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Generalized Stokes-Einstein equation for spherical particle suspensions

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The cooperative diffusion coefficient D_c for spherical particle suspensions is calculated using a "mode-coupling" method which extends previous calculations of D_c for critical fluids and semidilute polymer solutions. The renormalization of the viscosity in the velocity-velocity correlation function from the solvent to the suspension viscosity leads to a generalized Stokes-Einstein (SE) equation in which the suspension viscosity η replaces the solvent viscosity η_0 and the correlation length ξ (related to the osmotic compressibility) replaces the sphere radius R at nonvanishing suspension concentrations. Insertion of the leading order hard sphere virial expansions for η and the osmotic compressibility into our generalized SE equation gives a virial expansion for D_c which is consistent with theoretical estimates obtained by alternative methods. These leading order virial expansions are also consistent with experiments on model ("hard sphere") suspensions. Results are given for the virial expansion of spherical liquid droplets interacting via a contact attractive interaction. Further experiments are required to test the generalized SE equation at higher suspension concentrations.

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I. INTRODUCTION

Recent activity in the hydrodynamics of suspensions has been stimulated by the development of inelastic scattering techniques which allow routine estimates of the cooperative diffusion coefficient and other suspension properties [1]. Dynamic light scattering measurements complement the traditional tracer diffusion, sedimentation, and viscosity studies of suspensions and a comparison of these measurements on carefully prepared model suspensions has allowed a check on the internal consistency of available hydrodynamic theory for hard sphere suspensions [2,3]. Good agreement between theory and experiment has been obtained at low concentrations where the leading order virial expansions of transport properties should be sufficient [2,3]. Further theoretical development has been slow because of the complications caused by many-body excluded volume and hydrodynamic interactions and existing theories are inadequate for describing suspensions at intermediate and high concentrations [4].

The present paper develops a nonperturbative calculation of the cooperative diffusion coefficient D_c of spherical Brownian particle suspensions. We obtain a simple relation between D_c, the suspension viscosity η, and the osmotic compressibility, which can be represented as

$$D_c = k_B T / 6\pi\eta\xi \ , \qquad (1.1)$$

where $k_B T$ denotes thermal energy and ξ is a "correlation length." In the dilute limit (1.1) reduces to Einstein's equation [5] and ξ thus reduces to the particle radius R. We term Eq. (1.1) a "generalized Stokes-Einstein (SE) equation" since it is an obvious extension of the infinite dilution result [5,6].

An explicit determination of D_c is obtained through a "sum rule" relating ξ to the osmotic compressibility (see Sec. II). This procedure serves to specify D_c in terms of long wavelength suspension properties (η, Π), where Π is the osmotic pressure. From this sum rule we find an alternative expression for D_c for spherical particle suspensions

$$D_c / D_{c,0} = (\eta/\eta_0)^{-1} [(\partial\Pi/\partial\phi)/(\partial\Pi/\partial\phi)_0]^{1/2} \ , \qquad (1.2)$$

where the 0 subscript denotes the dilute solution limit and ϕ is the volume fraction of suspended particles. Equation (1.2) indicates that there are two competing factors which determine the concentration dependence of D_c for hard sphere suspensions. The "fluidity" $(\eta/\eta_0)^{-1}$ factor in Eq. (1.2) *decreases* with increasing concentration, while the osmotic compressibility factor in Eq. (1.2) *increases* with increasing concentration. In the absence of attractive interparticle interactions the osmotic contribution predominates so that D_c *increases* with concentration. Equation (1.2) is a useful representation of D_c since there are many known results (exact and approximate) for Π and η for spherical particle suspensions which can be inserted into Eq. (1.2) to estimate D_c. As a nontrivial example we consider a suspension of spherical liquid droplets, having a viscosity different from the solvent, interacting via a contact attractive interaction. The ratio of the droplet to the solvent viscosity, the "relative fluidity," z_η, and the attractive interaction, as measured by the dimensionless second osmotic virial coefficient $\bar{\psi}$, are found to have a large effect on D_c for liquid droplets. The predicted variation of the leading virial coefficient of D_c for "sticky liquid droplets" is found to be comparable to measurements on flexible polymer solutions.

