

Amorphous Polymers

diffuse scattering

due to short range order (featureless scattering)

- liquid
- inorganic glass
- glassy or rubbery polymer



amorphous halo

1. local structure (short range order)

-> radial distribution function

2. large scale density fluctuation (short range order)

Pair distribution ftn

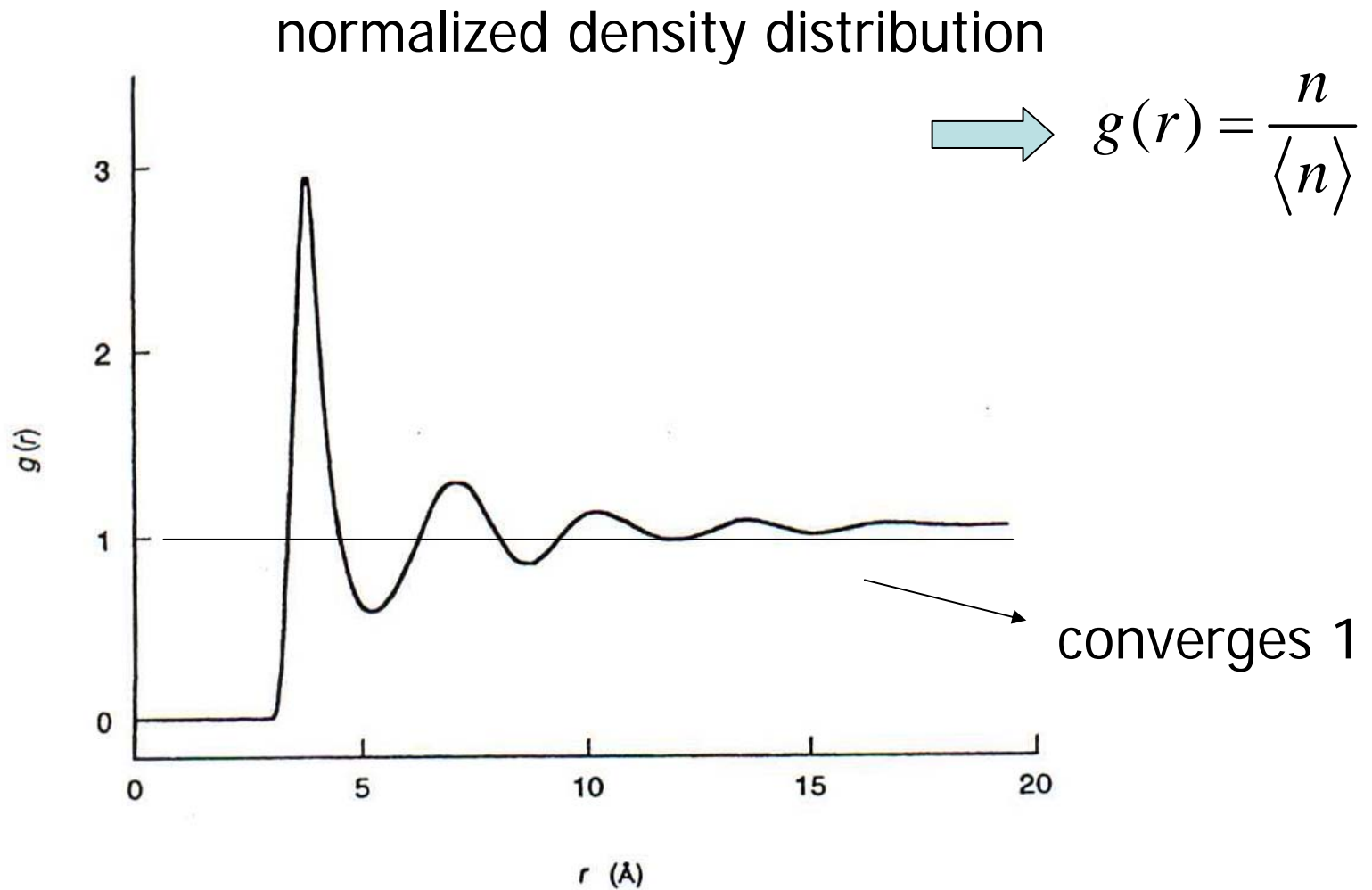
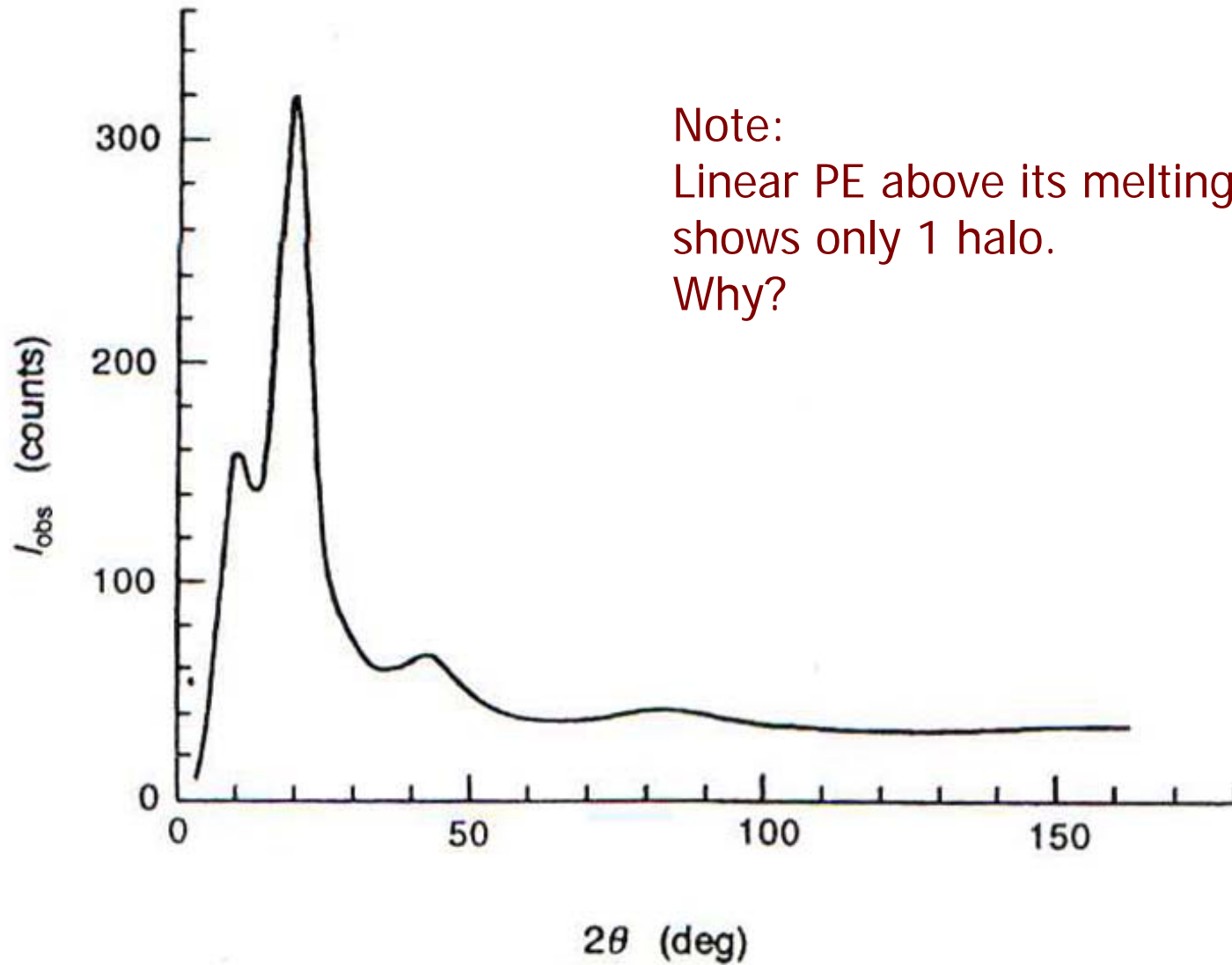


