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Light scattering from dilute macromolecular solutions*

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The polarized light scattering spectrum from a dilute solution of spherical macromolecules is customarily interpreted on the basis of independent particle diffusion. However, it is known that diffusion in such a system is governed by a many particle diffusion equation with cross-diffusion coefficients $\mathbf{D}_{ij}$ that depend on the inverse distance between all pairs of particles (i, j). Here we prove that the spectrum from the system described by the N-particle diffusion equation is identical to the spectrum obtained from the simple, but incorrect, independent particle diffusion model. The physical reason for this suprising simplication is that the $\mathbf{D}_{ij}$ are proportional to Oseen's tensor which holds for an incompressible fluid and hence has no longitudinal part. When short-range forces are taken into account as well as the long-range hydrodynamic interaction present in $\mathbf{D}_{ij}$, it is possible to obtain simple approximate expression for a k-dependent effective diffusion constant $D_{\text{eff}}(\mathbf{k})$. This expression is evaluated for the case where the macromolecules are treated as hard spheres and one obtains $D_{\text{eff}}(\mathbf{k})=D_0[1+2.0\phi]$ for low k where ϕ is the volume fraction of macromolecules in solution.

I. INTRODUCTION

The polarized light scattering spectrum from a solution of spherical macromolecules in an optically inert solvent is proportional[1] to

$$I(\mathbf{k},\omega)=\mathrm{Re}\int_0^\infty dt\,\exp(-i\omega t)G(\mathbf{k},t), \qquad (1.1)$$

where ω is the change in frequency and k the change in wave vector upon scattering. The coherent structure factor $G(\mathbf{k}, t)$ is defined by

$$G(\mathbf{k},t)=(1/N)\sum_{m=1}^{N}\sum_{n=1}^{N} \times\langle\exp[i\mathbf{k}\cdot\mathbf{R}_m(t)]\exp[-i\mathbf{k}\cdot R_n(0)]\rangle, \qquad (1.2)$$

where the sums are over all the macromolecules in the solution and $\mathbf{R}_m(t)$ denotes the position of particle m at time t.

Experiments on neutral macromolecular solutions have invariably been interpreted[2-8] on the basis that the solution is "dilute" and that interactions between the particles may be neglected in determining the diffusional motion of the particles. Thus it is assumed that the N-particle coordinate space distribution function $P(\mathbf{R}^N, t)$ is the product of single particle distribution functions

$$P(\mathbf{R}^N,t)=\prod_{j=1}^{N} p^{(1)}(\mathbf{R}_j,t) \qquad (1.3)$$

and that each single particle distribution function $p^{(1)}(\mathbf{R}, t)$ satisfies the single particle diffusion equation

$$\partial p^{(1)}(\mathbf{R},t)/\partial t=D_0\nabla^2 p^{(1)}(\mathbf{R},t). \qquad (1.4)$$

From these assumptions it follows that

$$G(\mathbf{k},t)=G(\mathbf{k},0)\exp[-D_0\mathbf{k}^2t] \qquad (1.5)$$

and that the spectrum is given by

$$I(\mathbf{k},\omega)=G(\mathbf{k},0)\{D_0\mathbf{k}^2/[\omega^2+(D_0\mathbf{k}^2)^2]\}. \qquad (1.6)$$

The width of the spectrum is determined by (D_0k^2) and does not depend upon concentration. The basis for adopting this infinite dilution picture for solutions that are actually at finite concentration is the experimental observation that the measured width is largely independent of concentration.

