Elastic scattering from cubic lattice systems with paracrystalline distortion. II.

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Our previous paper [Phys. Rev. B **36**, 1754 (1987)], in which Hosemann's paracrystal theory was extended to three-dimensional cubic systems, contained some errors. In this paper, we have corrected these errors and further refined the theory. The scattering profiles by our new theory are not so different from the previous ones; satisfactory, even better agreements with experimental data are also obtained with slightly larger distortion factor g.

In one of our preceding papers,[1] a paracrystal theory, which was first proposed by Hosemann,[2] was extended to face-centered-cubic (fcc), body-centered-cubic (bcc), and simple-cubic (sc) cases, and the scattering profiles were calculated numerically. However, the paper contained some errors. In the present paper we have corrected the errors, further refined the theory, and recalculated the paracrystalline lattice factors.

The range of integration for the operation of taking an orientation average, namely Eq. (16) in the original paper, is correct for sc lattices, but incorrect for fcc and bcc cases. For these cases, the following equation must be used instead of Eq. (16) in the original paper:

$$Z(q)=\frac{1}{4\pi}\int_0^{2\pi}d\phi\int_0^{\pi}d\theta\, Z_1(q,\theta,\phi)Z_2(q,\theta,\phi) \times Z_3(q,\theta,\phi)\sin\theta\ , \tag{1}$$

The correction is based on the nonorthogonality of the three fundamental vectors shown in Fig. 1 in the original paper. For sc lattices, no modification is necessary because its three fundamental vectors are orthogonal to each other.

This nonorthogonality of fundamental vectors of fcc and bcc symmetries also affects the distortion factor, $|F_k(\mathbf{q})|$. Equation (6) for $F_k(q)$ is not strictly correct for fcc and bcc lattices. In these cases, Eq. (6) in the original

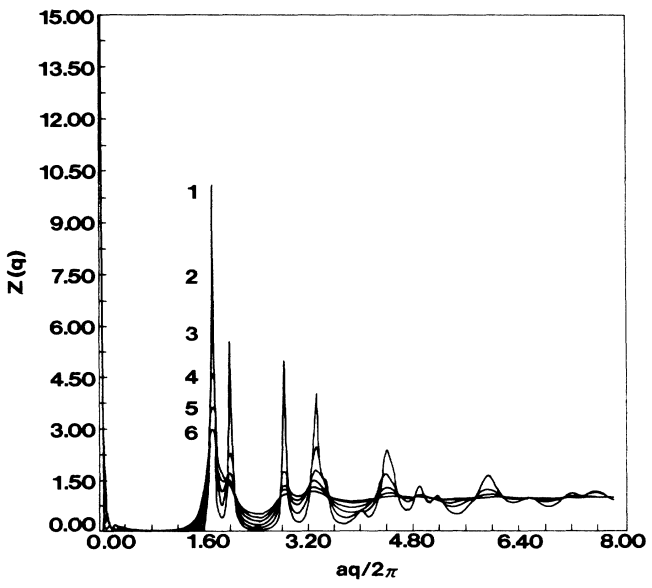

FIG. 1. Paracrystalline lattice factors for a fcc lattice. Curve 1, g=0.05; 2, 0.07; 3, 0.09; 4, 0.11; 5, 0.13; 6, 0.15.

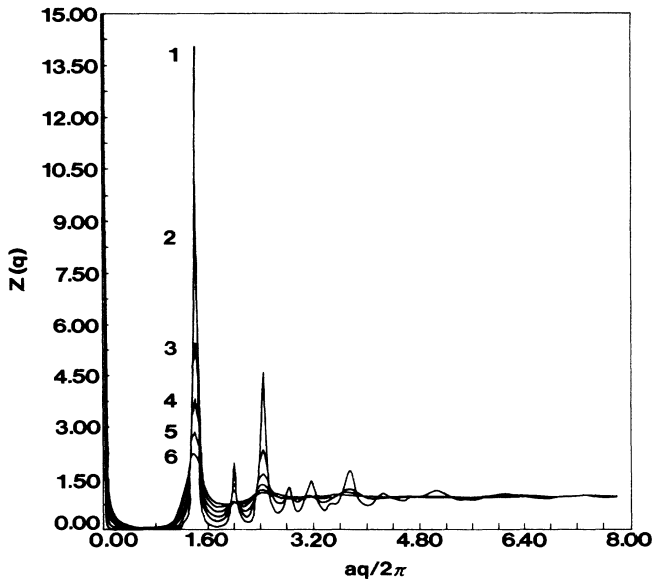

FIG. 2. Paracrystalline lattice factors for a bcc lattice. Curve 1, g=0.05; 2, 0.07; 3, 0.09; 4, 0.11; 5, 0.13; 6, 0.15.

