In conclusion, we have measured the containment of high-β plasmas ($\beta \simeq 0.3$ to 0.4) in the $2X$II magnetic mirror device and have observed evidence of a β limit. The magnitude and time dependence of this limit were consistent with those predicted for the mirror instability.

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[1]R. A. Dandl, H. O. Eason, P. H. Edmonds, A. C. England, G. E. Guest, C. L. Hedrick, J. T. Hogan, and J. C. Sprott, in *Proceedings of the Fourth International Conference on Plasma Physics and Controlled Nuclear Fusion Research, Madison, Wisconsin, 1971* (International Atomic Energy Agency, Vienna, Austria, 1972), Vol. 2, p. 607.

[2]For example, see H. P. Eubank, P. Noll, and F. Trappert, Nucl. Fusion 5, 68 (1965); V. A. Finlayson, F. H. Coensgen, and W. E. Nexsen, Jr., Nucl. Fusion 12, 659 (1972).

[3]W. S. Cooper, K. H. Berkner, and R. V. Pyle, Nucl. Fusion 12, 263 (1972); and K. W. Ehlers and W. B. Kunkel, in *Proceedings of the Second International Conference on Ion Sources, Vienna, Austria, 1972,* edited by I. Viehboeck, H. Winter, and M. Bruck (Österreichische Studiengesellschaft für Atomenergie GmbH, Vienna, Austria, 1972), p. 259.

[4]W. F. Cummins, Rev. Sci. Instrum. 41, 234 (1970).

[5]T. C. Simonen, F. H. Coensgen, W. F. Cummins, W. E. Nexsen, Jr., A. W. Molvik, and B. W. Stallard, Bull. Amer. Phys. Soc. 18, 1320 (1973).

[6]W. E. Nexson, Jr., W. F. Cummins, F. H. Coensgen, A. W. Molvik, and T. C. Simonen, Bull. Amer. Phys. Soc. 17, 985 (1972).

[7]J. G. Cordey and C. J. H. Watson, in *Proceedings of British Nuclear Energy Society Conference on Nuclear Fusion Reactors, Culham Laboratory, 1969* (United Kingdom Atomic Energy Authority, Culham, England, 1970), p. 122.

[8]L. S. Hall, Phys. Fluids 15, 882 (1972).

[9]J. P. Holdren, Nucl. Fusion 12, 267 (1972).

[10]For convenience, we will follow the custom of referring to this as the mirror instability, although this condition more precisely refers to the maximum perpendicular β for which equilibrium exists.

[11]J. G. Cordey and C. J. H. Watson, Nucl. Fusion 12, 287 (1972).

[12]L. S. Hall and T. C. Simonen, to be published.

Dynamics of Charged Macromolecules in Solution*

Dale W. Schaefer

Sandia Laboratories, Albuquerque, New Mexico 87115

and

Bruce J. Berne

Department of Chemistry, Columbia University, New York, New York 10027

Analysis of the scattered intensity and photocount correlation function of light scattered from charged R17 virus indicates incipient macromolecular ordering.

If a coherent light source is focused on a macromolecular solution, fluctuations are observed in the scattered light intensity. Fluctuations result since motion of the particles produces a constantly changing interference condition at the detector.[1] If the positions of the particles are uncorrelated, it is well established that the decay rate of intensity fluctuations is directly proportional to macromolecular diffusion constant.[2]

In the case of solutions in which the range of interparticle interaction is comparable to the interparticle distance d, macromolecular dynamics have remained quite obscure. This is the case, not only because of the theoretical difficulties associated with many-body systems, but also because of limited experimental data. In order to elucidate this problem we present data on both the magnitude and time dependence of light scattered from solutions of charged macromolecules (R17 virus) in which the range of the electrostatic interaction σ is comparable to d. Both the scattered intensity and the decay rate Γ of the field correlation function depend strongly on scattering angle indicating incipient translational ordering. These data are interpreted by the Zwanzig-Mori projection-operator formalism,[3-5] through which we demonstrate that the dependence of Γ on scattering angle is largely

determined by the decreased susceptibility of the system to fluctuations whose Fourier wavelength is greater than d. We show that this susceptibility can be measured through the integrated scattered light intensity.

