Density Fluctuation in Amorphous Polymers by Small Angle X-Ray Scattering

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ABSTRACT: Density fluctuations in an infinite volume can be obtained by extrapolating the scattering intensity to the zero scattering angle, while those in a finite volume having a radius of several tens of Angstrom can be obtained from intensities at non-zero scattering angles. Small angle X-ray scattering intensities for condensed phases were approximated by $I(s) = I(0) \exp(As^2)$. This s dependence of the intensity arises from the repulsive interaction between two particles. Since the density fluctuations in the above two types of volume (infinite and finite) were nearly the same in magnitude and temperature dependence for an amorphous polymer (PMMA), it was concluded that no density fluctuations due to structural inhomogeneity exist. The temperature dependence of the density fluctuations in a finite volume for PMMA and PC exhibited a second transition temperature T^* below T_g, the glass transition temperature.
KEY WORDS Density Fluctuation / Small Angle X-Ray Scattering (SAXS) / Amorphous Polymers / Amorphous Structure / SAXS Intensity Function /

A study of thermal density fluctuations in liquids and glasses including amorphous polymers by small angle X-ray scattering is of interest from two points of view. The first is its relation to the structure of amorphous states, which was investigated by Wendorff and Fischer.[1-3] The second is concerned with providing a way to subtract the "liquid-like" background scattering for semicrystalline polymers, polymer solutions and so on.

The temperature dependence of density fluctuations in liquids, oligomers and amorphous polymers was measured by Wendorff et al.,[1] Fischer et al.,[2,3] Rathje et al.[4] and Wiegand et al.[5] using small angle X-ray scattering (SAXS) techniques. Fischer et al.[1-3] measured the scattering intensity at s_{min} where the influence of a hole or large particle-scattering vanishes ($s = (2/\lambda) \sin \theta$, λ is the wavelength, 2θ, the

scattering angle), and calculated the density fluctuation $\overline{\delta N^2}/\bar{N}$ from

$$\frac{\overline{\delta N^2}}{\bar{N}} = \frac{I(s_{min})}{Nf^2(s_{min})} \tag{1}$$

where N is the number of atoms, $I(s)$, the scattering intensity and $f(s)$, the atomic structure factor. Ruland et al.[4,5] determined the density fluctuation by extrapolating the scattered intensity to the zero scattering angle using the empirical equation

$$\frac{\overline{\delta N^2}}{\bar{N}} = \lim_{s \to 0} \frac{I(s)}{Nf^2(s)} \tag{2}$$

where

$$I(s) = I(0) \exp(As^2) \qquad (s, \text{ small}) \tag{3}$$

with A, a constant.

These two methods yielded the temperature

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dependences of density fluctuation which were similar near the glass transition temperature but disagreed at low temperatures. In this paper, the physical basis of these methods is discussed.

THEORETICAL

Density Fluctuations in a Small Volume

The density fluctuation in a small fixed volume v taken in a large volume V ($v \ll V$) is given by Ruland[6] as follows:

$$\left(\frac{\overline{\delta n^2}}{\bar{n}}\right)_v = \int \frac{1}{n} I_e(s) \frac{1}{v} \Phi^2(2\pi sR) ds \qquad (4)$$

where n is the number of electrons in v, $(\overline{\delta n^2}/\bar{n})_v$ the density fluctuation averaged over V, $I_e(s)$ the observed scattering intensity in electron units, $v = (4/3)\pi R^3$ and

$$\Phi^2(x) = \left(3 \frac{\sin x - x \cos x}{x^3}\right)^2 \qquad (5)$$

The function $\Phi^2(x)$, derived from the Fourier transform of the self-convolution of the form factor, has a very sharp peak at $x = 0$[7] and decreases near zero for $x \gtrsim \pi$.

When v is very large, i.e., $R \to \infty$, $\Phi^2(2\pi sR)$ becomes a delta function, and eq 4 gives

$$\lim_{v \to \infty} \left(\frac{\overline{\delta n^2}}{\bar{n}}\right)_v = \frac{1}{n} I_e(0) \qquad (6)$$

This equation indicates that the method of Ruland et al. (eq 2) gives the density fluctuation in an infinite volume.