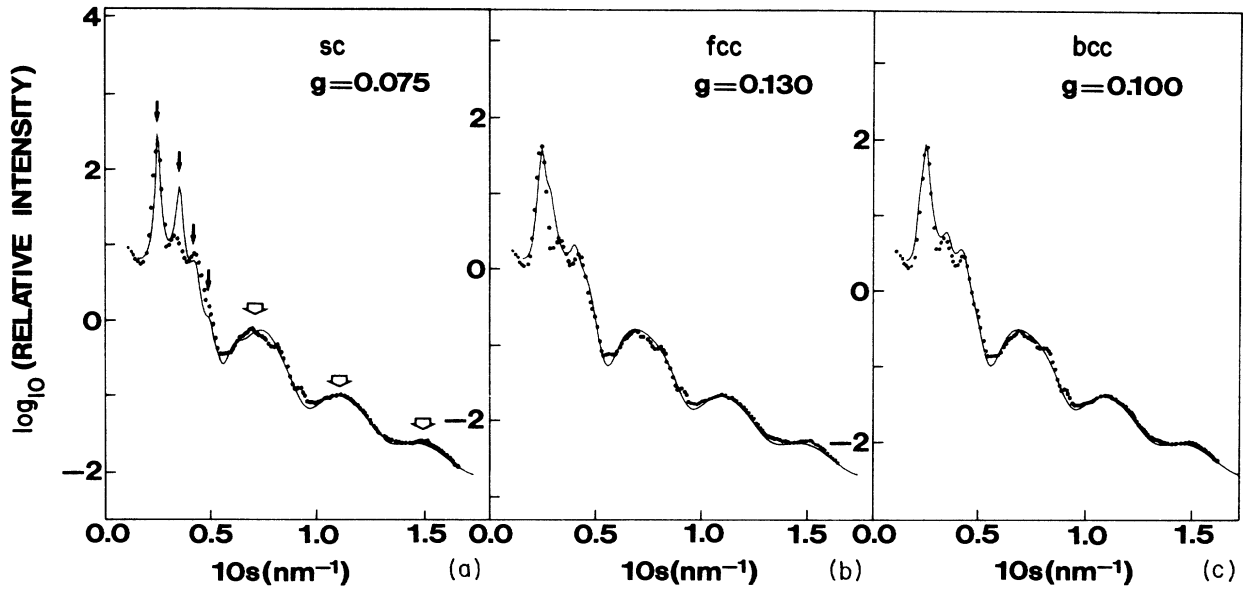

FIG. 3. Comparison of the experimental scattering curve of a styrene-isoprene block copolymer and the theoretical curves for cubic paracrystals: (a) sc, (b) fcc, and (c) bcc. Theoretical profiles were calculated for a given set of parameters $R=13.1$ nm, $\sigma_r=1.0$ nm, and $\sigma_s=0.5$ nm. The parameters g and a_n were 0.075 and 40.1 nm, respectively, for sc, 0.130 and 69.6 for fcc, and 0.100 and 56.7 for bcc.