There is, however, a need for theoretical justification of these simplifying assumptions. The reason is that the known, correct N-particle Smoluchowski diffusion equation[9-13] describing the dynamical motion of a dilute solution of heavy spherical particles does not have a solution of the form Eq. (1.3). This equation which may be obtained from stochastic considerations,[9] from molecular considerations,[10-13] or through reduction of the corresponding N-particle Fokker–Planck equation[14,15] is

$$\partial P(\mathbf{R}^N,t)/\partial t=\left[\sum_{i=1}^{N} D_0\nabla_i^2+\sum_{i,j=1}^{N}\nabla_i\cdot\mathbf{D}_{ij}\cdot\nabla_j\right]P(\mathbf{R}^N,t). \qquad (1.7)$$

The second term on the right hand side of this equation contains the interactions between the particles through cross diffusion tensors $\mathbf{D}_{ij}$ which are given by

$$\mathbf{D}_{ij}=(1-\delta_{ij})(k_BT)\mathbf{T}_{ij}\equiv\mathbf{D}(\mathbf{R}_i-\mathbf{R}_j), \qquad (1.8)$$

where δ_{ij} is the Kronecker delta, T the absolute temperature, and $\mathbf{T}_{ij}$ is Oseen's tensor[9,16] that describes the hydrodynamic interaction between particles i and j:

$$\mathbf{T}_{ij}=(8\pi\eta_0R_{ij})^{-1}\{\mathbf{I}+[(\mathbf{R}_{ij}\mathbf{R}_{ij})/R_{ij}^2]\}=\mathbf{T}(\mathbf{R}_i-\mathbf{R}_j). \qquad (1.9)$$

In this equation η_0 is the solvent shear viscosity, $\mathbf{I}$ is the unit tensor, and $\mathbf{R}_{ij}$ is the vector distance between particles i and j. The N-particle diffusion equation Eq. (1.7) is valid when the particles are widely separated and consequently it does not contain the concentration effects that arise when the particles are sufficiently close to feel the direct short-range interaction potential. Also the equation has not been proven to be valid for charged systems.

Potentially the most important dynamical concentration effect in the macromolecular solution might arise from the interaction term in the N-particle diffusion equation. This interaction term takes into account the hydrodynamic interaction which is always present between macromolecules in solution. Since the hydrodynamic interaction is of long-range, i.e., $\mathbf{D}_{ij} \sim R_{ij}^{-1}$ these effects might well be imagined to be dramatic. It is necessary to understand why the simple current interpretation that ignores these interactions is successful.

The purpose of this article is to present a simple and exact mathematical analysis which demonstrates that the spectrum computed according to the complete N-particle diffusion equation is identical to the spectrum given in Eq. (1.6) obtained from the independent particle diffusion model. In short the long-range interaction terms in the correct N-particle diffusion equation do not contribute to the spectrum and one need not be concerned that these terms lead to concentration effects in light scattering experiments. The result of the simple independent particle model is correct but the reasoning used in the past to obtain the result is not.

In the next section the derivation of an expression for the spectrum for the N-particle diffusion model is presented. The physical basis for the absence of long-range interaction effects on the spectrum is discussed. In Sec. III it is shown that the N-particle diffusion equation Eq. (1.7) has the novel feature of yielding exact closed equations for reduced distribution functions of the N-particle system. The paper concludes with remarks concerning extensions of the model and analysis presented to more general cases where interesting concentration effects may well arise from the long-range hydrodynamic interaction.

II. LIGHT SCATTERING SPECTRUM

For the N-particle diffusion model the dynamical structure factor $G(\mathbf{k}, t)$ may be computed according to Eq. (1.2) as

$$G(\mathbf{k}, t)=\sum_{m,n} V^{-N} \int d\mathbf{R}^N d\hat{\mathbf{R}}^N \exp[i\mathbf{k}\cdot \mathbf{R}_m] \times\exp[-i\mathbf{k}\cdot \mathbf{R}_n] P(\mathbf{R}^N t \,|\, \hat{\mathbf{R}}^N, 0), \qquad (2.1)$$

where $P(\mathbf{R}^N, t \,|\, \hat{\mathbf{R}}^N, 0)$ satisfies the N-particle diffusion equation Eq. (1.7)

$$\partial P(\mathbf{R}^N, t \,|\, \hat{\mathbf{R}}^N, 0)/\partial t = L(\mathbf{R}^N) P(\mathbf{R}^N, t \,|\, \hat{\mathbf{R}}^N, 0), \qquad (2.2)$$

$$L(\mathbf{R}^N)=\sum_i D_0 \nabla_i^2+\sum_{i,j} \nabla_i \cdot \mathbf{D}_{ij} \cdot \nabla_j \qquad (2.3)$$

with initial condition

$$P(\mathbf{R}^N, 0 \,|\, \hat{\mathbf{R}}^N, 0)=\delta(\mathbf{R}^N-\hat{\mathbf{R}}^N). \qquad (2.4)$$

In this expression for the equilibrium correlation function $G(\mathbf{k}, t)$ use has been made of the fact that the equilibrium solution to the N-particle diffusion equation is simply V^{-N}.