In Sec. III we derive the generalized SE equation (1.1) using methods that extend the mode-coupling calculations of Ferrell [7] and Brochard and DeGennes [8] for D_c of critical fluids and semidilute polymer solutions, respectively. Although our calculations share a common conceptual basis, relating to the consideration of the coupling of solvent velocity and solute concentration fluctuations, our implementations of these ideas is rather distinct from previous calculations. The angular preaveraging approximation, which is conventionally employed in mode-coupling calculations [7–9], is examined and *avoided* in the present calculations, for example. Section IV compares the "generalized Stokes-Einstein equation" Eq. (1.2) to previous virial expansion calculations for D_c and to experimental measurements of D_c at low concentrations. Favorable agreement is obtained in these comparisons. In Sec. IV we also consider a nonperturbative "generalized Svedberg equation" [10] relating D_c to the sedimentation coefficient Λ and the osmotic compressibility. The virial expansion of Λ is then obtained for hard spheres and interacting liquid droplets by combining this equation with Eq. (1.2). Some technical details of our calculations are given in the Appendices.

II. DYNAMIC STRUCTURE FACTOR AND THE COOPERATIVE DIFFUSION COEFFICIENT D_c

A. General results

Consider a suspension of N spherical Brownian particles in a large container of volume V. Local fluctuations in the microscopic density arising from thermal fluctuations or from imposed perturbations of the suspension relax according to the diffusion equation where D_c defines the cooperative diffusion coefficient. Since D_c reflects both the viscosity of the suspension and the interparticle interaction through the osmotic compressibility we begin our derivation of D_c by defining the microscopic particle density and the associated density-density correlator, the dynamic structure factor.

The microscopic particle density $n(\mathbf{r},t)$ is defined in the usual way,

$$n(\mathbf{r},t)=\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i(t)) , \tag{2.1}$$

where $\mathbf{r}_i$ denotes the center of mass position for the ith particle. If we denote the volume average of a suspension property P by

$$\langle P\rangle_v=\frac{1}{V}\int d\mathbf{r}\,P(\mathbf{r}) , \tag{2.2}$$

then the average particle density equals

$$N/V=\langle n(\mathbf{r},t)\rangle_v=\phi/(4\pi R^3/3)\equiv\bar{n} , \tag{2.3}$$

where ϕ is the particle volume fraction. Consideration of a suspension of spheres having a distribution of sizes ("polydisperse") requires a generalization of the density definition

$$n(\mathbf{r},t)=\sum_{j}\sum_{i=1}^{N_j}\delta(\mathbf{r}-\mathbf{r}_{ij}(t)) , \tag{2.4}$$

where $\sum_j n_j=N$ and n_j is the number of spheres having radius R_j. The conclusions of the development below, however, are unchanged from the simpler case of a solution of monodisperse ($R_j=R$) spheres and, for the sake of notational simplicity, we confine our development to the monodisperse case. We combine Eqs. (2.1) and (2.3) to define the density-density correlator

$$S(\mathbf{R},\tau)=\langle[n(\mathbf{r},t)-\bar{n}][n(\mathbf{r}',t')-\bar{n}]\rangle_v , \tag{2.5a}$$

where

$$\mathbf{R}=\mathbf{r}-\mathbf{r}',\quad \tau=|t-t'| . \tag{2.5b}$$

The variables $\mathbf{R}$ and τ are appropriate for suspensions which are homogeneous on average in space and time. The Fourier transform of Eq. (2.5a) defines the dynamic structure factor

$$S(\mathbf{k},\tau)=\left\langle\sum_{i,j}e^{i\mathbf{k}\cdot[\mathbf{r}_i(\tau)-\mathbf{r}_j(0)]}\right\rangle_v ,\quad k\neq0,\quad k=|\mathbf{k}| . \tag{2.6}$$

For $k=0$, Eq. (2.6) needs to be replaced by Eq. (A4) and this point is further discussed below and in Appendix A.