Figure 4.1 Pair distribution function of liquid argon at 84 K obtained by neutron scattering measurement.



Note:
Linear PE above its melting point
shows only 1 halo.
Why?

Figure 4.2 Intensity of x-ray scattering from atactic polystyrene, as observed using $\text{CuK}\alpha$ radiation.

$I(q)$

$$= Nb^2 + b^2 \sum_{j=1}^N \sum_{j \neq k} \langle e^{-iqr_{jk}} \rangle$$

$$= Nb^2 + Nb^2 \int_{\nu} n_2(r) e^{-iqr} dr$$

$$= Nb^2 + Nb^2 \int_{\nu} [n_2(r) - \langle n \rangle] e^{-iqr} dr + Nb^2 \int_{\nu} \langle n \rangle e^{-iqr} dr$$

$$= Nb^2 + Nb^2 \int_{\nu} [g(r) - 1] e^{-iqr} dr + Nb^2 \langle n \rangle \delta(q)$$

self-correlation

pair-correlation

sample as a whole
or null scattering
(unobservable)

Interference function (or reduced intensity function)

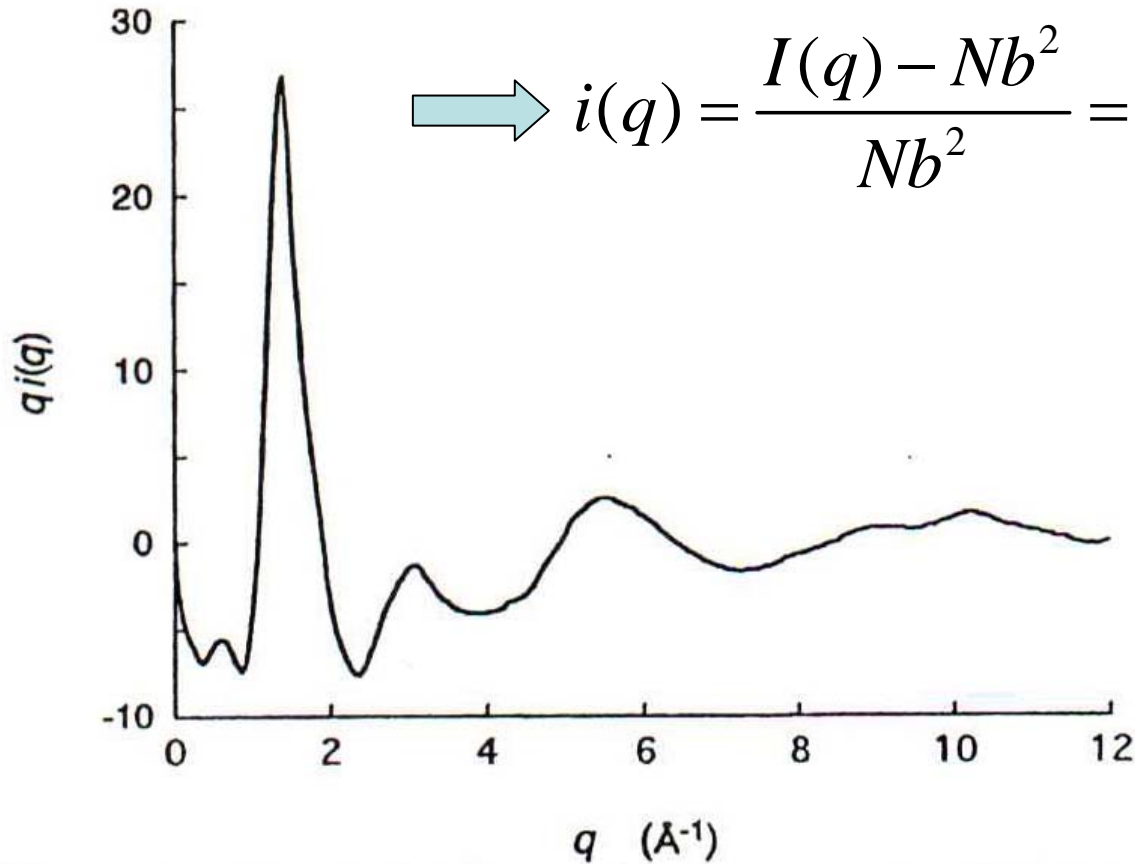


Figure 4.3 Plot of $qi(q)$ for atactic polystyrene, where $i(q)$ is the interference function defined by (4.13). (From Mitchell and Windle.¹⁰)