If the observed intensity $I_e(s)$ is nearly constant or changes very slowly with s for $0 \le sR \le 1$, the term $(1/n)I_e(s)$ can be taken out of the integral in eq 4 and because

$$\int \frac{1}{v} \Phi^2(2\pi sR) ds = 1 ,$$

we obtain

$$\left(\frac{\overline{\delta n^2}}{\bar{n}}\right)_v \cong \frac{1}{n} I_e(s_a) \qquad (s_a, \text{ small}) \qquad (7)$$

where s_a is an arbitrary value of s such that $0 \le s_a R \le 1$. Equation 7 indicates that the density fluctuation in v is given by eq 1, which was used by Fischer et al. However, in this method, $I_e(s)$ must change very slowly at small s.

The Functional Shape of the SAXS Intensity in Fluid or Amorphous State

The scattering intensity $I(s)$ for gas phases or isolated molecules decreases monotonically with an increase in s in the neighborhood of $s = 0$, while $I(s)$ of liquids and glasses becomes very small in this region of s and a new peak possibly due to intermolecular interactions appears. Amorphous polymers show the same scattering behavior as the latter. For polymers, it is impossible to observe the scattering intensity in the gas phase. However, the scattering intensity for a molecule in the bulk state can be measured by neutron scattering from a deuterated polymer dispersed in the matrix of a protonated polymer (or vice versa).[8]

As Debye[9] showed theoretically, the decrease in scattering intensity in a condensed phase at s small compared with the size of isolated molecules is due to repulsive interaction of the particles. Harvey[10] demonstrated this experimentally by measuring the pressure dependence of scattering from N_2 gas. Fournet[11] attempted to improve Debye's approximation using the Born and Green theory.[12]

When there exists an attractive interaction of the type $-1/r^6$ between atoms, Enderby et al.[13] showed that the structure factor $S(s) = I(s)/Nf^2(s)$ may be described by the following equation for small values of s,

$$S(s) = S(0) + a_2 s^2 + a_3 s^3 + \cdots \qquad (8)$$

where the s^3 term reflects the attractive interaction. For a low density van der Waals gas, Albers et al.[14] rigorously evaluated the s^3 and s^5 terms from interactions of the types $1/r^6$ and $1/r^8$, respectively. They suggest that a measurement with the very high accuracy (about 0.2%) is necessary to detect the difference between

eq 8 and 9,

$$S(s) = S(0) + b_2 s^2 + b_4 s^4 + \cdots \qquad (9)$$

Ruland *et al.*[4,5] found experimentally the SAXS intensity for liquids or glassy polymers may be represented by eq 3. This implies that eq 9 describes accurately the experimental SAXS intensity.

For simplicity, we consider a monoatomic liquid. The structure factor $S(s)$ is represented by

$$S(s) = 1 + \rho \int e^{-2\pi i s r} [g(r) - 1] \, dr \qquad (10)$$

where ρ is the number density, and $g(r)$, the radial distribution function. The density fluctuation in a given large volume can be obtained from

$$\frac{\overline{\delta N^2}}{\bar{N}} = \frac{\overline{N^2} - \bar{N}^2}{\bar{N}} = S(0) \qquad (11)$$

In order to discuss the effect of intermolecular interference on SAXS intensity, it is relevant to use the Ornstein–Zernike equation

$$h(r) = c(r) + \rho \int_0^\infty c(|r - r'|) h(r') 4\pi r'^2 \, dr' \qquad (12)$$

where $h(r) = g(r) - 1$ is the net correlation function and $c(r)$, the direct correlation function. In terms of the Fourier transform of these functions

$$\hat{c}(s) = \int c(r) e^{-2\pi i s r} \, dr \qquad (13)$$

$$\hat{h}(s) = \int h(r) e^{-2\pi i s r} \, dr \qquad (14)$$

the structure factor $S(s)$ can be expressed as

$$S(s) = 1 + \rho \hat{h}(s) \qquad (15)$$

$$= \frac{1}{1 - \rho \hat{c}(s)} \qquad (16)$$

Equation 15 is pertinent when $S(s)$ at relatively large s (or small r) is considered, because $h(r)$ can be obtained from an actual structure as the pair correlation function. On the other hand,

eq 16 is very useful when s is small (or r is large), since the direct correlation between two particles is short-ranged.