It is also convenient to perform a Fourier transform of $S(\mathbf{k},\tau)$ in time,

$$S(\mathbf{k},\omega)=\int_{-\infty}^{\infty}dt\,e^{i\omega\tau}S(\mathbf{k},\tau) , \tag{2.7}$$

which allows us to obtain a direct connection between the initial decay rate $\Gamma_{\mathbf{k}}^{(0)}$ of the dynamic structure factor [11] through the cumulant relation

$$\Gamma_{\mathbf{k}}^{(0)}=-\frac{\partial}{\partial\tau}\ln\left[\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{i\omega\tau}S(\mathbf{k},\omega)\right]_{\tau\to0^+} . \tag{2.8}$$

Some illustrative calculations, related to $\Gamma_{\mathbf{k}}^{(0)}$ and helpful for the development below, are given in Appendix A. If we define the fluctuation of the number density $\rho(\mathbf{r},t)$ as

$$\rho(\mathbf{r},t)=n(\mathbf{r},t)-\bar{n} , \tag{2.9a}$$

then $\Gamma_{\mathbf{k}}^{(0)}$ can be rewritten, using Eqs. (2.5)–(2.8), in the form

$$\Gamma_{\mathbf{k}}^{(0)}=-\left[\int d\mathbf{r}'\int d\mathbf{r}\,e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\frac{\partial}{\partial t}\times\langle\rho(\mathbf{r},t)\rho(\mathbf{r}',t')\rangle_v/S(\mathbf{k},0)\right]_{\tau\to0^+} , \tag{2.9b}$$

where $S(\mathbf{k},0)$ is given by Eq. (A4). We next focus on the numerator term in (2.9b).

Assuming that the continuity equation

$$\frac{\partial}{\partial t}n(\mathbf{r},t)+\mathrm{div}\,\mathbf{j}=0 \tag{2.10}$$

holds for both macroscopic and microscopic densities we can define [12] a current $\mathbf{j}$

$$\mathbf{j}=\sum_{i=1}^{N}v_i(t)\delta(\mathbf{r}-\mathbf{r}_i(t)) , \tag{2.11}$$

where $v_i(t)$ is the velocity of the ith particle. Equation (2.11) does not explicitly account for the fact that our particles are immersed in a fluid, however. Thus, we let $v_f(\mathbf{r},t)$ be the fluid velocity and $v_i(t)$ is taken to be the velocity of the particle center of mass $v_i(t)=d\mathbf{r}_i(t)/dt$. Imposition of the nonslip boundary condition then gives rise to the constraint

$$v_f(\mathbf{r},t)=v_i(t) \ . \tag{2.12}$$

Obviously, this result should be modified to account for the finite size of the Brownian spheres. This complication is ignored in the present treatment so that some inaccuracy can be expected at high volume fractions where packing effects become important ($\phi>0.4$). Neglect of the finite particle size should be appropriate for situations in which the spontaneous velocity fluctuations occur at scales larger than the size of the Brownian particles.

By Fourier transforming Eq. (2.10) we obtain

$$\frac{\partial}{\partial t}n_{\mathbf{k}}(t)+i\mathbf{k}\cdot\mathbf{j}(\mathbf{k},t)=0 \ , \tag{2.13}$$

where

$$\mathbf{j}(\mathbf{k},t)=\frac{1}{(2\pi)^3}\int d\mathbf{k}'v(\mathbf{k}',t)n(\mathbf{k}-\mathbf{k}',t) \ . \tag{2.14}$$

with the help of Eqs. (2.12)–(2.14) we can write Eq. (2.9) as

$$S(\mathbf{k},0)\Gamma_{\mathbf{k}}^{(0)}=\int_0^t dt''\mathbf{k}\cdot\langle\, \mathbf{j}(\mathbf{k},t)\mathbf{j}(-\mathbf{k},t'')\rangle\cdot\mathbf{k}\Big|_{\tau\to 0^+} \ . \tag{2.15}$$