An alternative expression for $G(\mathbf{k}, t)$ is

$$G(\mathbf{k}, t)=\sum_{m,n} V^{-N} \int d\mathbf{R}^N \exp[-i\mathbf{k}\cdot \mathbf{R}_m] \exp[L(\mathbf{R}^N)t] \times\exp[i\mathbf{k}\cdot \mathbf{R}]. \qquad (2.5)$$

This expression may be evaluated by considering the differential equation satisfied by $G(\mathbf{k}, t)$:

$$\partial G(\mathbf{k}, t)/\partial t=\sum_{m,n} V^{-N} \int d\mathbf{R}^N \exp[-i\mathbf{k}\cdot \mathbf{R}_m] L(\mathbf{R}^N) \times \exp[L(\mathbf{R}^N)t] \exp[i\mathbf{k}\cdot \mathbf{R}_n]. \qquad (2.6)$$

Substitution of the definition of $L(\mathbf{R}^N)$, Eq. (2.3), followed by integration by parts leads to the equation

$$\partial G(\mathbf{k}, t)/\partial t = -D_0 \mathbf{k}^2 G(\mathbf{k}, t)+\sum_{m,n} V^{-N} \int d\mathbf{R}^N \times \exp[-i\mathbf{k}\cdot \mathbf{R}_n] \sum_{j\,(\neq n)} (i\mathbf{k}\Delta_j) : \mathbf{D}_{nj} \times \exp[L(\mathbf{R}^N, t)] \exp[i\mathbf{k}\cdot \mathbf{R}_n], \qquad (2.7)$$

where

$$[i\mathbf{k}\nabla_j : \mathbf{D}_{nj}]=\sum_{\alpha,\beta} [ik_\alpha (\partial/\partial R_{\beta j}) D_{nj}^{\alpha\beta}] \quad \alpha, \beta = x, y, z. \qquad (2.8)$$

and the gradient with respect to $\mathbf{R}_j$ operates only on $\mathbf{D}_{nj}$. The key step in the analysis is to recognize that the second term on the right hand side of Eq. (2.7) is identically zero. The reason is that

$$\sum_\beta (\partial/\partial R_{\beta j}) D_{nj}^{\alpha\beta}=0 \qquad (2.9)$$

as can be verified by direct substitution of the definition of $\mathbf{D}_{nj}$ given in Eqs. (1.8) and (1.9). It is also true that

$$\nabla_{\mathbf{R}} \cdot \mathbf{D}(\mathbf{R}-\mathbf{R}')=\nabla_{\mathbf{R}'} \cdot \mathbf{D}(\mathbf{R}-\mathbf{R}')=0. \qquad (2.10)$$

Consequently it follows that for the N-particle diffusion model

$$\partial G(\mathbf{k}, t)/\partial t=-D_0 \mathbf{k}^2 G(\mathbf{k}, t), \qquad (2.11)$$

which leads to an identical expression for the dynamic structure factor $G(\mathbf{k}, t)$ as in the independent particle model, Eq. (1.5). Hence the spectrum for the N-particle diffusion model and the independent particle model are the same and given by Eq. (1.6). The assertion that both models lead to identical light scattering spectra that do not exhibit concentration effects is established. The N-particle diffusion model is a rare example of an interacting many particle model where the dynamical structure factor is given exactly by zeroth order independent particle dynamics.