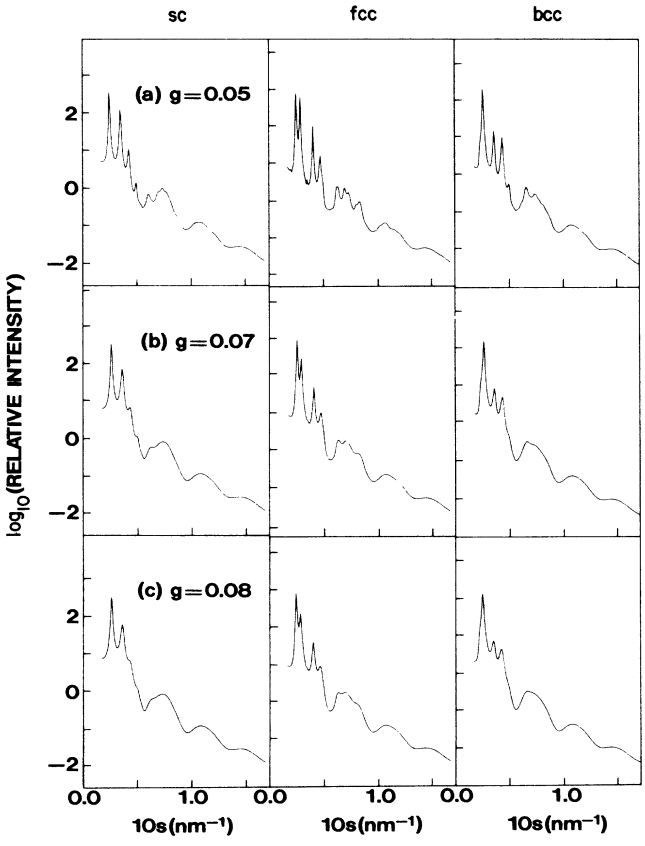

FIG. 4. Theoretical scattering curves of cubic paracrystals. (a) $g=0.05$, (b) $g=0.07$, and (c) $g=0.08$. Other parameters are the same as in Fig. 3.

paper should be

$$|F_k(\mathbf{q})|=\exp\{-\tfrac{1}{2}(\Delta a^2/a^2)[(\mathbf{q}\cdot\mathbf{a}_1)^2+(\mathbf{q}\cdot\mathbf{a}_2)^2+(\mathbf{q}\cdot\mathbf{a}_3)^2]\}$$
$$=\exp\{-\tfrac{1}{8}\Delta a^2q^2[(\sin\theta\sin\phi+\cos\theta)^2+(-\sin\theta\cos\phi+\cos\theta)^2+(-\sin\theta\cos\phi+\sin\theta\sin\phi)^2]\} \quad (2)$$

for fcc, and

$$|F_k(\mathbf{q})|=\exp\{-\tfrac{1}{8}\Delta a^2q^2[(\sin\theta\cos\phi+\sin\theta\sin\phi+\cos\theta)^2+(-\sin\theta\cos\phi-\sin\theta\sin\phi+\cos\theta)^2+(-\sin\theta\cos\phi+\sin\theta\sin\phi-\cos\theta)^2]\} \quad (3)$$

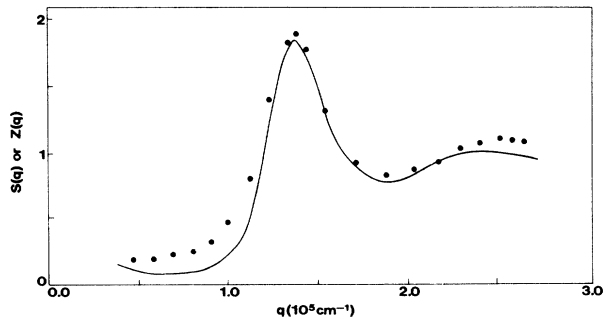

FIG. 5. Comparison of the experimental interference function $S(q)$ with the theoretical paracrystalline lattice factor $Z(q)$. The circles denote $S(q)$ for a latex suspension by Ottewill with a volume fraction of 10^{-3} and a particle radius of 256 Å. The line denotes $Z(q)$ for a fcc lattice, $a_n=5597$ Å and $g=0.22$.

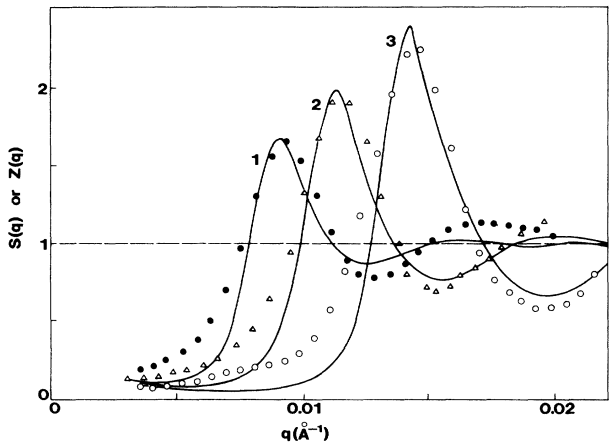

FIG. 6. Comparison of the experimental interference function $S(q)$ obtained by neutron scattering for latex solutions by Cebula *et al.* with theoretical lattice factors $Z(q)$. ●, △, and ○ represent $S(q)$ observed for a latex particle of $R=157$ Å at volume fractions 0.04, 0.08, and 0.13, respectively. Curves 1, 2, and 3 represent $Z(q)$ for fcc structures with ($a_n=830$ Å, $g=0.24$), ($a_n=679$ Å, $g=0.21$), and ($a_n=539$ Å, $g=0.18$), respectively.