Expanding $\hat{c}(s)$ in powers of s yields

$$\hat{c}(s) = \int_0^\infty c(r) \left[1 - \frac{(2\pi s r)^2}{6} + \frac{(2\pi s r)^4}{120} - \cdots \right] 4\pi r^2 \, dr$$

$$= c_0 - \frac{2\pi^2}{3} c_2 s^2 + \frac{2\pi^4}{15} c_4 s^4 - \cdots \qquad (17)$$

where

$$c_n = \int_0^\infty c(r) 4\pi r^{n+2} \, dr \qquad (18)$$

The structure factor for small s can be approximated by

$$S(s) \cong \frac{1}{1 - \rho c_0} \exp \left[-\left(\frac{(2/3)\pi^2 \rho c_2}{1 - \rho c_0} \right) s^2 \right] \qquad (19)$$

With eq 11 and 19, the density fluctuation can be related to the zeroth moment of the direct correlation function c_0 by

$$\frac{\overline{\delta N^2}}{\bar{N}} = \frac{1}{1 - \rho c_0} \qquad (20)$$

which indicates that $\rho c_0 < 1$. The sign of the second moment c_2 depends on the physical state of the material. Experimentally, c_2 is positive near the critical point but negative for normal liquid or glassy states.

In normal liquid or glassy states with which we are concerned here, one of the most important direct correlations between two particles is the repulsive interaction or the excluded volume effect. The hard sphere model is pertinent for our purposes. It is well established that the Percus–Yevick equation[15] is a very good approximation for describing liquid states which have no long-range interactions such as those of dipoles. An exact solution to the Percus–Yevick equation for the hard sphere model was found by Wertheim[16] and Thiele.[17] The direct correlation function $c_{PY}(r)$ for this Percus–Yevick equation is represented by

$$c_{PY}(r) = \begin{cases} -\dfrac{1}{(1-\eta)^4}\left[(1+2\eta)^2 \right. \\ \quad -6\eta\left(1+\dfrac{\eta}{2}\right)^2\left(\dfrac{r}{\sigma}\right) \\ \left. \quad +\dfrac{\eta}{2}(1+2\eta)^2\left(\dfrac{r}{\sigma}\right)^3\right] & (r < \sigma) \\ 0 & (r > \sigma) \end{cases} \quad (21)$$

where $\eta = (1/6)\pi\sigma^3\rho$ and σ is the diameter of the hard sphere. Hence, for $s\sigma \ll 1$, we obtain

$$S_{PY}(s) \cong \frac{(1-\eta)^4}{(1+2\eta)^2}$$

$$\times \exp\left[\frac{\pi^2\eta(16-11\eta+4\eta^2)}{5(1+2\eta)^2}(s\sigma)^2\right] \quad (22)$$

It is obvious that c_2 in eq 19 is negative for $0 < \eta < 0.74$ where $\eta = 0.74$ corresponds to the closest packing of spheres. The density fluctuation is described by

$$\frac{\overline{\delta N^2}}{\bar{N}} = \frac{(1-\eta)^4}{(1+2\eta)^2} \quad (23)$$

Equation 22 suggests that the repulsive interaction between two particles is significantly responsible for the decrease in scattered intensity or $S(s)$ at small scattering angles in the condensed state of a substance. For small s, the atomic structure factor can be approximated by

$$f^2(s) \cong n_e^2 \exp(-ks^2) \quad (s, \text{ small}) \quad (24)$$

where n_e is the number of electrons in the sphere and k is a constant. The observed scattering intensity in the region of small s may be expressed by

$$I(s) =$$

$$I(0)\exp\left[\left(\frac{\pi^2\eta(16-11\eta+4\eta^2)}{5(1+2\eta)^2}\sigma^2-k\right)s^2\right] \quad (25)$$

which provides the physical basis for eq 3.

EXPERIMENTAL

A Kratky camera equipped with Ni-filtered CuK_α radiation and a xenon-filled proportional counter combined with a pulse-height discriminator was used to obtain density fluctuation by the method based on eq 1. Absolute scattered intensities were determined by a comparison with scattering from a standard sample.[18] The values of s_{min} were 0.020 Å^{-1} for PS and 0.017 Å^{-1} for PMMA and PC.

To evaluate the s dependence of the intensity (see eq 3), the Kratky camera and a Guinier–Simon camera (FR553, N.V. Verenigde Instrumenten-fabrieken Enraf-Nonius, Holland) with CuK_α radiation and a bent quarz monochromator were used for amorphous polymers and liquid benzene, respectively. The range of 2θ for benzene was limited to $2\theta > 5°$ on the basis of experimental considerations. Corrections for the slit-like collimation were not made for the reason stated in the Appendix.