It remains to examine the physical basis for the simplification encountered in the N-particle diffusion model. The simplification is a direct consequence of the property of the Oseen tensor exhibited in Eq. (2.10):

$$\nabla_{\mathbf{R}}\cdot \mathsf{T}(\mathbf{R}-\mathbf{R}') = \nabla_{\mathbf{R}'}\cdot \mathsf{T}(\mathbf{R}-\mathbf{R}') = 0. \tag{2.12}$$

The reason why the Oseen tensor has no longitudinal part may be appreciated by considering the assumptions that are employed in obtaining this quantity. The Oseen tensor is the Green's function for the linearized Navier–Stokes equations for the velocity field v under the assumption that the fluid may be considered as incompressible and that inertial effects may be neglected.[9,16] Thus

$$\mathbf{v}(\mathbf{R}) = \mathsf{T}(\mathbf{R}-\mathbf{R}')\cdot \mathbf{F}_0 \tag{2.13}$$

is the solution to the equation

$$\rho\partial \mathbf{v}(R,t)/\partial t = 0 = \eta\nabla^2\mathbf{v} - \nabla p + \mathbf{F}_0\delta(\mathbf{R}-\mathbf{R}') \tag{2.14}$$

with the additional constraint of an incompressible fluid:

$$\nabla_{\mathbf{R}}\cdot \mathbf{v}(\mathbf{R}) = 0. \tag{2.15}$$

It follows immediately from the condition for an incompressible fluid Eq. (2.15) that the velocity field v(R) given in Eq. (2.13) will be entirely transverse and hence that Eq. (2.12) is satisfied. In terms of spatial Fourier transforms one has

$$\hat{\mathbf{v}}(\mathbf{k}) = \hat{\mathsf{T}}(\mathbf{k})\cdot \mathbf{F}_0 \exp[i\mathbf{k}\cdot\mathbf{R}'] \tag{2.16}$$

with

$$\hat{\mathsf{T}}(\mathbf{k}) = (\eta k^2)^{-1}[\mathsf{1} - \mathbf{k}\mathbf{k}/k^2]. \tag{2.17}$$

The condition of an incompressible fluid is $i\mathbf{k}\cdot\hat{\mathbf{v}}(\mathbf{k}) = 0$ so that one has $[i\mathbf{k}\cdot\hat{\mathsf{T}}(\mathbf{k})] = 0$.

III. EXACT DECOUPLING OF THE N-PARTICLE DIFFUSION EQUATION

An additional consequence of the property Eq. (2.10) is that the N-particle diffusion yields exact closed equations for reduced n-particle distribution functions of the system. The reduced distribution function $p^{(n)}(\mathbf{R}^n, t)$ is defined by

$$p^{(n)}(\mathbf{R}^n, t) = \int d\mathbf{R}^{N-n} P(\mathbf{R}^N, t) \quad n < N. \tag{3.1}$$

This quantity is useful for obtaining the nonequilibrium average of phase functions $\chi^{(n)}[\mathbf{R}^n(t)$ that depend on a subset of the macromolecules:

$$\overline{\chi^{(n)}(t)} = \int d\mathbf{R}^N \chi^{(n)}(\mathbf{R}^n) P(\mathbf{R}^N, t) = \int d\mathbf{R}^n \chi(\mathbf{R}^n) p^{(n)}(\mathbf{R}^n, t). \tag{3.2}$$

In order to obtain a kinetic equation for $p^{(n)}$ one integrates the diffusion equation

$$\partial P(\mathbf{R}^N, t)/\partial t = L(\mathbf{R}^N) P(\mathbf{R}^N, t) \tag{3.3}$$

over the coordinates of $(N-n)$ particles. With the observation that $L(\mathbf{R}^N)$ may be written as

$$L(\mathbf{R}^N) = \sum_{i=1}^{N} D_0 \nabla_i^2 + \sum_{i,j}^{N} \mathsf{D}_{ij} : \nabla_i \nabla_j \tag{3.4}$$

because of the property Eq. (2.10) one easily obtains the kinetic equation

$$\partial p^{(n)}(\mathbf{R}^n, t)/\partial t = L(R^n) p^{(n)}(\mathbf{R}^n, t) + \sum_{i=1}^{N} \sum_{j=n+1}^{N} \int d\mathbf{R}^{N-n} \mathsf{D}_{ij} : \nabla_i \nabla_j P(\mathbf{R}^N, t). \tag{3.5}$$