The key to the application of the Zwanzig-Mori treatment is to choose (by physical insight) those dynamical properties which change slowly in time and to project an arbitrary property onto the subspace of these slow variables and its orthogonal complement which, by definition, contains all the rapidly decaying properties.[5] If the subspaces are judiciously chosen, a large separation of time scales results and solution of the memory equation for the time correlation function is possible. We find that the single slow variable $C(K,t)$, the amplitude of the Kth Fourier component of the macromolecular concentration, is sufficient to explain most of the features of the data presented below. We have

$$C(K,t) = N^{-1}\sum_j \exp[i\vec{K}\cdot\vec{r}_j(t)]$$

$$= N^{-1}\sum_j \exp[iKz_j(t)], \tag{1}$$

where $\vec{r}_j$ is the position of the jth macromolecule and N is the number of macromolecules. $\vec{K}$ is presumed to lie in the z direction. Conveniently, $C(K,t)$ is proportional to the scattered light field, $\vec{K}$ being the scattering vector.

The memory equation for $\mathcal{C}(t) \equiv \langle C(0)|C(t)\rangle$, the correlation function of the $C(t)$, becomes[3,5]

$$d\mathcal{C}(t)/dt = -\int_0^\infty d\tau\, \mathcal{K}(\tau)\mathcal{C}(t-\tau). \tag{2}$$

The memory function $\mathcal{K}(\tau)$ is related to the correlation function of the random force conjugate to C and cannot, in general, be calculated. Nevertheless Eq. (2) may be formally solved if $C(t)$ is the only slowly decaying property. In this case (Markov approximation) $\mathcal{K}(\tau)$ lies wholly within the subspace of rapidly decaying properties. Within this approximation, then, $\mathcal{C}(t) = \exp(-\Gamma t)$, where

$$\Gamma(K) \equiv K^2 D(K)S^{-1}(K). \tag{3}$$

The kinetic factor $D(K)$ is related to $J_z(K,t)$, the Kth Fourier component of the particle flux in the z direction:

$$D(K) \equiv \int_0^\infty d\tau \langle J_z(K,0)|J_z(K,\tau)\rangle_Q, \tag{4}$$

where the subscript Q indicates that the average is performed in the fast subspace. $D(K)$ reduces to the diffusion constant in the limits $K \to 0$, $d \to \infty$. $S(K) = \langle C|C\rangle$, the susceptibility or structure factor, is just the integrated scattered light intensity.

Equation (3) indicates that $\Gamma(K)$ is determined partly by $D(K)$, a measure of the functional drag, and partly by $S(K)$, a measure of the susceptibility of the system to fluctuations of wave vector K. Since $D(K)$ is determined primarily by interaction with the solvent, it is reasonable to believe that $D(K)$ will be a weak function of K. Therefore, the K dependence of Γ is expected to reflect inversely the K dependence of $S(K)$.

Because of the importance of $S(K)$ in determining the form of $\Gamma(K)$ it is worth noting how $S(K)$ changes as σ increases.[6,7] For weakly correlated systems ($\sigma < d$), $S(K)$ is less than unity for small K and approaches unity for $K\sigma > 2\pi$.[7] As σ becomes comparable to d it is reasonable to expect a broad maximum in $S(K)$ at $Kd \gtrsim 2\pi$. This maximum is analogous to the lowest order peak in the x-ray structure factor of dense fluids.[6] Finally, for $\sigma \gg d$ the system should display long-range order and $S(K)$ will show a sharp "Bragg" peak at $Kd = 2\pi$.

