where $K_1^* = gN_0v^n$, and $g$ is a geometrical factor (which is $4\pi/3$ for spheres as in eq 1 and 2). The slope in eq 5 for the relationship between log $[-(\ln (1 - v^c)]$ and log $t$, $(n + a)$, is smaller than $n$, its original Avrami exponent.

## Crystallization with Changing Growth Rate

Linear crystal growth rates that change as crystallization proceeds have been observed earlier and mainly been linked to the influence of transport processes on crystallization.[1] For example, crystallization from dilute solution at large supercooling showed a nonlinear crystal-size increase with time,[22] and copolymers were shown to exhibit a sizable slow-down in spherulitic growth rate on close approach of two spherulites.[23,24] Such slow-down of crystal growth can often be treated as a Stefan problem[25] and leads usually to a boundary position that changes with the square root of time.[1] More substantial reduction in crystal growth rate is possible if the interface volume is large and crystallization leads to increasing restriction of the amorphous fraction, as can occur in the production of major fractions of rigid amorphous polymers.[15-19] In the cases of copolymers, such as in the HBA/HNA copolyesters,[12,21] a translational motion along the chain direction is largely hindered by the earlier grown crystals, and noncrystallizable counits cannot thus diffuse out from the growth-front of the crystal surface. We call such a phenomenon a "soft impingement." To treat this case, we assume that the crystal growth rate is a fraction of time:

$$v = v_0t^m \qquad (6)$$

where $m$ is negative when $v$ decreases with increasing time. Equation 3 can now be cast in the form of

$$\log [-(\ln (1 - v^c))] = \log g + \log N + n \log v_0 + n(m + 1) \log t$$

$$\log [-(\ln (1 - v^c))] = \log K_2^* + n(m + 1) \log t \qquad (7)$$

where $K_2^* = gNv_0^n$, and $n(m + 1)$ is the slope of log $t$. Such a slope is smaller than $n$ since $m$ is negative. If the crystal growth is diffusion-controlled, for instance, in which case $v$ would scale as $t^{-1/2}$,[26] according to eq 7, the slope of log $t$ becomes $0.5n$, and it would be 0.5, 1, and 1.5 for one-, two-, and three-dimensional growth, respectively.

Combining these two effects of nonnegligible volume fraction of nuclei and changing crystal growth rate, we may have

$$\log [-(\ln (1 - v^c))] = \log g + \log N_0 + n \log v_0 + [n(m + 1) + a] \log t$$

$$\log [-(\ln (1 - v^c))] = \log K^* + [n(m + 1) + a] \log t \qquad (8)$$

where $K^* = gN_0v_0^n$, and $n(m + 1) + a$ is called as an apparent coefficient of log $t$. Both negative contributions ($m$ and $a$) lead to the smaller value of the apparent coefficient one observed from experiments.

**Acknowledgment.** This work was supported at the University of Akron by the Research Challenge fund and at The University of Tennessee by the National Science Foundation, Polymers Program, Grant DMR 8317097.