The second term on the right hand side of Eq. (3.5) may be shown to vanish identically by integration by parts with respect to $\mathbf{R}_j$ the coordinate of particle j and use of the property Eq. (2.10). It follows that the exact kinetic equation for the reduced n-particle distribution function is

$$\partial p^{(n)}(\mathbf{R}^n, t)/\partial t = L(\mathbf{R}^n) p(\mathbf{R}^n, t), \tag{3.6}$$

where the operator $L(\mathbf{R}^n)$ is given either by Eq. (2.3) or equivalently Eq. (3.4). The reduced kinetic equation is of the same form as the N-particle diffusion equation itself. In particular one has for the single particle reduced distribution function

$$\partial p^{(1)}(\mathbf{R}, t)/\partial t = D_0 \nabla_{\mathbf{R}}^2 p^{(1)}(\mathbf{R}, t). \tag{3.7}$$

The microscopic expression for the concentration of particles is

$$c(\mathbf{r}, t) = \sum_n \delta(\mathbf{r} - \mathbf{R}_n(t)) \tag{3.8}$$

and the nonequilibrium average of this concentration is given by

$$\bar{c}(\mathbf{r}, t) = \sum_n \int dR^N \delta(\mathbf{r} - \mathbf{R}_n) P(\mathbf{R}^N, t) = \sum_{n=1}^{N} \int d\mathbf{R}_n \delta(\mathbf{r} - \mathbf{R}_n) p^{(1)}(\mathbf{R}_n, t). \tag{3.9}$$

We obtain as an immediate consequence of the decoupling property Eq. (3.6) that the nonequilibrium concentration exactly satisfies the diffusion equation

$$\partial \bar{c}(\mathbf{r}, t)/\partial t = D_0 \nabla_{\mathbf{r}}^2 \bar{c}(\mathbf{r}, t), \tag{3.10}$$

In terms of spatial Fourier coefficients

$$\bar{c}_{\mathbf{k}}(t) = \int d\mathbf{r} \exp(-i\mathbf{k}\cdot\mathbf{r}) \bar{c}(\mathbf{r}, t) \tag{3.11}$$

one has

$$\partial \bar{c}_{\mathbf{k}}(t)/\partial t = -D_0 k^2 \bar{c}_{\mathbf{k}}(t). \tag{3.12}$$

The coherent structure factor $G(\mathbf{k}, t)$ may be expressed as

$$G(\mathbf{k}, t) = (1/N)\langle c_{\mathbf{k}}(t) c_{-\mathbf{k}}(0)\rangle \tag{3.13}$$

and it follows that the usually approximate procedure of employing the average transport equation Eq. (3.12) to evaluate the equilibrium correlation function yields the exact result Eq. (1.5).

IV. OTHER SOURCES OF CONCENTRATION DEPENDENCE

The analysis of the preceding sections is based on the adoption of the N-particle diffusion equation Eq. (1.7) as an adequate model for dilute macromolecular solutions. Two important limitations of the model must be kept in mind. First, the form of Oseen's tensor Eq. (1.9) and hence the position dependent cross diffusion coefficients $\mathbf{D}_{ij}$ are based on the assumption of an incompressible fluid. If this assumption is relaxed and one employs the form of Oseen's tensor appropriate to a compressible fluid the form of the diffusion equation will change and the cross diffusion coefficients will become "frequency dependent." This may be reflected in the light scattering spectrum by concentration dependent deviations from the Lorentzian linewidths in the high frequency wings. We are presently considering the more general situation of macromolecular diffusion in a compressible fluid and the light scattering spectrum from such a system.