Alternatively, we have

$$S(\mathbf{k},0)\Gamma_{\mathbf{k}}^{(0)}=\frac{1}{(2\pi)^6}\int_0^t dt''\int d\mathbf{k}'\int d\mathbf{k}''\langle\,\mathbf{k}\cdot v(\mathbf{k}',t)v(\mathbf{k}-\mathbf{k}'',t)\cdot\mathbf{k}n(\mathbf{k}-\mathbf{k}',t)n(-\mathbf{k}',t'')\rangle\Bigg|_{\tau\to 0^+} \ , \tag{2.16}$$

where $\langle\cdots\rangle$ denotes a "thermal average," which is assumed to be equivalent to the volume average in Eq. (2.2).

The "preaveraging" approximation (commonly employed in the dynamics of critical fluids [7–9] and in polymer solution dynamics [11]) may be introduced by "breaking" the average in Eq. (2.16),

$$\mathbf{k}\cdot\langle\, v(\mathbf{k}',t)v(\mathbf{k}-\mathbf{k}',t'')\rangle\cdot\mathbf{k}\langle\, n(\mathbf{k}-\mathbf{k}',t)n(-\mathbf{k}'',t'')\rangle \ . \tag{2.17}$$

Thus the decoupled current-current correlator $\langle\,\mathbf{jj}\,\rangle$ admits an easy calculation if we employ the velocity-velocity correlator for fluids given by

$$\langle\, v_{ik}(t)v_{jk'}(t')\rangle$$
$$=(2\pi)^3\delta(\mathbf{k}+\mathbf{k}')\left[\delta_{ij}-\frac{k_ik_j}{k^2}\right]\frac{2k_BT}{\eta k^2}\delta(t-t') \ . \tag{2.18}$$

We note that the decoupling approximation Eq. (2.17) requires that the viscosity in (2.18) is the *suspension* viscosity rather than the solvent viscosity at nonvanishing particle concentrations (see below). The correlator in Eq. (2.18) can be obtained in a standard way [13] from the low Reynolds number approximation to the Navier-Stokes equation

$$\frac{\partial}{\partial t}v(\mathbf{r},t)=-\frac{1}{\rho}\nabla P+\tilde{\Gamma}\nabla^2 v(\mathbf{r},t) \ , \tag{2.19}$$

where ρ is the solvent density, P is the hydrodynamic pressure, and $\tilde{\Gamma}=\eta/\rho$ is the kinematic viscosity. Adding to Eq. (2.19) the randomly fluctuating forces and using the incompressibility condition

$$\operatorname{div} v=0 \tag{2.20}$$

produces an explicit expression for the velocity correlator

$$\langle\, v_{ik}(t)v_{jk'}(t')\rangle=(2\pi)^3\delta(\mathbf{k}+\mathbf{k}')\left[\delta_{ij}-\frac{k_ik_j}{k^2}\right]$$
$$\times\frac{2k_BT}{\rho\Gamma}\frac{\Gamma}{2}e^{-\Gamma|t-t'|} \ , \tag{2.21}$$

where $\Gamma=\tilde{\Gamma}k^2$. Finally, taking the limit $\Gamma\to\infty$ gives the approximation

$$\lim_{\Gamma\to\infty}\frac{\Gamma}{2}e^{-\Gamma|t-t'|}\simeq\delta(t-t') \ , \tag{2.22}$$

leading to Eq. (2.18). The approximation Eq. (2.22) is very helpful because it allows us to replace the correlator $\langle\, n(\mathbf{k}-\mathbf{k}',t)n(-k'',t'')\rangle$ by an equal time correlator. Using the auxiliary result of Eq. (A4), we then obtain the nonperturbative relation

$$\langle\, n(\mathbf{k}-\mathbf{k}',t)n(-\mathbf{k}'',t)\rangle=\bar{n}\left[\frac{\partial\bar{n}}{\partial\Pi}\right]_T k_BT \ . \tag{2.23}$$

Note that Eq. (2.23) is independent of k in view of Eq. (A4).

