_m)} = e^{-2W_q} N \sum_{\boldsymbol{G}} \delta(\boldsymbol{q}-\boldsymbol{G})$$

1st-order elastic diffuse scattering

$$S_1(\boldsymbol{q}) = e^{-2W_q} \frac{1}{N} \sum_{n,m} e^{-i\boldsymbol{q}(\boldsymbol{R}_n-\boldsymbol{R}_m)} \langle \boldsymbol{q}\boldsymbol{u}(\boldsymbol{R}_n) \cdot \boldsymbol{q}\boldsymbol{u}(\boldsymbol{R}_m) \rangle$$

$$= e^{-2W_q} N \left| \boldsymbol{q}\boldsymbol{u}_{\boldsymbol{q}} \right|^{\boldsymbol{2}}$$

Debye-Waller factor

$$W_q = \frac{1}{2} \langle (\boldsymbol{q}\boldsymbol{u})^2 \rangle$$

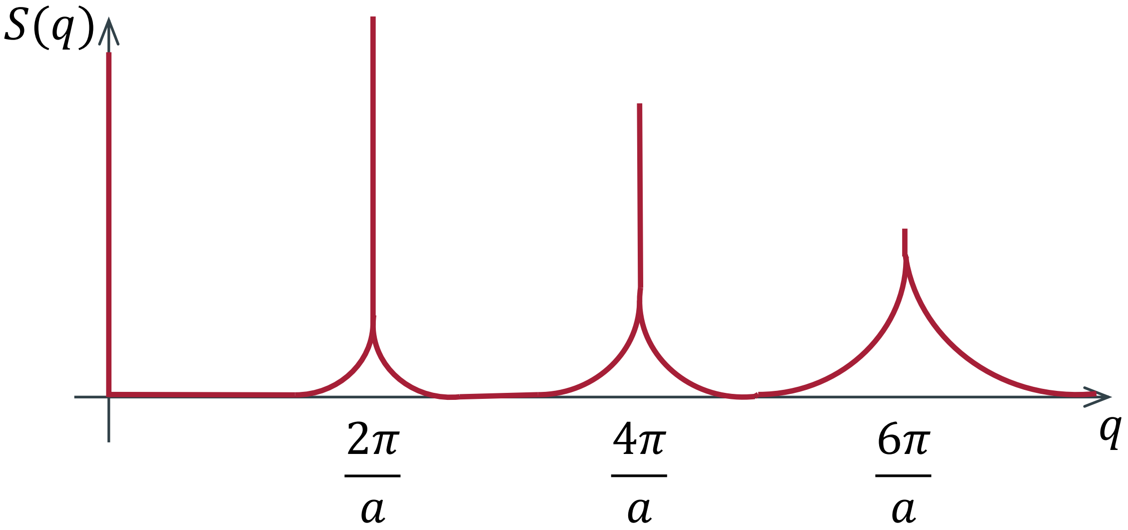
Fourier transform of the displacement field

$$u_{\boldsymbol{q}} = \frac{1}{V} \int u(\boldsymbol{r}) e^{-i\boldsymbol{q}\boldsymbol{r}} d\boldsymbol{r}$$