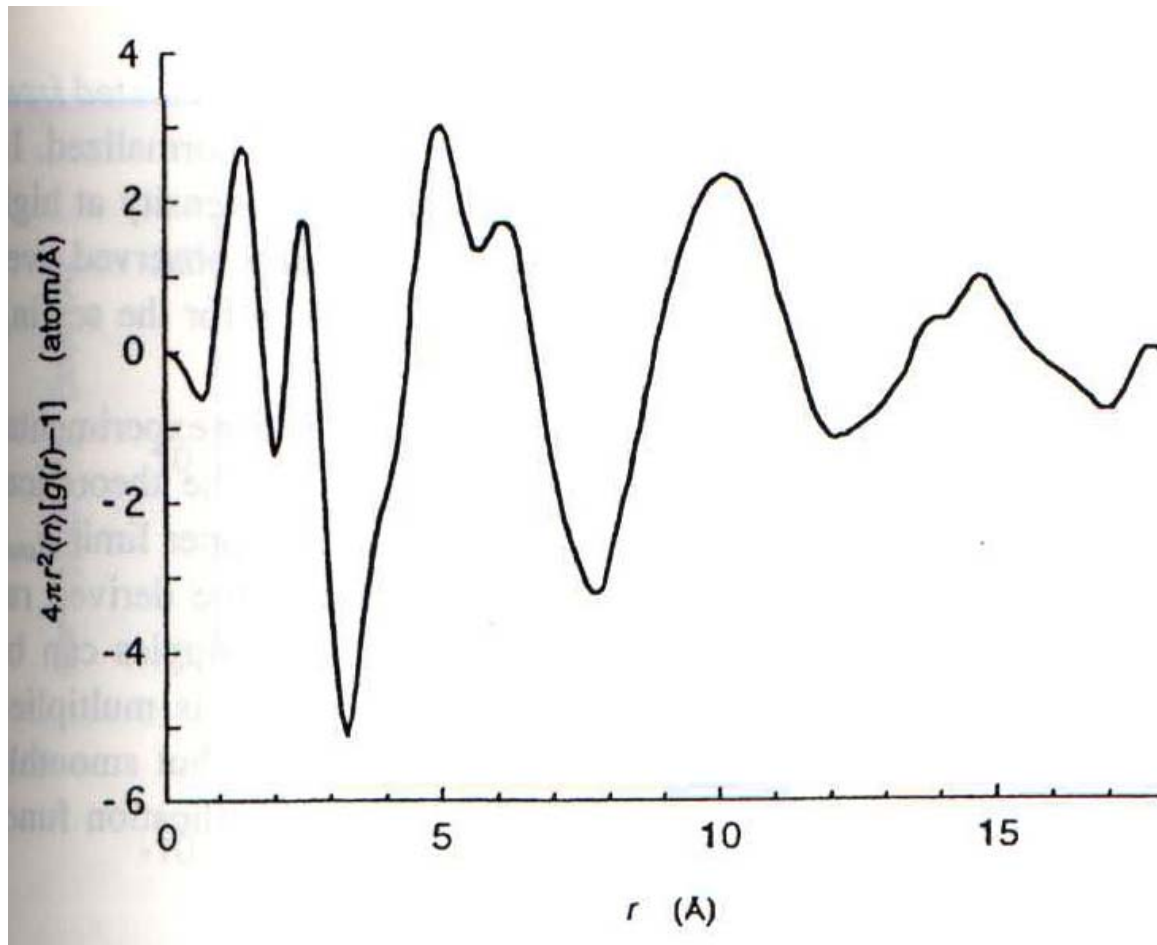


Figure 4.4 Gross radial distribution function $\hat{g}(r)$ of polystyrene given by the inverse Fourier sine