## References and Notes

(1) Wunderlich, B. *Macromolecular Physics. Crystal Nucleation, Growth, Annealing*; Academic: New York, 1976; Vol. 2.
(2) Avrami, M. *J. Chem. Phys.* **1939**, *7*, 1103; **1940**, *8*, 212; **1941**, *9*, 177.
(3) Kolmogoroff, A. N. *Izv. Akad. Nauk SSSR, Ser. Math.* **1937**, *1*, 335.
(4) Johnson, W. A.; Mehl, R. T. *Trans. Am. Inst. Min., Metall. Pet. Eng.* **1939**, *135*, 416.
(5) Evans, U. R. *Trans. Faraday Soc.* **1945**, *41*, 365.
(6) Poisson, S. D. *Recherches sur la Probability des Jugements en matière criminelle et en matière civile*; Bachelier: Paris, 1837; p 206.
(7) Dole, M. *Kolloid Z.* **1959**, *165*, 40.
(8) Wunderlich, B. *J. Chem. Phys.* **1958**, *29*, 1395.
(9) Fischer, E. W. *Pure Appl. Chem.* **1978**, *50*, 1219.
(10) Hanna, S.; Windle, A. H. *Polymer* **1988**, *29*, 207.
(11) Wunderlich, B. *Macromolecular Physics. Crystal Structure, Morphology, Defects*; Academic: New York, 1973; Vol. 1.
(12) Cheng, S. Z. D. *Macromolecules* **1988**, *21*, 2475.
(13) Bhattacharya, S. K.; Misra, A.; Stein, R. S.; Lenz, R. W.; Hahn, P. E. *Polym. Bull. (Berlin)* **1986**, *16*, 465.
(14) Grebowicz, J.; Cheng, S. Z. D.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 675.
(15) Suzuki, H.; Wunderlich, B. *Makromol. Chem.* **1985**, *189*, 1109.
(16) Cheng, S. Z. D.; Cao, M.-Y.; Wunderlich, B. *Macromolecules* **1986**, *19*, 1868.
(17) Cheng, S. Z. D.; Wunderlich, B. *Macromolecules* **1987**, *20*, 1630.
(18) Cheng, S. Z. D.; Wu, Z. Q.; Wunderlich, B. *Macromolecules* **1987**, *20*, 2082.
(19) Cheng, S. Z. D.; Wunderlich, B. *Macromolecules* **1988**, *21*, 789.
(20) Butzbach, G. D.; Wendorff, J. H.; Zimmermann, H. J. *Polymer* **1986**, *27*, 1337.
(21) Cao, M.-Y. Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, NY 12180-3590, 1988.
(22) Holland, V. F.; Lindenmeyer, P. H. *J. Polym. Sci.* **1962**, *57*, 589.
(23) Price, F. P.; Kilb, R. W. *J. Polym. Sci.* **1962**, *57*, 395.
(24) Barnes, W. J.; Luetzel, W. G.; Price, F. P. *J. Phys. Chem.* **1961**, *65*, 1742.
(25) Stefan, J. *Ann. Phys. (Leipzig)* **1891**, *42*, 269.
(26) Schultz, J. *Polymer Materials Science*; Prentice-Hall: Englewood Cliffs, NJ, 1974.

---

# Multiple Scattering Correction to the Second Virial Coefficient Measured by Small-Angle Scattering

A. T. BOOTHROYD

*Department of Physics, University of Warwick, Coventry, CV4 7AL, U.K.*

*Received May 4, 1988*

## Introduction

When solutions are very dilute, the elastic scattering from the individual solute molecules adds linearly, so the intensity of radiation scattered coherently with wavevector transfer, $Q$, is just proportional to the mass of the molecule, $M$, the concentration, $c$, and the single-chain form factor, $P(Q)$. For larger concentrations, interparticle interferences become important, and the scattering then depends upon higher powers of the concentration. Zimm[1] derived an approximate expression for the coherent partial differential cross section by assuming that two molecules interact at only one point at any one time:

$$\frac{d\Sigma}{d\Omega}(Q) \approx KcMP(Q)[1 - 2A_2(Q)cMP(Q)] \qquad (1)$$

$P(Q)$ is defined here to be unity at zero $Q$. In the small $Q$ limit, $A_2$ is the second virial coefficient in the power series expansion of the osmotic pressure and indicates deviations from van't Hoff's law for ideal solutions. The second virial coefficient is an important quantity because it represents the strength of the intermolecular interactions.[2] It is usual to write eq 1 in the reciprocal,

$$Kc\left(\frac{d\Sigma}{d\Omega}\right)^{-1} \approx \frac{1}{MP(Q)} + 2A_2c \qquad (2)$$

because this form comes closer to accounting for neglected higher order terms than does eq 1.

Equation 2, known as the Zimm equation, has been the basis for analyzing low $Q$ scattering data for many years.

0024-9297/88/2221-3328$01.50/0

The method is to run a series of concentrations and to extrapolate the scattering from each to $Q = 0$. The second virial coefficient may then be obtained directly from the gradient of a plot of $Kc(\mathrm{d}\Sigma(0)/\mathrm{d}\Omega)^{-1}$ versus $c$.

At low $Q$, coherent scattering may be regarded as arising from the difference in scattering power between the solute and solvent. This "contrast" is relatively small in light scattering experiments. With neutrons, however, it can be much larger and may lead to quite strong scattering, especially when deuteriated molecules are used. In such circumstances, there is a possibility that problems may arise from the multiple scattering of radiation.

The effects of multiple scattering upon the angular dependence of small-angle scattering have been calculated[3,4] and shown to be unimportant in most experiments. In any case, the problems can always be reduced with a thinner sample, or lower concentrations. However, it has not been recognized before that multiple scattering also affects the value of $A_2$ obtained by the method described above.