The samples used were (1) polystyrene (PS), $M_w = 4 \times 10^5$, thermally polymerized by Dettenmaier et al.,[19] taking care to minimize heterogeneity effects due to additives,[20] (2) poly(methyl methacrylate) (PMMA), (PMMA240, Röhm GmbH), $M_w = 7 \times 10^6$, and (3) polycarbonate (PC), (Makrolon, Bayer AG Dormagen), $M_w = 3.5 \times 10^4$. All the samples were 2 mm in diameter.

RESULTS AND DISCUSSION

Density Fluctuations

In order to compare the theoretical equations with the experimental density fluctuations of amorphous polymers, it is relevant to consider a monomer as the scattering unit. Hence, N in eq 1 and 2 is regarded as the number of monomers. The density fluctuations per monomer obtained by the method based on eq 2 for PS and PMMA at room temperature and the values of σ calculated from eq 23 are given in Table I; where σ represents the

Table I. Density fluctuations per monomer $(\overline{\delta N^2}/\bar{N})_{monomer}$ determined by the method based on eq 2 at room temperature and the values of σ calculated from eq 23

Sample[b]	$(\overline{\delta N^2}/\bar{N})_{monomer}$	ρ g cm^{-3}	σ Å
PS	0.010	1.05	5.5
PMMA	0.016	1.18	5.1
Benzene	0.026[a]	0.879	5.0

[a] Calculated from eq 28.
[b] PS, polystyrene; PMMA, poly(methyl methacrylate).

diameter of a monomer. Here, ρ in $\eta = (1/6)\pi\sigma^3\rho$ was assumed to be the macroscopic number density. Although the values of σ are apparently reasonable, we must note the fact that the radial distribution function $g_{PY}(r)$ for the hard sphere model has the first (or the innermost) peak at $r \cong \sigma$. Experimentally, the first intermolecular peak positions for PS, PMMA and benzene were 10.0,[21] 6.8,[22] and 5.3 Å,[23] respectively; they were obtained from radial distribution function analyses. These values for amorphous polymers do not agree with the σ values in Table I. Therefore, the packing units of amorphous polymers should be larger than those of one monomer. If the packing unit consists of z monomers, the density fluctuation per packing unit[6] is given by

$$\left(\frac{\overline{\delta N^2}}{\bar{N}}\right)_z = \frac{1}{z}\left(\frac{\overline{\delta N^2}}{\bar{N}}\right)_{monomer} \quad (26)$$

When determined consistently from the observed density fluctuations and σ, z was found to be 5 for PS and 2 for PMMA.

Density fluctuations measured by the above two methods (eq 1 and 2) should coincide within several percent when the change in scattering intensity in the region of small s is moderate. This was confirmed by a comparison of Fischer et al.'s data[3] for PMMA with Rathje et al.'s[4] and also by our measurements on PS, PMMA, and PC at room temperature
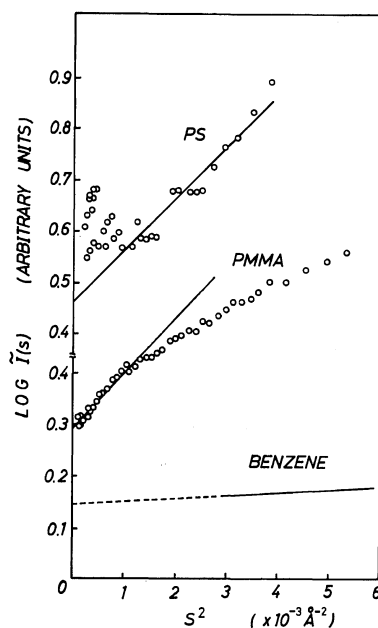
Figure 1. Small angle X-ray scatterings measured at room temperature for various substances. Plots shift arbitrarily along the ordinate.

(see Figure 1). Hence, the calculations based on the density fluctuations in a finite volume give almost the same results.