The features discussed above were studied through measurements of the total counting rate and clipped photocount correlation function for light scattered from solutions of R17 virus at 25°C. R17 is a highly stable spherical virus of radius 139 Å.[8] Solutions were prepared by dialysis against pure water and subsequent titration with NaOH. Data were also taken at high ionic strength (1M NaCl) in which case the effects of charge were absent. The scattered intensity $S(K)$ was measured as a function of the scattering angle θ for all solutions [$K = 2K_0\sin(\theta/2)$, where K_0 is the magnitude of the wave vector of the incident light]. To permit normalization of $S(K)$ to that of noninteracting particles of the same concentration, the intensity of all the samples was measured at $\theta = 90°$ relative to a standard solution of 0.109-μm-diam polystyrene spheres. The mean decay rate $\bar{\Gamma}$ of $\mathcal{C}(t)$ was determined from the initial decay of the clipped photocount correlation function.[8,9] In addition, since the measured correlation functions were nonexponential, the width of the distribution of decay rates $\langle(\Delta\Gamma)^2\rangle/\bar{\Gamma}^2$ was determined through data analysis by the method of cumulants.[9]

Data for $S(K)$ are shown in Fig. 1 for solutions with $Z = 0$ (1M NaCl), $Z = 500$, and $Z = 3600$, where $Z = $ (moles of NaOH added)/(moles of R17). Several features of these data should be noted. (a) $S(0)$ is less than unity for $Z \neq 0$ as expected from thermodynamic analysis.[7] In fact, a simple hard-sphere analysis of $S(0)$ indicates that for both samples $\sigma \approx 1150\ \text{Å} \approx d/2$. Although the charge is
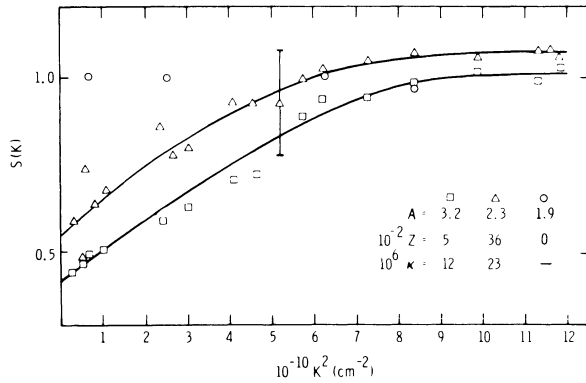
FIG. 1. K dependence of the scattering cross section for solutions of R17 virus in water (triangles, squares) and 1M NaCl (circles). Z = (moles NaOH added)/(moles R17). A = absorbance at 260 nm (1 cm path). κ = conductance (Ω^{-1} cm^{-1}). The absorptivity (Ref. 15) at 260 nm is $2.9 \times 10^{7} M^{-1}$ cm^{-1}. The source used was a krypton ion laser with wavelength 4762 or 6764 Å.

FIG. 2. K dependence of the mean decay rate.

certainly larger for $Z = 3600$, the conductivity κ of the solution is twice that for $Z = 500$ indicating more effective shielding by small ions. The larger κ is due to inadvertent introduction of KCl during an attempt to measure the pH with a glass electrode. (b) $S(K)$ is an increasing function of K^2 for $K \to 0$. This dependence was observed by Pusey et al.[8] and is expected for repulsive forces.[10] (c) For $Z \neq 0$, $S(K)$ appears to be greater than unity for $K^2 \sim 11 \times 10^{10}$, indicating a broad peak in $S(K)$. The error bars, of course, do not exclude $S(K) = 1$. In either case, the data clearly indicate $\sigma \lesssim d$ (very short range order) for both systems.

Data for $\bar{\Gamma}$ are plotted in Fig. 2. For the $Z = 500$ data, cumulant analysis showed that $\langle(\Delta\Gamma)^2\rangle/\bar{\Gamma}^2$ varied from 0.24 ± 0.03 at small K to 0.15 ± 0.03 for large K. The corresponding numbers for $Z = 3600$ were 0.34 ± 0.03 and 0.25 ± 0.02. A temperature-dependent viscosity correction was applied to $\bar{\Gamma}$, assuming $\bar{\Gamma}/K^2 \propto$ (solvent viscosity)$^{-1}$, to reduce the data to standard conditions (water at 20°C). As suggested above, the K dependence of $\bar{\Gamma}/K^2$ is inversely related to $S(K)$ in Fig. 1.