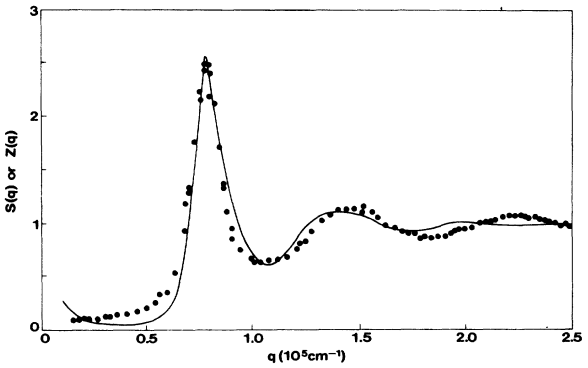

FIG. 7. Comparison of the experimental interference function $S(q)$ with theoretical paracrystalline lattice factor $Z(q)$. The circles denote $S(q)$ obtained by light scattering for a latex suspension by Versmold *et al.*, 0.34×10^{18} particles/m^3. The line denotes $Z(q)$ for a fcc structure, $a_n=9824$ Å and $g=0.17$.

for bcc, by using Eqs. (17)–(22) and (26)–(28) in the original paper. These equations must be used instead of Eq. (6) in the original paper.

When we compare the theoretical profile with the experimental one in terms of the total scattering curve, $I(q)$, the particle scattering factors $\langle|f_0|^2\rangle$ and $|\langle f_0\rangle|^2$ are necessary, as is clear from Eq. (1) in the original paper. Our previous calculation was done with an assumption that $\langle|f_0|^2\rangle=|\langle f_0\rangle|^2$. This relation is correct for scattering from spheres only at the limit of no size distribution, but becomes incorrect for polydisperse systems. Here, we have recalculated theoretical $I(q)$ without this assumption and calculated $|\langle f_0\rangle|^2$ as well as $\langle|f_0|^2\rangle$ based upon the model previously adopted.[3]

Paracrystalline lattice factors, $Z(q)$'s, for fcc and bcc by our corrected theory, are shown in Figs. 1 and 2, which correspond to Figs. 4 and 5 in the original paper, respectively. Scattering profiles are not so different from those by our previous calculation, but in general the height of diffraction peaks becomes higher at the same g value.[4] A marked upturn at very small-angle regions is observable also for a fcc system.

The small-angle x-ray (SAXS) data of block copolymer films, in which a microphase separation occurs and the spherical domains are arranged in an ordered manner, was compared with the corrected theory in Fig. 3 which corresponds to Fig. 9 in the original paper. A very good agreement with the paracrystalline model can be obtained for a bcc lattice. A good agreement with a bcc lattice was also obtained by our previous calculation, but the agreement is much better now. Here it must be noted that the corresponding g value becomes larger than the previous one. The typical scattering profiles for these systems are shown in Fig. 4 which correspond to Fig. 10 in the original paper.

The comparison of experimental interference functions obtained by light scattering and small-angle neutron-scattering (SANS) data with the theoretical paracrystalline lattice factors were shown in Figs. 5–7. For all cases, a fcc lattice is assumed, and agreements between the theory and experiments are satisfactory. The g factors used in the fittings are slightly larger than the previous ones.

The relation between the peak height and g value, and the influence of the size of the crystal, is now being analyzed.

Valuable comments were received from Dr. Norio Nemoto and Dr. Masukazu Hirata (Kyoto University) to whom our sincere gratitude is due.

[1]H. Matsuoka, H. Tanaka, T. Hashimoto, and N. Ise, Phys. Rev. B **36**, 1754 (1987).

[2]R. Hosemann and S. N. Bagchi, *Direct Analysis of Diffraction by Matter* (North-Holland, Amsterdam, 1966).

[3]T. Hashimoto, M. Fujimura, and H. Kawai, Macromolecules **13**, 1660 (1980).

[4]In our recent review article (Ref. 5), the integration range had already been corrected, while the distortion factor $|F_k(\mathbf{q})|$ had not been modified. As shown in Ref. 5, the peak height became lower at the same g-value condition.

[5]N. Ise, H. Matsuoka, and K. Ito, Macromolecules **22**, 1 (1989).