transform of $q_i(q)$ according to (4.22). (From Schubach *et al.*⁷)

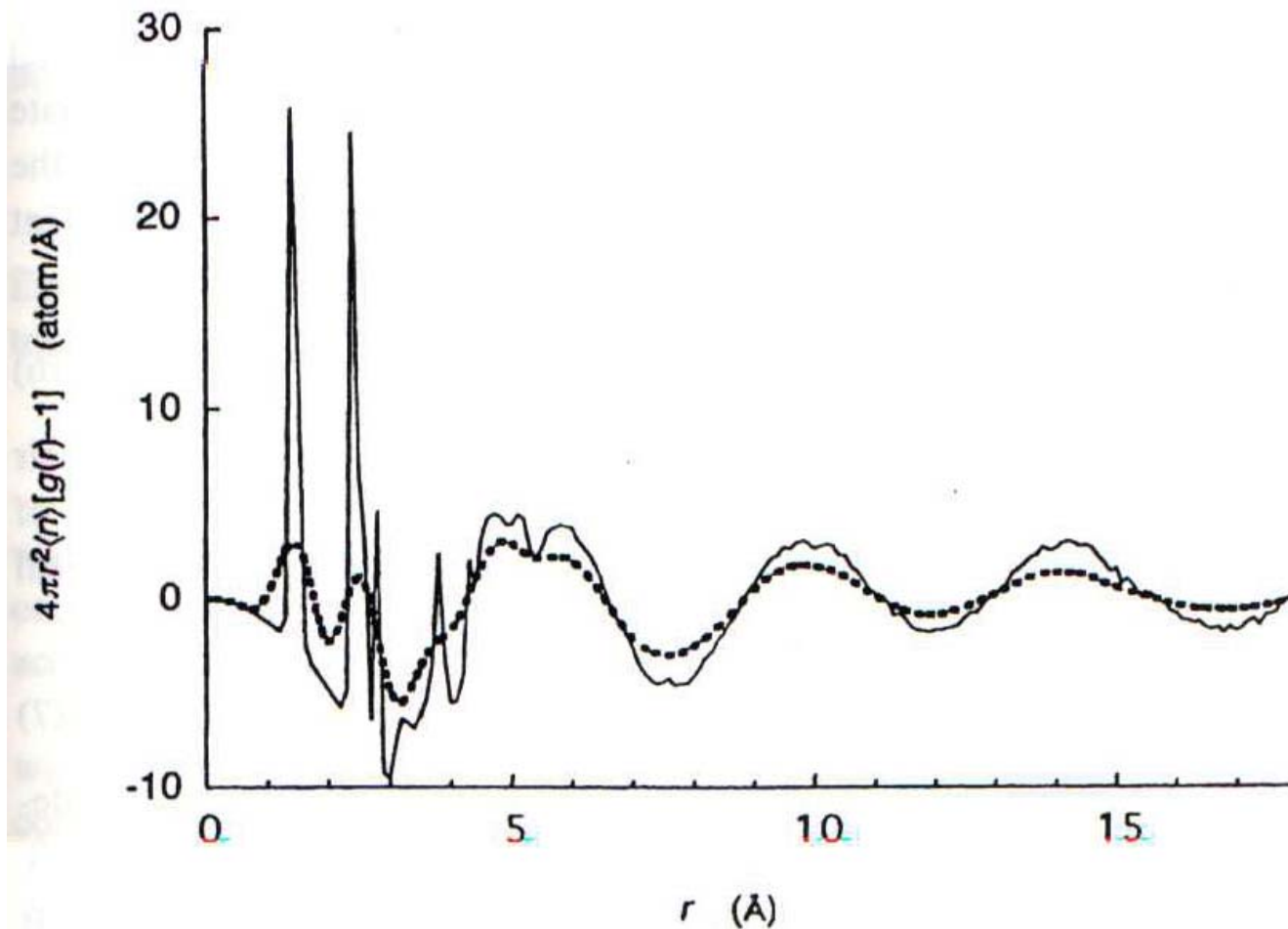
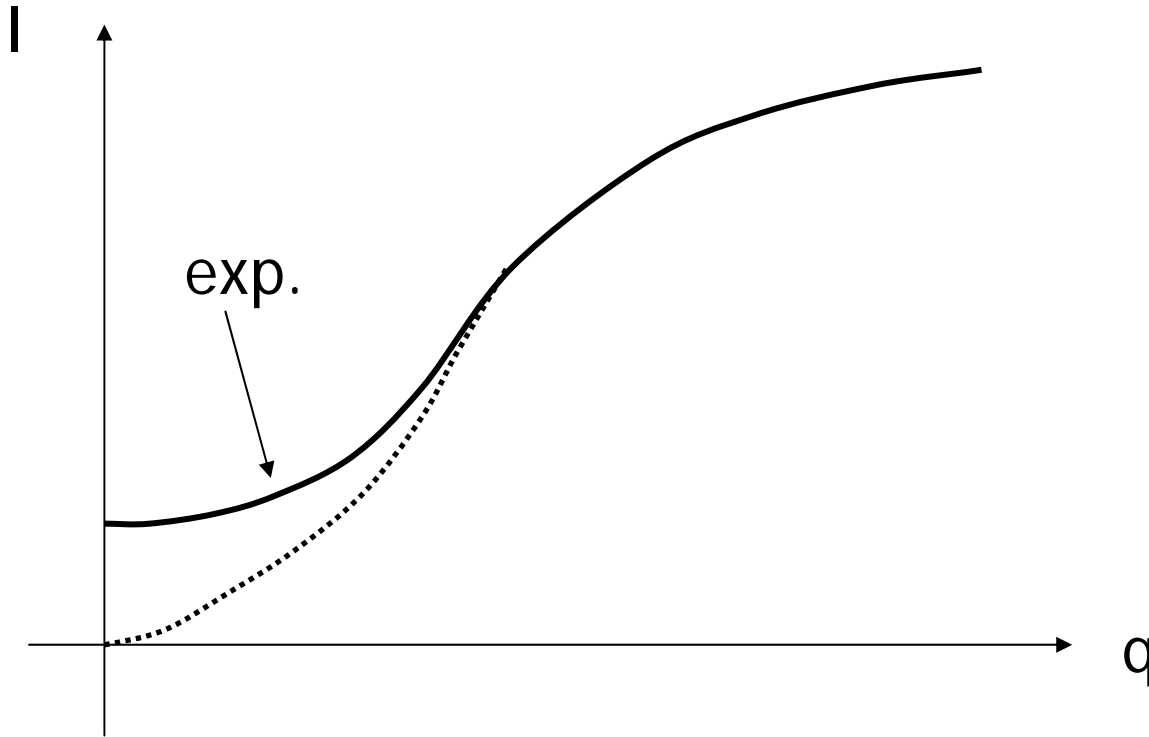