Two observations can be made concerning the kinetic factor $D(K)$ in Fig. 3: (a) $D(K)$ is a decreasing function of charge. This behavior is expected for repulsive forces although the effects are not as great as predicted by Pyun and Fixman's hard-sphere theory[11] when the hard-sphere diameter is calculated from $S(0)$ in Fig. 1. (b) The
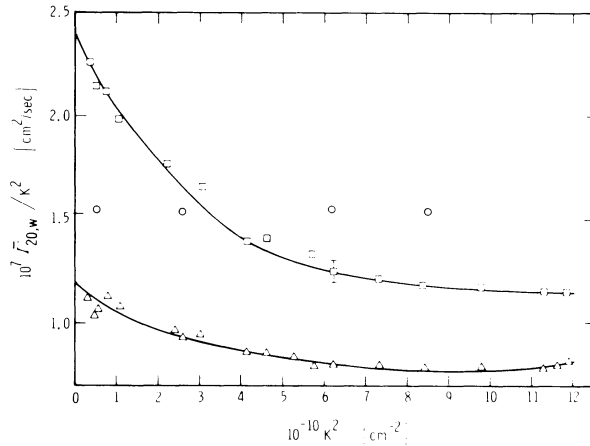
weak dependence of $D(K)$ on K is consistent with the one-dimensional computer simulations of Pusey.[10]

Insight into the meaning of $D(K)$ can be obtained by analyzing the collective decay rate Γ [Eq. (3)] in terms of single and pair correlations.[5,12] This is accomplished by treating the slow subspace as a combination of single-particle variables $C^{(i)}(t) \equiv \exp[i\vec{K} \cdot \vec{r}_i(t)]$ as well as the multiparticle variable $C(t)$. Following this procedure, the collective decay rate Γ can be written in terms of Γ_s, the single-particle decay rate, and Γ_d, a two-particle dynamic correlation factor:

$$D(K) = \Gamma S(K) K^{-2} = (\Gamma_s + N\Gamma_d) K^{-2}, \qquad (5)$$

$$\Gamma_s = K^2 \int_0^{\infty} d\tau \langle J_z^{(1)}(K,0) | J_z^{(1)}(K,\tau)\rangle_Q, \qquad (6)$$

$$\Gamma_d = K^2 \int_0^{\infty} d\tau \langle J_z^{(1)}(K,0) | J_z^{(2)}(K,\tau)\rangle_Q. \qquad (7)$$

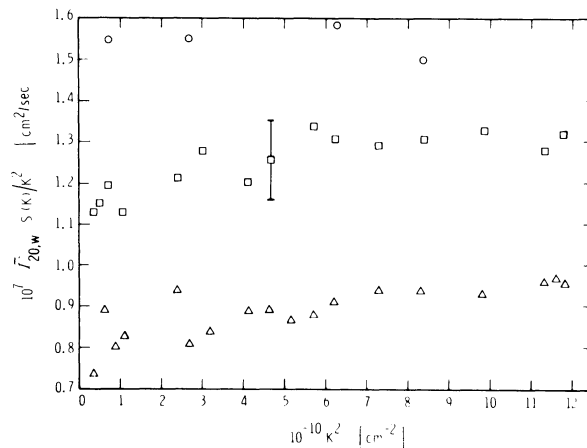Although the data lack sufficient accuracy and

FIG. 3. K dependence of the kinetic factor.

precision to establish definitively the form of Γ_d, it appears that Γ_d is a positive quantity with a maximum coincident with the maximum in $S(K)$. This conclusion rests on the assumption that Γ_s is a K-independent decreasing function of charge.