B. Correlation length and δ-function regularization

At low suspension concentrations the density correlation function falls off sharply and in the infinite dilution limit a δ-function decay is formally obtained [see (A3)]. More generally, the decay of the density correlation function reflects the interparticle interactions at finite particle concentration. Following Landau and Lifshitz [13(a)] and more recently Ferrell [7], we introduce a regularization of the δ function to account for the finite decay range ("correlation length") of the density correlation function

$$\delta(|\mathbf{R}|)=\lim_{\xi\to 0^+}\frac{1}{4\pi\xi^2}\frac{1}{|\mathbf{R}|}\exp\left[-\frac{|\mathbf{R}|}{\xi}\right] \ . \tag{2.24}$$

We then replace the δ function in our formalism by this regularization and determine ξ self-consistently through its calculated relation to other properties. Given the formal nature of this procedure, it is important to check the consistency of this method with exact results for hard sphere suspensions in dilute solutions. This consistency check is considered below.

First, we observe that $S(\mathbf{k}=0,0)$ is related to the osmotic compressibility $(\partial\Pi/\partial\bar{n})_T$ via the sum rule [13(a)]

$$k_B T\bar{n}\left[\frac{\partial\bar{n}}{\partial\Pi}\right]_T=\int dR\, S(\mathbf{R},0)\equiv S(\mathbf{k}=0,0)\ . \tag{2.25}$$

Substitutions of Eq. (A3) into the right-hand side of Eq. (2.25) with the δ function regularized according to Eq. (2.24) produces the identity due to the relation $1=\int_0^\infty dx\, xe^{-x}$. The Fourier-transformed and regularized expression for $S(\mathbf{R},0)$ can now be written as

$$\langle n(\mathbf{k}-\mathbf{k}',t)n(-\mathbf{k}'',t)\rangle$$

$$=(2n)^3\delta(\mathbf{k}-\mathbf{k}'-\mathbf{k}'')\frac{\bar{n}\left[\dfrac{\partial\bar{n}}{\partial\Pi}\right]_T k_B T}{(k'')^2+\xi^{-2}}\frac{1}{\xi^2} \tag{2.26}$$

instead of Eq. (2.23). The combined use of Eqs. (2.16)–(2.18) and (2.26) produces

$$\Gamma_{\mathbf{k}}^{(0)}=\frac{2k_B T}{g(\mathbf{k})}\int\frac{d\mathbf{g}}{(2\pi)^3}\mathbf{k}^T\cdot H(\mathbf{q})\cdot\mathbf{k}g(\mathbf{k}+\mathbf{q})\ , \tag{2.27}$$

where $g(\mathbf{k})=(k^2+\xi^{-2})^{-1}$ and the Fourier transformed Oseen tensor [11] $\underline{H}(\mathbf{k})$ is defined by

$$H_{ij}(\mathbf{k})=\left[\delta_{ij}-\frac{k_i k_j}{k^2}\right]\frac{1}{\eta k^2}(2\pi)^3\delta(\mathbf{k}+\mathbf{k}')\ , \tag{2.28}$$

where we have employed Eqs. (2.21) and (2.22). [Again we emphasize that the viscosity in Eq. (2.28) is the suspension viscosity rather than the solvent viscosity.] It is also important that although Eq. (2.27) was derived previously [7,9,11], the present derivation allows us to develop our formalism *beyond* the preaveraging approximation. This generalization is developed below.