The second limitation of the N-particle diffusion model adopted here is that the direct short-range forces between the solute macromolecules has not been included in Eq. (1.7). These short-range forces will give rise to conventional concentration effects that arise from solute–solute or solvent–solute interaction. When the direct short-range forces are included, the form of the N-particle diffusion equation becomes[9]

$$\partial P(\mathbf{R}^N, t)/\partial t = [L(\mathbf{R}^N, t) + \delta L(\mathbf{R}^N)]P(\mathbf{R}^N, t), \qquad (4.1)$$

where the operator $L(R^N)$ is given by Eq. (2.3) or alternatively Eq. (3.4) and the operator $\delta L(R^N)$ is given by

$$\delta L(\mathbf{R}^N) = -\beta D_0 \sum_{i=1}^{N} \nabla_{\mathbf{R}} \cdot \mathbf{F}_i - \beta \sum_{i,j=1}^{N} \nabla_{\mathbf{R}_i} \cdot \mathbf{D}_{ij} \cdot \mathbf{F}_j . \qquad (4.2)$$

In Eq. (4.2) $\mathbf{F}_i$ is the force on macromolecule "i"

$$\mathbf{F}_i = -\nabla_{\mathbf{R}_i} U(\mathbf{R}^N), \qquad (4.3)$$

where $U(\mathbf{R}^N)$ is the direct potential energy of interaction between the macromolecules which we assume is composed of the sum of pair interactions $U(R_{ij})$.

In order to investigate the concentration effects that may be expected from these direct interactions between the macromolecules we examine the equation for the reduced one-particle distribution function which according to Eqs. (3.1) and (4.1) is given by

$$\partial p^{(1)}(\mathbf{R}_1, t)/\partial t = D_0 \nabla^2_{\mathbf{R}_1} p^{(1)}(\mathbf{R}_1, t) + (N-1)\int d\mathbf{R}_2\, \delta L(1,2) p^{(2)}(\mathbf{R}_1, \mathbf{R}_2, t) \qquad (4.4)$$

with

$$\delta L(1,2) = -\beta D_0 \nabla_{\mathbf{R}_1} \cdot [\nabla_{\mathbf{R}_1} U(\mathbf{R}_{12})] + \beta \nabla_{\mathbf{R}_1} \cdot \mathbf{D}_{12} \cdot [\nabla_{\mathbf{R}_2} U(R_{12})]. \qquad (4.5)$$

This equation clearly is the first in a hierarchy that couples together all the reduced distribution functions. Thus a definitive determination of the concentration dependence of the single particle distribution function requires a detailed analysis of the density expansion of the system Eq. (4.1). This detailed analysis is not justified since the N-particle diffusion model which is adopted here as the basis for a theory of the concentration dependence of the diffusion coefficient is too primitive a model. For example the Oseen expression for $\mathbf{D}_{ij}$ is only valid for small values of (σ/R_{ij}) corresponding to large interparticle separations. Accordingly rather than undertake a complete analysis we shall make a simple physical statement of the expected low concentration form of $p^{(2)}(\mathbf{R}^2, t)$.

The two particle reduced distribution function may be expressed as

$$p^{(2)}(\mathbf{R}_1, \mathbf{R}_2, t) = W(\mathbf{R}_1, t \mid \mathbf{R}_2, t) p^{(1)}(\mathbf{R}_2, t), \qquad (4.6)$$

where w is the time dependent conditional probability of finding particle "1" at $\mathbf{R}_1$ at time t, given particle "2" is at $\mathbf{R}_2$ at time t. Our assumption is that w may be adequately approximated by its equilibrium form

$$W_{\mathrm{eq}}(\mathbf{R}_1 \mid \mathbf{R}_2) = (1/V) g(R_{12}), \qquad (4.7)$$

where $g(R_{12})$ is the equilibrium radial distribution function for the macromolecules in solution. The low concentration form of $g(R_{12})$ is $g_0(R_{12}) = \exp[-\beta u(R_{12})]$. Thus we assume that $p^{(2)}(R^2, t)$ is of the form

$$p^{(2)}(t) = (1/V)\exp[-\beta U(R_{12})] p^{(1)}(R_2, t). \qquad (4.8)$$

When this expression is substituted into Eq. (4.4) one obtains

$$\partial p^{(1)}(R_1, t)/\partial t = D_0 \nabla^2_{\mathbf{R}} p^{(1)} + c \int d\mathbf{R}_2\, \delta L(1,2) g_0(R_{12}) p^{(1)}(\mathbf{R}_2, t), \qquad (4.9)$$