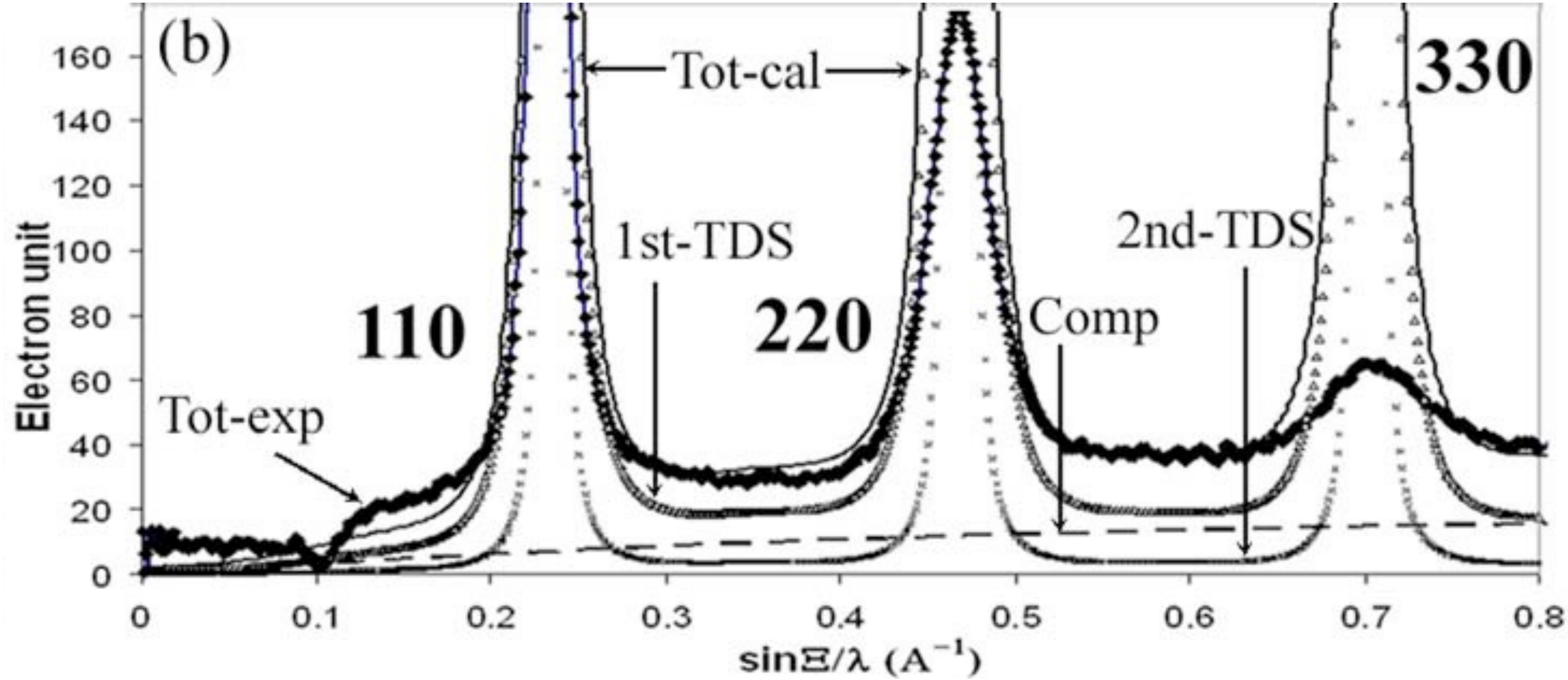
# Thermal diffuse scattering

1st-order elastic thermal diffuse scattering

$$S_1(\boldsymbol{q}) = e^{-2W_q} N\left|\boldsymbol{q}\boldsymbol{u}_{\boldsymbol{q}}\right|^{\boldsymbol{2}} \propto e^{-2W_q}\, q^2\, \frac{k_b T}{mc^2(G-q)^2}$$