C. Generalized Stokes-Einstein relation

The computation of $\Gamma_{\mathbf{k}}^{(0)}$ is actually rather cumbersome [7,9] even within the preaveraging approximation Eq. (2.27). The situation is simpler if only the calculation of the diffusion coefficient is required. Using Eqs. (A7) and (2.15) we obtain

$$\begin{aligned}D_c&=\frac{\partial}{\partial k^2}\Gamma_{\mathbf{k}}^{(0)}|_{\mathbf{k}=0}\\&=\tfrac{1}{6}\sum_{i=1}^{3}\frac{\partial^2}{\partial k_i^2}\Gamma_{\mathbf{k}}^{(0)}|_{\mathbf{k}=0}\\&=\tfrac{1}{6}\int_0^t dt''\langle\mathbf{j}(0,t)\cdot\mathbf{j}(0,t'')\rangle|_{\tau\to0^+,\mathbf{k}=0}/S(0,0)\ .\end{aligned} \tag{2.29}$$

From the theory of Brownian motion [12] in the infinite dilution limit we also have the definition

$$\begin{aligned}D&\equiv\lim_{t\to\infty}\frac{1}{6}\frac{d}{dt}\langle[\mathbf{r}(t)-\mathbf{r}(0)]^2\rangle\\&=\lim_{t\to\infty}\frac{1}{6}\int_0^t d\tau'\langle v(t)\cdot v(\tau')\rangle\ .\end{aligned} \tag{2.30}$$

In the case of a nonslip boundary condition [see Eq. (2.12)] we can simply replace the particle velocities v by those for the fluid. Consistency between Eqs. (2.29) and (2.30) requires

$$\langle v(\tau)\cdot v(\tau')\rangle=\langle\mathbf{j}(0,\tau)\cdot\mathbf{j}(0,\tau')\rangle/S(0,0)\ . \tag{2.31}$$

This result is independent of the preaveraging approximation and is based only on the nonslip boundary condition prescribed by Eq. (2.12). The imposition of the nonslip boundary condition is nontrivial (as it is explained in the Appendix B) and is related to the assumption of the incompressibility of the fluid given by Eq. (2.20).

Equation (2.12) could also be used as a starting point for a field-theoretic approach to concentrated suspensions of hard spheres, polymers, or even semiflexible membranes. The mathematical framework for such a field theory was suggested in the work of Lund and Regge [14(a)] and others [14(b),14(c)] in different physical contexts. We shall develop this formalism specifically for the hydrodynamics of sphere suspensions in a separate work. The important qualitative aspect of this formulation for the present work lies in the insight it gives into the renormalization of the viscosity in the velocity-velocity correlator [e.g., Eq. (2.18)]. The field theory leads to a description of suspension hydrodynamics in which the suspension particles are represented by a scalar field interacting with a field representing the hydrodynamic interaction fluctuations ("photon field" in an analogous electrodynamic problem). The interaction between these fields is controlled by a coupling parameter involving the suspension viscosity. The renormalization of the coupling constant caused by the field interactions corresponds to the viscosity renormalization adopted rather formally in Eq. (2.18). Moreover, the sum rule Eq. (1.2) serves to fix the renormalization scheme in the field theory so that the present formulation is complementary to the field-theoretic approach.

To understand better the significance of Eq. (2.31), we first consider the infinite dilution limit. Using Eq. (2.18) and Fourier transforming it to real space we obtain

$$\langle v_i(\mathbf{r},\tau)\cdot v_j(\mathbf{r}',\tau')\rangle=\frac{k_B T}{4\pi\eta}\frac{1}{|\mathbf{r}-\mathbf{r}'|}(\delta_{ij}+n_i n_j)\delta(\tau-\tau')\ , \tag{2.32}$$

where $n_i=(r-r')_i/|\mathbf{r}-\mathbf{r}'|$. In view of Eq. (2.31), we take the trace of both sides of Eq. (2.32) to obtain

$$\langle v(\mathbf{r},\tau)\cdot v(\mathbf{r}',\tau')\rangle=\frac{k_B T}{\pi\eta}\frac{1}{|\mathbf{r}-\mathbf{r}'|}\delta(\tau-\tau')\ . \tag{2.33}$$

This expression should now be properly averaged to eliminate the explicit r dependence. By analogy with Eq.