The s Dependence of SAXS Intensity

The SAXS intensity for PS, PMMA, and benzene at room temperature is plotted against s^2 in Figure 1. The linear ranges in log I vs. s^2 are narrower than those shown by Ruland et al.[4,5] According to what was mentioned in the THEORETICAL section, the approximation of eq 3 should be better for smaller scattering angles. For estimating the constant A in eq 3 from the hard sphere model, the atomic structure factor $f(s)$ for a sphere with a uniform distribution of electrons was assumed to be

$$f^2(s) = n_e^2\Phi^2(\pi s\sigma)$$
$$\cong n_e^2\exp(-2.181\sigma^2 s^2) \quad (s, \text{ small}) \quad (27)$$

The observed values of A are summarized in Table II, along with those calculated. The value of A_{calc} for benzene is about the same as

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Table II. The constant A in $I(s) = I(0) \exp(As^2)$ determined at room temperature or calculated from eq 25 and 27 under the assumption of a packing unit with z monomers

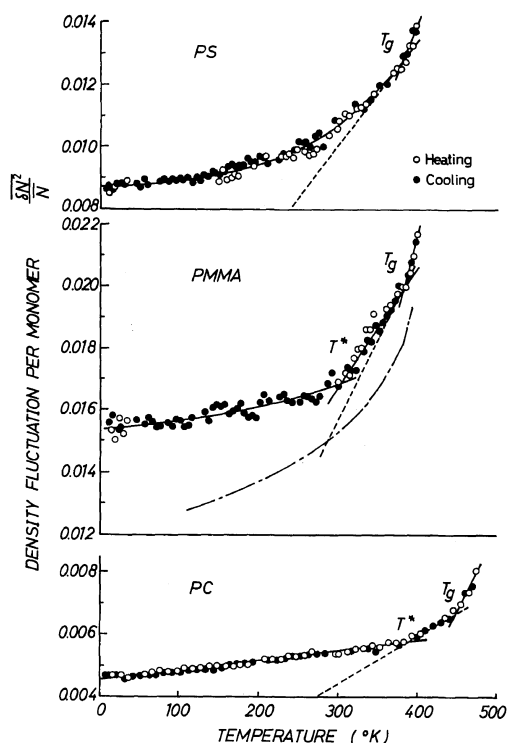| Sample	A_{obs} Å^2	A_{calc} Å^2	z
PS	~240	34	5
PMMA	~260	24	2
Benzene	~10	19	1

Figure 2. Temperature dependence of density fluctuation in a finite volume of PS, PMMA, and PC. The dotted lines describe the relation given by eq 29. The dot-dashed line for PMMA shows the data by Rathje and Ruland.[4]

that of A_{obs}. However A_{calc} and A_{obs} for polymers (PS and PMMA) show large differences, suggesting that chain connectivity must be considered in the calculation. It is evident that the present model is too simple to account for all aspects of SAXS intensity and is concerned with the equilibrium state, whereas the observations were performed on polymers in the glassy state.

Temperature Dependence of Density Fluctuation

The temperature dependence of density fluctuations in a finite volume for PS, PMMA, and PC is shown in Figure 2. It is similar to that reported by Rathje et al.[4] and Wiegand et al.[5] The magnitude of the density fluctuations measured by the two methods for PMMA above room temperature also coincided within several percent. This means that PMMA has no special structural density fluctuations in a range exceeding several tens of Angstrom.[3]

For PMMA and PC, a second transition temperature T^* was observed below T_g, but this was not seen clearly for PS. No such transition temperatures were reported by Rathje et al. For comparison, their data for PMMA are shown in Figure 2 (the dot-dashed line). The transition temperature T^* appeared since the density fluctuations in a finite volume decrease with temperature below T^* more slowly than those in an infinite volume. The increase in the constant A below T^* probably

contributes to the appearance of T^* at least to some extent. Since these transition temperatures were observed with respect to density fluctuation in a finite volume, they may be related to the molecular motion in a region of several tens of Angstrom, but the exact relation still remains unclear.

The temperature dependence of density fluctuation may be described by the following relations:

1) Above T_g,

$$\frac{\overline{\delta N^2}}{\overline{N}} = \rho k_B T \beta_T \qquad (28)$$

where k_B is the Boltzmann constant, T, the absolute temperature and β_T, the isothermal compressibility.

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2) Below but near T_g,

$$\frac{\overline{\delta N^2}}{\overline{N}} = \rho k_B T \beta_T(T_g) \qquad (29)$$

which was derived by Wendorff and Fischer.[1] The dotted lines in Figure 2 show the latter relation.