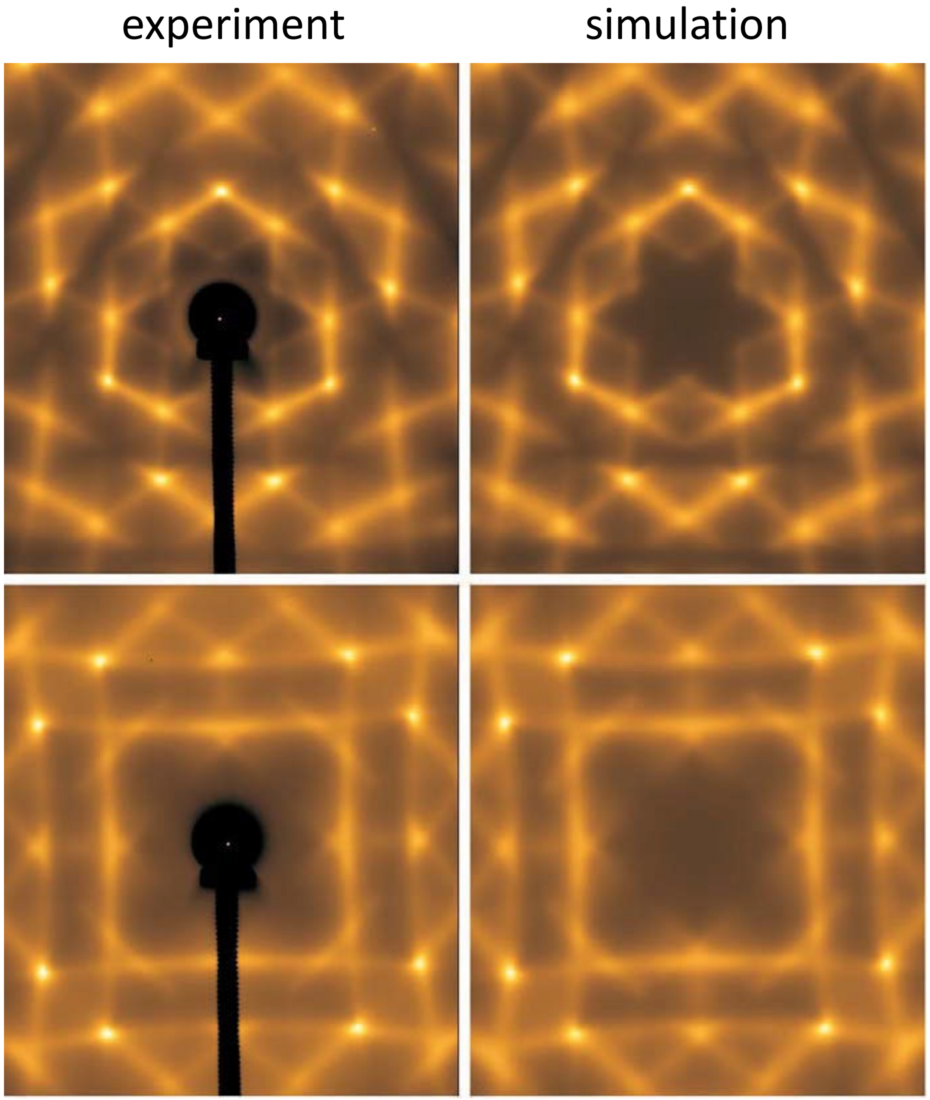
# Thermal diffuse scattering



X-ray thermal diffuse scattering from vanadium

Y. Ding et al., Appl. Phys. Lett. **88**, 061903 (1999)

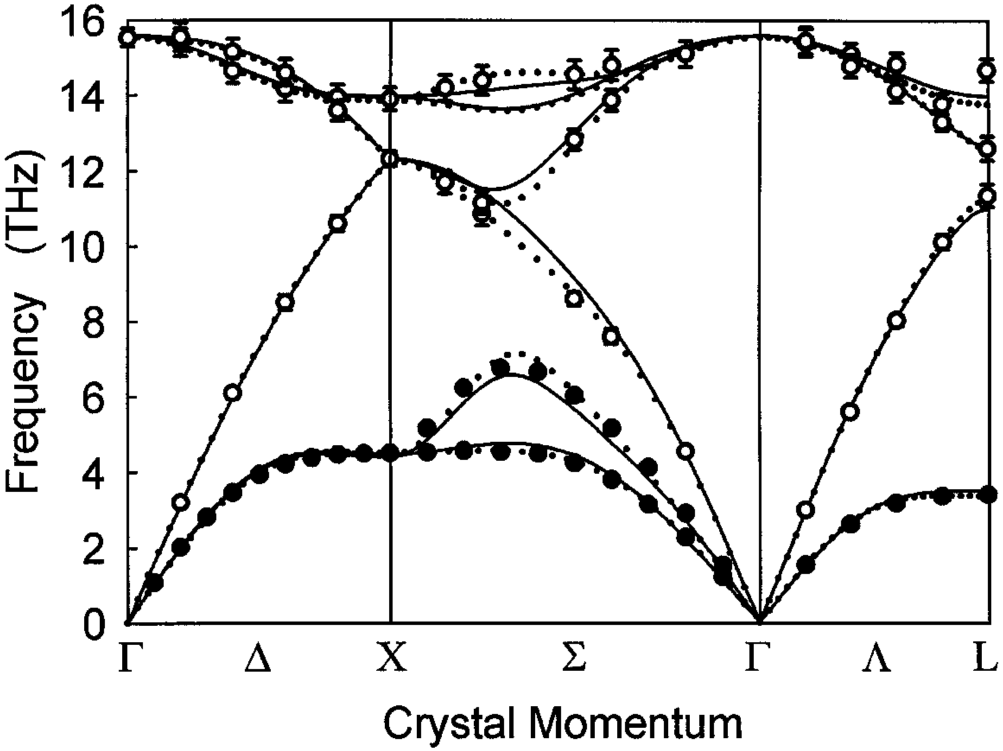
# Thermal diffuse scattering



Thermal diffuse scattering (TDS) from Si. The data were collected in a transmission geometry (photon energy 28 keV) using an image plate detector. The data were collected on the UNI-CAT beamline at the Advanced Photon Source in an exposure time of ~10 s. The top and bottom left panels show the data taken with a (111) and a (100) axis parallel to the incident beam respectively. The data are plotted on a logarithmic scale.