That this is so can be seen from the consideration of a dilute solution whose single-scattered intensity is described by eq 1 and 2, that is, one in which $2A_2cM \ll 1$. To a good approximation, the single scattering is proportional to $c$, so the leading term of the double-scattered intensity is proportional to $c^2$. Thus, there is an extra $Q$-dependent contribution to eq 1 whose concentration dependence is the same as that of the interaction term. When the concentration is varied and the spectra subjected to a Zimm analysis, the resulting second virial coefficient, $A_2'$, will be smaller than the actual value, $A_2$.

## Calculations

In order to estimate the importance of this correction, two extreme cases are considered. The first is when the wavelength, $\lambda$, of the radiation is much smaller than the size of the particles so that the coherent signal decays very rapidly with the angle. This is typical of small-angle neutron experiments. For any sample geometry, the ratio of double- to single-scattered intensities may be approximated by

$$\frac{I_2}{I_1} \approx \frac{KcMt\lambda^2}{\langle S^2 \rangle} F(u) \tag{3}$$

where $t$ is the sample thickness, $\langle S^2 \rangle$ is the mean squared radius of gyration of the scattering particles, and $u = Q^2\langle S^2 \rangle$. The function $F(u)$ depends upon the form of $P(Q)$:

$$F(u) = \frac{1}{(4\pi)^2 P(u)} \int_0^{2\pi} \mathrm{d}\phi \int_0^{\infty} \mathrm{d}u'\, P(u')P(u' + u + 2(uu')^{1/2} \cos \phi) \tag{4}$$

When $I_2$ from eq 3 is included in eq 1, the effective second virial coefficient is seen to be

$$A_2' = A_2 - \frac{Kt\lambda^2}{2\langle S^2 \rangle} F(0) \tag{5}$$

If $P(Q)$ is the Lorentzian function used by Goyal et al.,[4] then $F(0) = 0.12$. A similar calculation using the Debye function for Gaussian polymers gives $F(0) = 0.094$. Thus, a value of $F(0) = 0.1$ may be presumed typical. Approximate values of the other constants for hydrogenous polymers in deuteriated solvents are $K = 0.01$ mol cm$^2$ g$^{-2}$, $t = 0.2$ cm, and $\lambda^2/\langle S^2 \rangle = 0.1$, so that the correction to $A_2$ is of the order $10^{-5}$ mol cm$^3$ g$^{-2}$. This is an order of magnitude lower than typical second virial coefficients in good solvents.

The second example concerns isotropic scattering, which occurs when $\lambda^2 \gg \langle S^2 \rangle$, as in many light scattering experiments (although the polarisation of the scattering does give some angular dependence). It also applies to incoherent neutron scattering, but since the incoherent intensity is usually much smaller than the coherent signal, the corrections for incoherent–incoherent multiple scattering will not be estimated explicitly here. The double-scattered intensity for isotropic scattering in the infinite slab geometry was derived by Vineyard,[5] and for weak scatterers at zero angle the ratio is

$$\frac{I_2}{I_1} \approx \frac{KcMt}{\tau} \frac{2 \ln 2 - 1}{8\pi} \tag{6}$$

where $\tau = -(\ln T)$, and $T$ is the transmission of the sample.

Equation 6 is still proportional to $c$ as long as $T$ is independent of $c$, i.e., when the radiation is attenuated by processes other than scattering from the solute particles. Thus, the measured second virial coefficient is

$$A_2' = A_2 - \frac{Kt}{2\tau} 0.015 \tag{7}$$

With the same neutron constants as before, and a transmission of 90% ($\tau = 0.1$), the correction is of the order $10^{-4}$ mol cm$^3$ g$^{-2}$.

## Conclusions

The aim of this note is to point out that multiple scattering can still be present in the results of small-angle experiments even when it has an apparently negligible effect upon the angular dependence of the scattered radiation. The estimates above show that the correction to the measured second virial coefficient is small under normal circumstances. Corrections for cases intermediate to those discussed above are more complicated functions of $\tau$ and $\langle S^2 \rangle/\lambda^2$, but the magnitude of the effect will be in between the extremes represented by eq 5 and 7. The problem is worst for samples with a high contrast factor, so it is unimportant in light scattering, but may become significant for second virial coefficients measured by neutron scattering.

**Registry No.** Neutron, 12586-31-1.

## References and Notes

(1) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1093.

(2) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.

(3) Schelten, J.; Schmatz, W. *J. Appl. Crystallogr.* **1980**, *13*, 385.

(4) Goyal, P. S.; King, J. S.; Summerfield, G. C. *Polymer* **1983**, *24*, 131.

(5) Vineyard, G. H. *Phys. Rev.* **1954**, *96*, 93.