Figure 4.5 From the result of a molecular dynamics simulation, the x-ray scattering intensity was calculated, and from it $\hat{g}(r)$, given in the broken curve, was derived, by using exactly the same procedure as was used to treat experimental x-ray scattering intensities. The solid curve is the C-C atom pair distribution function calculated directly from the simulation result. (From Mondello *et al.*¹³)

Thermal Density Fluctuation of Amorphous Polymers

Intensity near '0' of amorphous polymers



$I(q)$ doesn't converge toward '0' due to ... density fluctuation or else such as fluid in homogeneity

thermal fluctuation

thermal E

isothermal compressibility

$$\frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle} = \langle N \rangle kT \beta_T$$

avg number density = $\langle N \rangle / V$

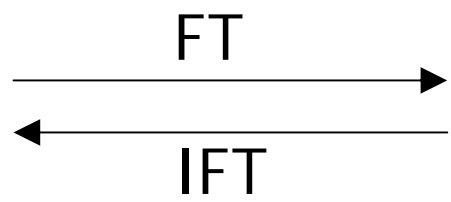
As β_T goes up, $\langle (\Delta N)^2 \rangle$ becomes more significant.

$$A(\vec{q}) = \int \rho(\vec{r}) e^{-i\vec{r}\cdot\vec{q}} d\vec{r}$$

SLDD

Scattering amplitude

$$\rho(\vec{r}) = \rho_u(\vec{r}) * z(\vec{r})$$



$$A(\vec{q}) = F(\vec{q})Z(\vec{q})$$

Form factor

lattice factor

autocorrelation

$$\begin{aligned} \Gamma_\rho(\vec{r}) &= V \langle \rho(\vec{u}) \rho(\vec{u}') \rangle \\ &= \int \rho(\vec{r}) \rho(\vec{u} + \vec{r}) d\vec{u} \end{aligned}$$