The only feature of the data which cannot be understood in terms of the above treatment is the nonexponential behavior of measured correlation functions. It is possible that this behavior is due to the presence of a small amount of highly extended ribonucleic acid released from ruptured particles. Indeed, when the R17 solution used was dialyzed back to 1M NaCl the measured D was found to be 10% less than that of native R17 indicating some denaturation. It is also possible that the subspace $C(t)$ chosen above does not include all the slow properties, thus compromising the Markov approximation leading to Eq. (3). It is reasonable, for example, that the counterions track the macroion and thus assume slow dynamical properties. In any case, expansion of the slow subspace leads to discouraging theoretical complications.

The only microscopic theory with which these data can be compared is that of Stephen,[13] who treated scattering from electrolytes in the Debye-Hückel limit. Unfortunately the strong intermacroion forces present in the solutions studied here invalidate Stephen's assumptions. Nevertheless, it is interesting to note that Stephen's theory, when specialized to our case, gives

$$\frac{\Gamma(K)}{K^2} = \frac{(K^2 + q_+{}^2 + q_-{}^2)D_-D_+}{(K^2 + q_+{}^2)D_+ + (K^2 + q_-{}^2)D_-}. \qquad (8)$$

q_- and q_+ are the inverse Debye screening length for the macroions and small ions as defined by Stephen, and D_- and D_+ are the corresponding hydrodynamic diffusion constants. Although Eq. (8) predicts the trends observed, the data cannot be fitted even if D_- is taken from Fig. 3 and q_- is adjusted.

Finally, it should be noted that the correlations observed here are not due to "dispersion effects" studied by Kirkwood and Shumaker,[14] which arise because of fluctuating multipoles and lead to attractive forces. If these forces were the dominant cause of short-range correlation, we would expect $S(K)$ to decrease with K as $K \to 0$, which is contrary to experiment.

[1]D. W. Schaefer, in *Laser Applications to Optics and Spectroscopy*, edited by S. F. Jacobs, M. O. Scully, M. Sargent, III, and J. F. Scott (Addison-Wesley, Reading, Mass., 1974).

[2]S. B. Dubin, J. H. Lunacek, and G. B. Benedek, Proc. Nat. Acad. Sci. U.S. **57**, 1164 (1967).

[3]R. Zwanzig, in *Lectures in Theoretical Physics*, edited by W. E. Brittin, B. W. Downs, and J. Downs (Interscience, New York, 1961), p. 106.

[4]H. Mori, Progr. Theor. Phys. **33**, 423 (1965).

[5]B. J. Berne and R. Pecora, *Chemical and Biological Applications of Light Scattering* (Interscience, New York, 1974), Chap. 11; B. J. Berne, in *Physical Chemistry*, edited by D. Henderson (Academic, New York, 1971), Vol. VIII-B, p. 539.

[6]P. A. Egelstaff, *An Introduction to the Liquid State* (Academic, London, 1967), Chap. 6.

[7]P. Doty and R. F. Steiner, J. Chem. Phys. **20**, 85 (1952).

[8]P. N. Pusey, D. W. Schaefer, D. E. Koppel, R. D. Camerini-Otero, and R. M. Franklin, J. Phys. (Paris), Colloq. **33**, C1-163 (1972).

[9]D. E. Koppel, J. Chem. Phys. **57**, 4814 (1972).

[10]P. N. Pusey, in *Photon Correlation and Light Beating Spectroscopy*, edited by H. Z. Cummins and E. R. Pike (Plenum, New York, 1974).

[11]C. W. Pyun and M. Fixman, J. Chem. Phys. **41**, 937 (1964).

[12]T. Keyes and D. Kivelson, J. Chem. Phys. **56**, 1057 (1972).

[13]M. J. Stephen, J. Chem. Phys. **55**, 3878 (1971).

[14]J. G. Kirkwood and J. B. Shumaker, Proc. Nat. Acad. Sci. U.S. **38**, 863 (1952).

[15]R. D. Camerini-Otero, P. N. Pusey, D. E. Koppel, D. W. Schaefer, and R. M. Franklin, Biochemistry **13**, 960 (1974).