M. Holt et al., Phys. Rev. Lett. **83**, 3317 (1999)

# Thermal diffuse scattering



$$S_1(\boldsymbol{q}) \propto e^{-2W_q} \sum_{s=1}^{6} \frac{|\boldsymbol{q}\boldsymbol{e}_s|^2}{\omega_s} \coth\left(\frac{\hbar\omega_S}{2\mathrm{k_B T}}\right)$$

Phonon dispersion curves of Si. Open and closed circles are neutron scattering data from Solid curves are derived from a best fit to the x-ray scattering intensity patterns. Dotted curves are obtained from an independent fit to the neutron data using the same lattice dynamics model and can be regarded as an interpolation of the neutron data.

M. Holt et al., Phys. Rev. Lett. **83**, 3317 (1999)

# What to remember

- The structure of the material can be conveniently described by density-density correlation function

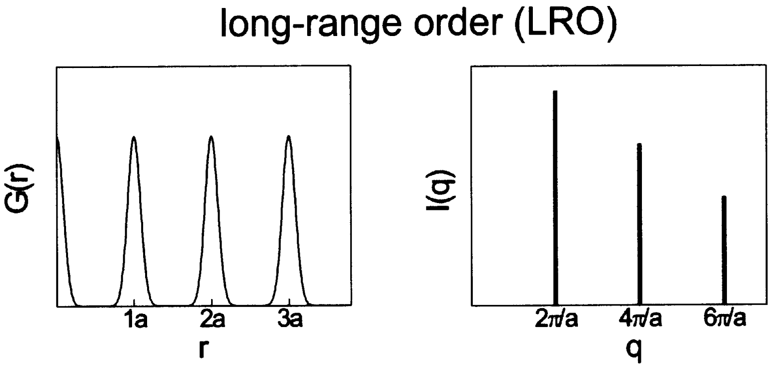
$$G(\vec{r}_1, \vec{r}_2) = \langle n(\vec{r}_1) n(\vec{r}_2) \rangle = \left\langle \sum_{\alpha\alpha'} \delta(\vec{r}_1 - \vec{r}_\alpha)\delta(\vec{r}_2 - \vec{r}_{\alpha'}) \right\rangle$$

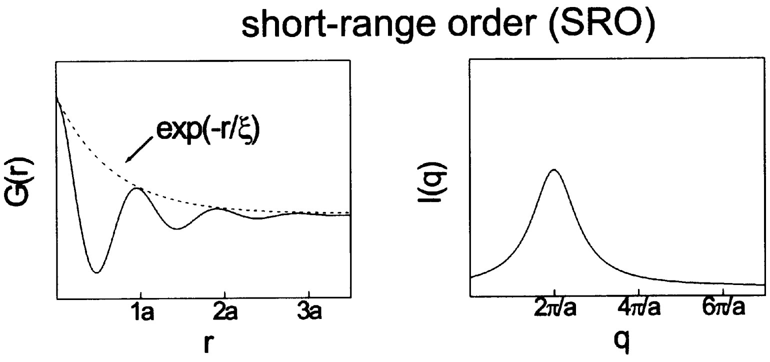
- The diffraction can be described by the structure factor

$$S(\vec{q}) = \frac{1}{N} \left\langle \sum_{\alpha\alpha'} e^{-i\vec{q}(\vec{r}_\alpha - \vec{r}_{\alpha'})} \right\rangle = \int e^{-i\vec{q}\vec{r}} G(\vec{r}) d\vec{r}$$

- Diffraction is sensitive to the mutual distances between the atoms, not to their absolute positions, therefore diffraction can directly probe the correlation function

- The long-range order corresponds to a slow (algebraic) decay of the correlation function. The short-range order corresponds to a fast (exponential) decay of the correlation function.


long-range order (LRO)


short-range order (SRO)