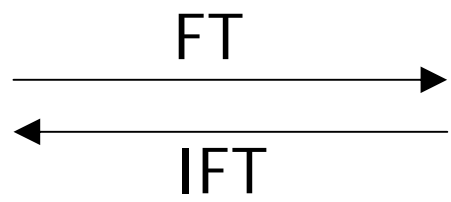
squaring

$$\begin{aligned} I(\vec{q}) &= A(\vec{q}) \cdot A^*(\vec{q}) \end{aligned}$$

$$I(\vec{q})$$

$$\Gamma_\rho(\vec{r})$$

Autocorrelation ftn



$$I(\vec{q}) = \int \Gamma_\rho(\vec{r}) e^{-i\vec{r}\cdot\vec{q}} d\vec{r}$$

SLDD

$$\rho(\vec{r}) = \rho_u(\vec{r}) * z(\vec{r})$$

autocorrelation

$$\Gamma_\rho(\vec{r})$$

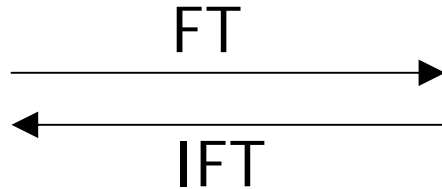
$$= V \langle \rho(\vec{u}) \rho(\vec{u}') \rangle$$

$$= \int \rho(\vec{r}) \rho(\vec{u} + \vec{r}) d\vec{u}$$



$$\Gamma_\rho(\vec{r})$$

Autocorrelation ftn



$$I(\vec{q})$$

$$I(\vec{q}) = \int \Gamma_\rho(\vec{r}) e^{-i\vec{r} \cdot \vec{q}} d\vec{r}$$

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

$$\Gamma_\rho(\vec{r})$$

$$= V \langle \rho(\vec{u}) \rho(\vec{u}') \rangle$$

$$= \int \rho(\vec{r}) \rho(\vec{u} + \vec{r}) d\vec{u}$$

$$= \int [\eta(\vec{u}) + \langle \rho \rangle] [\eta(\vec{u} + \vec{r}) + \langle \rho \rangle] d\vec{u}$$

$$= \int \eta(\vec{u}) \eta(\vec{u} + \vec{r}) d\vec{u} + \langle \rho \rangle^2 \int d\vec{u} + \langle \rho \rangle \int \eta(\vec{u}) d\vec{u} + \langle \rho \rangle \int \eta(\vec{u} + \vec{r}) d\vec{u}$$

$$\sim \int \eta(\vec{u}) \eta(\vec{u} + \vec{r}) d\vec{u} + \langle \rho \rangle^2 V$$

macroscopic dimension

=0

$$\sim \Gamma_\eta(\vec{r})$$

null scattering or scattering at $q=0$
 Experimentally unobservable

Invariant $Q = \int I(\vec{s}) d\vec{s} = \frac{1}{(2\pi)^3} \int I(\vec{q}) d\vec{q}$

for isotropic materials,

$$Q = 4\pi \int s^2 I(s) ds = \frac{1}{2\pi^2} \int q^2 I(q) dq$$

$$Q = \int \Gamma_{\rho}(\vec{r}) \left[\int e^{-i2\pi\vec{s}\cdot\vec{r}} d\vec{s} \right] d\vec{r}$$



$$= \int \Gamma_{\rho}(\vec{r}) \delta(\vec{r}) d\vec{r}$$

$$= \Gamma_{\rho}(0)$$

thermal fluctuation

thermal E

isothermal compressibility

$$\frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle} = \langle N \rangle kT \beta_T \dots \lim_{q \rightarrow 0} \frac{I(q)}{Nb^2} = \frac{I(0)}{Nb^2}$$

avg number density = $\langle N \rangle / V$

As β_T goes up, $\langle (\Delta N)^2 \rangle$ becomes more significant.

local number density

shape factor

$$N_v(r) = \int_v n(R) \sigma(R-r) dR$$

$$= n(r) * \sigma(-r)$$

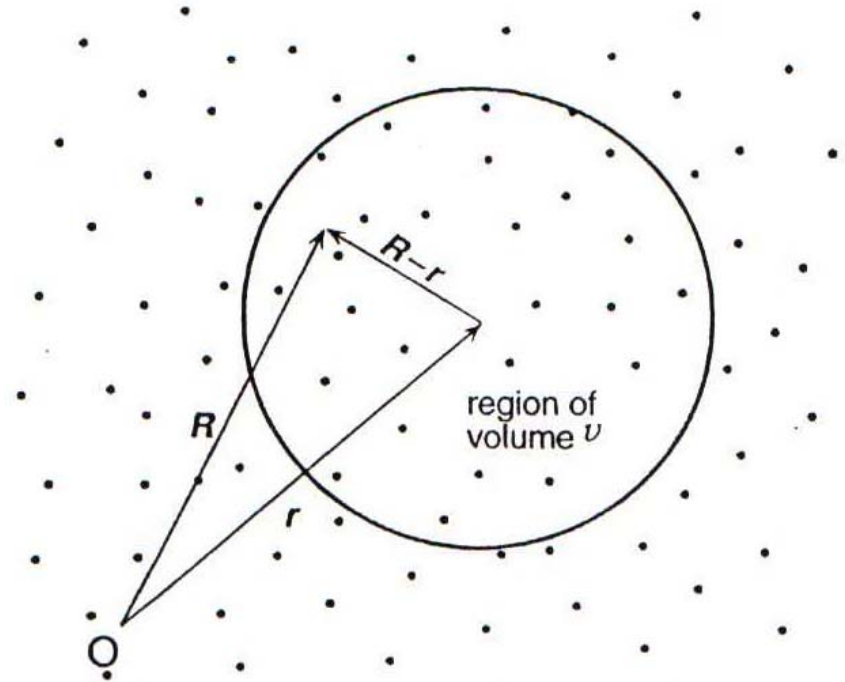


Figure 4.10 Diagram illustrating Equation (4.33). O is the arbitrarily chosen origin of the coordinate system. The center of the region of volume v is specified by vector r .