where $c = (N-1)/V$ is the concentration of macromolecules. This equation may be solved in terms of spatial Fourier transforms of the one-particle distribution function $\hat{p}^{(1)}(\mathbf{k}, t)$. If one takes the Fourier transform of Eq. (4.9) one obtains

$$\partial \hat{p}^{(1)}(\mathbf{k}, t)/\partial t = [-\mathbf{k}^2 D_0 - c D_1(\mathbf{k})]\, \hat{p}^{(1)}(\mathbf{k}, t), \qquad (4.10)$$

where the first concentration correction to the diffusion coefficient is given by

$$D_1(\mathbf{k}) = \int d\mathbf{R} \exp[i\mathbf{k} \cdot \mathbf{R}]$$

$$[D_0\nabla_{\mathbf{R}} - \nabla_{\mathbf{R}}\cdot \mathbf{D}(\mathbf{R})]\cdot \nabla_{\mathbf{R}}\{\exp[-\beta U(R_{12})] - 1\}. \tag{4.11}$$

For hard spheres of diameter σ, the k-dependent diffusion correction can be evaluated exactly. The result is

$$D_1(\mathbf{k}) = \pi D_0\sigma\{-\cos(k\sigma) + [\sin(k\sigma)/k\sigma]\}\quad, \tag{4.12}$$

where use has been made of Stokes' law $D_0 = [kT/3\pi\eta_0\sigma]$.

According to Eq. (3.9) the nonequilibrium average of the local concentration for a system where each particle is equivalent, is given by

$$\bar{c}(t) = N\int d\mathbf{R}_1\,\delta(r - R_1)\,p^{(1)}(\mathbf{R}_1, t). \tag{4.13}$$

It follows from Eqs. (4.13) and (4.10) that the diffusion equation, in terms of spatial Fourier coefficients satisfies the transport equation

$$\partial\bar{c}_{\mathbf{k}}/\partial t = [-D_0k^2 - cD_1(k)]\,\bar{c}_{\mathbf{k}}(t). \tag{4.14}$$

If this macroscopic transport equation is employed to compute the light scattering spectrum according to Eqs. (1.1) and (3.13) one obtains a Lorentzian line shape

$$I(\mathbf{k}, \omega) = G(\mathbf{k}, 0)\{\Gamma(\mathbf{k})/[\omega^2 + (\Gamma(k))^2]\} \tag{4.15}$$

with a width $\Gamma(\mathbf{k}) = D_0k^2 + cD_1(\mathbf{k})$. Thus when concentration effects are taken into account, the width of the spectrum is no longer proportional to k^2.

For small values of $(k\sigma)$, $D_1(\mathbf{k})$ may be expanded and to order $(k\sigma)^2$ one obtains the ordinary diffusion equation

$$\partial\bar{c}_{\mathbf{k}}/\partial t = -D_{\mathrm{eff}}k^2\bar{c}_{\mathbf{k}} \tag{4.16}$$

with an effective, concentration dependent, diffusion constant given by

$$D_{\mathrm{eff}} = D_0(1 + c\pi\sigma^3/3). \tag{4.17}$$

In terms of the volume fraction $\phi = (4\pi\sigma^3/24)c$ the effective diffusion constant is $D_{\mathrm{eff}} = D_0(1 + 2\phi)$. The coefficient of the first concentration correction to the diffusion coefficient K is closely related to the first concentration correction to the friction coefficient,[17] sedimentation coefficient,[17,18] and viscosity[18] of dilute macromolecular solutions,

$$D = D_0(1 + k\phi). \tag{4.18}$$

Our result $K = 2$ should be compared with the results of more detailed microscopic theories: Burgers[19] obtained $K = 1.143$; Fixman[17] obtained $K = 0.843$, although this result has been criticized by Kapustin and Khazanovich.[20] The experimental results of Cheng and Scharchmann[21,18] suggest $K = 2.94$. Related theoretical work has been presented by Saito,[22] Yamakawa,[23] and Rotne and Prager.[24]

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