3) At very low temperatures (near $T=0$ (K)), the density fluctuation consists of frozen-in disorder and thermal vibrations which occur under constraints imposed by the frozen structure. This structure of density fluctuation has been proposed by Ruland et al.[4,5]

CONCLUSIONS

Two methods are available for measuring the density fluctuations of liquids and glasses including amorphous polymers by small angle X-ray scattering.

(1) The density fluctuation in an infinite volume can be obtained by extrapolating the scattering intensity to the zero scattering angle. The density fluctuation in a finite volume whose radius is several tens of Angstrom can be obtained by measuring the scattering intensity at a single value of s ($\neq 0$).

(2) The X-ray scattering intensity for condensed phases (fluids and glasses) at small scattering angles can be approximated by $I(s) = I(0) \exp(As^2)$. This s dependence of the scattering intensity arises from repulsive interaction between two particles.

(3) The observed slopes A_{obs} of $\log I(s)$ vs. s^2 plots for polymers are much larger than those calculated on the basis of the hard sphere model. Chain connectivity must be considered in the calculation.

(4) The density fluctuations in PMMA measured by the above two methods have nearly the same magnitude and temperature dependence, suggesting this amorphous polymer to have no special structural density fluctuations in a range exceeding several tens of Angstrom.

(5) PMMA and PC have a second tran-

sition temperature T^* below T_g, which may be related to the molecular motion in the region of several tens of Angstrom.

APPENDIX

Smearing Effect

In a small angle X-ray scattering measurement, a slit-like collimation system instead of a point collimation one is used to obtain strong scattered intensity. For an infinitely narrow beam, the observed smeared intensity $\tilde{I}(s)$ is related to the desmeared (pinhole) scattering intensity $I(s)$ by

$$\tilde{I}(s) = \int_{-\infty}^{+\infty} V(y) I(\sqrt{s^2 + y^2}) \, dy \qquad (30)$$

where $V(y)$ is a weighting function depending on the collimation and receiving system. If $I(s)$ is represented by eq 3, eq 30 gives

$$\tilde{I}(s) = CI(0) \exp(As^2) \qquad (31)$$

where

$$C = \int_{-\infty}^{+\infty} V(y) \exp(Ay^2) \, dy \qquad (32)$$

Therefore, when the density fluctuation is measured by the method based on eq 1, it is only necessary to note the constant term C. The s dependence of $\tilde{I}(s)$ is the same as that of $I(s)$.

The actual scattering intensity for polymers is not described by eq 3 but by

$$I(s) = \begin{cases} I(0) \, \text{esp} \, (As^2) & (s \leq s_0) \\ I(0) \exp(As^2) + p(s) & (s > s_0) \end{cases} \qquad (33)$$
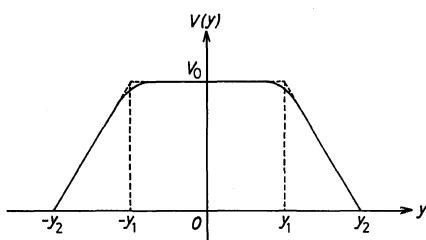
The smeared intensity is then given by

Figure 3. The weighting function $V(y)$.

$$\tilde{I}(s) = \left[2 \int_0^\infty V(y) I(0) \exp{(Ay^2)} \mathrm{d}y \right] \exp{(As^2)}$$
$$+ 2 \int_{\sqrt{s_0^2 - s^2}}^{y_2} V(y) p(\sqrt{s^2 + y^2}) \mathrm{d}y \quad (s \le s_0)$$

$$(34)$$

where s_0 is the deflecting point of $I(s)$ on the curve for $\exp{(As^2)}$, and y_1 and y_2 given in Figure 3. Experimentally, the function $p(s)$ changes gradually in the range $s_0 < s < y_2$, where $s_0 \cong 0.03 \sim 0.06$, $y_1 \cong 0.026$, and $y_2 \cong 0.078$ (Å^{-1}) for the present samples and experimental conditions. Hence, the contribution of the second term on the right-hand side of eq 34 to the slope of the $\log \tilde{I}(s)$ vs. s^2 plot is very small, and this plot gives A directly. Since its contribution to the intercept is not very small, the correction for the slit effect must be made for a correct determination of density fluctuations.

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