$$\Delta N_v(r) = N_v(r) - \langle N_v \rangle$$

$$= \Delta n(r) * \sigma(-r)$$

$$\text{where } \Delta n(r) = n(r) - \langle n \rangle$$

$$\langle (\Delta N_v)^2 \rangle$$

$$= \frac{\int_v (\Delta N_v)^2 dr}{V} = \frac{\int_v (\Delta n(r) * \sigma(-r))^2 dr}{V} = \frac{\int_v (\Delta n(r) * \sigma(-r))^2 dr}{V(2\pi)^3}$$

$$\text{since } \int_{-\infty}^{\infty} |f(r)|^2 dr = \frac{\int_{-\infty}^{\infty} |F\{f(r)\}|^2 dq}{(2\pi)^3} \text{ and convolution theorem,}$$

$$\longrightarrow \langle (\Delta N_v)^2 \rangle = \frac{\int_v |F(\Delta n(r))|^2 |F(\sigma(-r))|^2 dq}{V(2\pi)^3}$$

$$\langle (\Delta N_v)^2 \rangle = \frac{\int_v \frac{I(q)}{b^2} \left[\sum(q) \right]^2 |F(\Delta n(r))|^2 |F(\sigma(-r))|^2 dq}{V(2\pi)^3}$$

$$\lim_{v \rightarrow \infty} \langle (\Delta N)^2 \rangle = \frac{v}{V} \lim_{q \rightarrow 0} \frac{I(q)}{b^2} \quad N = \langle n \rangle V$$

$$\lim_{v \rightarrow \infty} \frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle} = \lim_{q \rightarrow 0} \frac{I(q)}{Nb^2} = \frac{I(0)}{Nb^2} = \langle N \rangle kT \beta_T$$

$$\lim_{v \rightarrow \infty} \frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle} = \lim_{q \rightarrow 0} \frac{I(q)}{Nb^2} = \frac{I(0)}{Nb^2} = \langle N \rangle kT \beta_T$$



for backgnd calculation

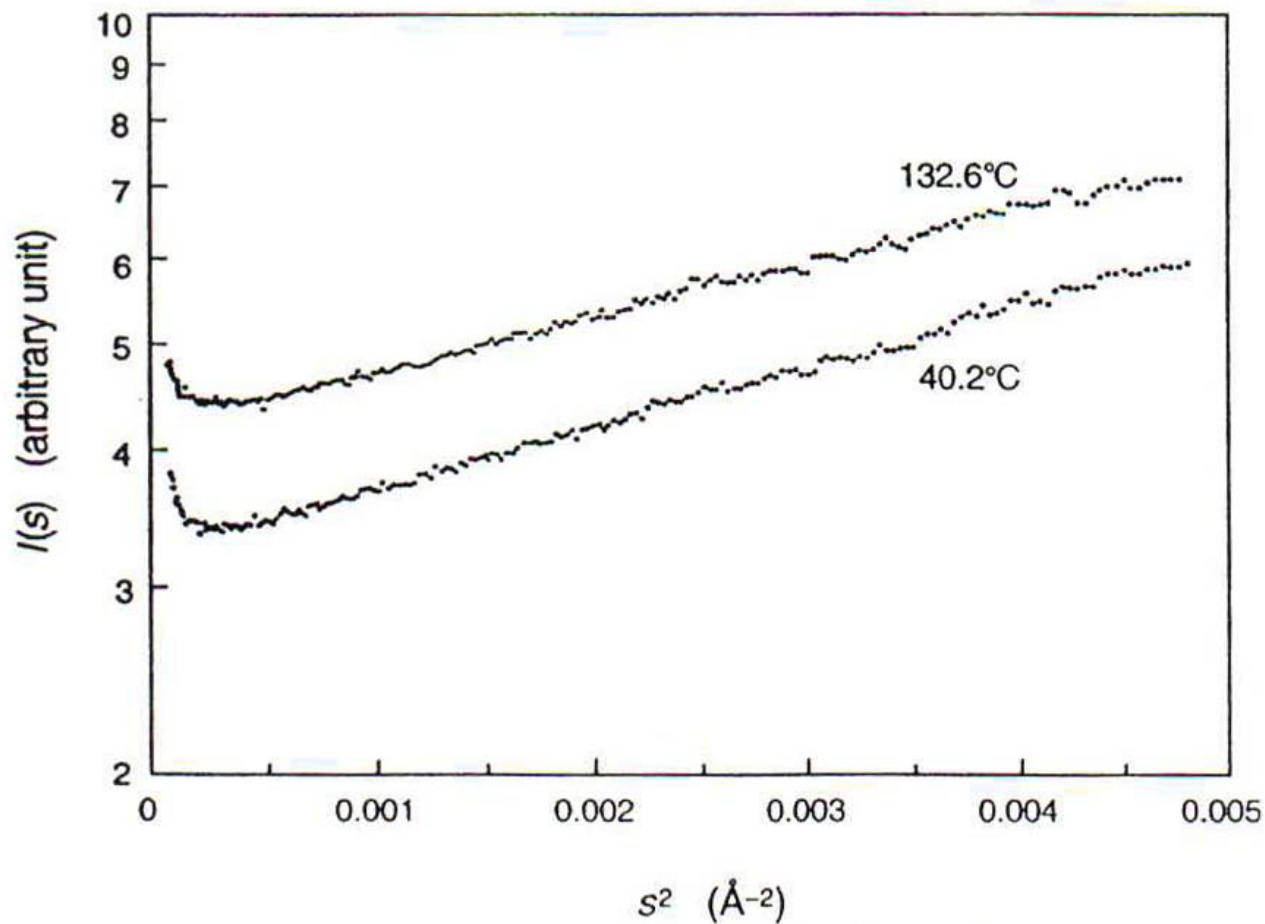


Figure 4.11 X-Ray scattering data obtained with atactic polystyrene at temperatures above and below the glass transition temperature, showing how the intensity $I(q)$, arising mostly from density fluctuations, depends on q as q approaches zero. (From Roe and Curro.¹⁹)

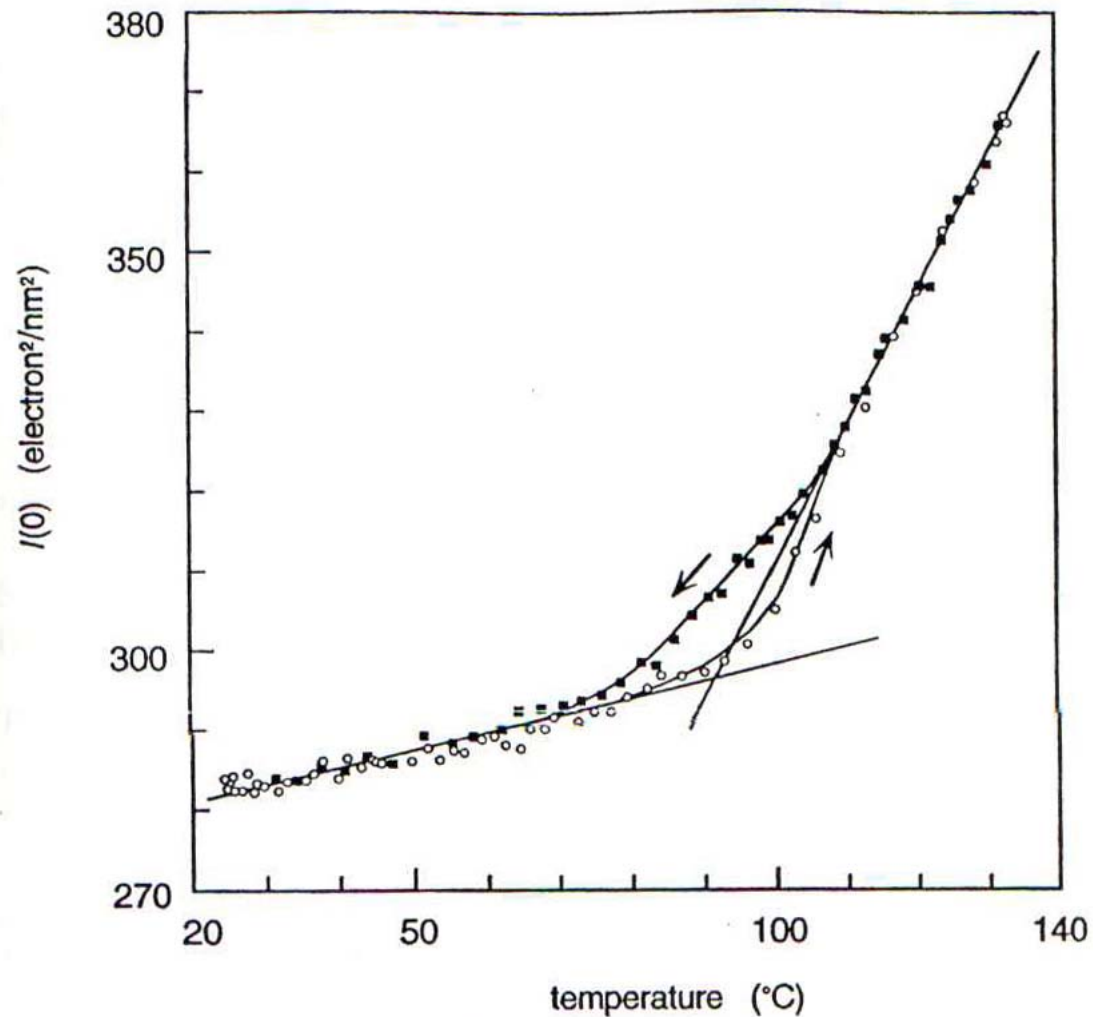


Figure 4.12 Points are the extrapolated x-ray scattering intensity $I(0)$, obtained with atactic polystyrene on heating and cooling through the glass transition temperature. (From Roe and Curro.¹⁹)