(2.2), we then introduce the surface average (sphere case only) as

$$\langle \cdots \rangle_S = \left[\frac{1}{4\pi} \right]^2 \int d\Omega \int d\Omega' \cdots \ , \tag{2.34}$$

where

$$\int d\Omega = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \ .$$

Combining Eqs. (2.33) and (2.34) gives

$$\langle v(\tau)\cdot v(\tau') \rangle = \frac{k_B T}{\pi\eta} \delta(\tau-\tau') \left\langle \frac{1}{|\mathbf{r}(\Omega)-\mathbf{r}(\Omega')|} \right\rangle_S \ . \tag{2.35}$$

Next, using the fact that

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{|\mathbf{r}'|^l}{|\mathbf{r}|^{l+1}} \frac{4\pi}{2l+1} Y_{lm}^*(\Omega') Y_{lm}(\Omega) \ , \quad |\mathbf{r}| > |\mathbf{r}'| \tag{2.36}$$

and combining this result with Eqs. (2.34) and (2.35) produces the simple result

$$\langle v(\tau)\cdot v(\tau') \rangle = \frac{k_B T}{\pi\eta R} \delta(\tau-\tau') \ , \tag{2.37}$$

where R is the hydrodynamic radius of the Brownian sphere. Finally, substituting Eq. (2.37) into Eq. (2.30) recovers the familiar Stokes-Einstein result

$$D_{c,0} = \frac{k_B T}{6\pi\eta_0 R} \ , \tag{2.38}$$

where the superscript 0 denotes the infinite dilution limit. η_0 is the solvent viscosity. Notice that this result was obtained without the preaveraging approximation and is based only on the nonslip boundary condition Eq. (2.12). The more familiar method of obtaining Eq. (2.38) employs a preaveraging approximation [7]. In this case it is convenient to rewrite the right-hand side of Eq. (2.31) as

$$\begin{aligned} \langle \mathbf{j}(\mathbf{0},\tau)\cdot\mathbf{j}(\mathbf{0},\tau') \rangle / S(\mathbf{0},0) &= \int d\mathbf{r}\, \delta(\tau-\tau') \operatorname{Tr} H_{ij}(\mathbf{r}) \\ &\quad \times \langle \rho(\mathbf{r})\rho(\mathbf{0}) \rangle \Big/ \int d\mathbf{r} \langle \rho(\mathbf{r})\rho(\mathbf{0}) \rangle \ , \end{aligned} \tag{2.39}$$

where $\delta(\tau-\tau') \operatorname{Tr} H_{ij}(\mathbf{r})$ is given by the right-hand side of Eq. (2.33) and the density-density correlator $\langle \rho(\mathbf{r})\rho(\mathbf{0}) \rangle$ is given by Eq. (A3), where the δ function is regularized according to Eq. (2.24). A simple calculation combining the right-hand side of Eqs. (2.39) and (2.31) with Eq. (2.30) yields the generalized Stokes-Einstein equation Eq. (1.1) so that at least in the infinite dilution limit, $R=\xi$. At the same time, the sum rule Eq. (2.25) implies [13(a)]

$$S(\mathbf{0},0) \sim \xi_s^2 \ , \tag{2.40}$$

where ξ_s is the static correlation length and the exponent 2 is exact at the level of mean-field theory. By using Eqs. (2.38) and (2.40) and invoking the complementary and continuity arguments, we identify the correlation length ξ in Eq. (1.1) with ξ_s (up to a constant factor). Thus we obtain a dimensionless expression for D_c at finite concentrations,

$$\frac{D_c}{D_{c,0}} = \frac{(\xi_s/\xi_0)^{-1}}{(\eta/\eta_0)} \ , \tag{2.41}$$

where $\xi_0 = R$. Alternatively, in view of Eq. (2.40), we may express D_c in terms of the suspension relative viscosity η/η_0 and the relative osmotic compressibility,

$$\frac{D_c}{D_{c,0}} = \frac{1}{(\eta/\eta_0)} \left[\frac{S(\mathbf{0},0)}{S_0(\mathbf{0},0)} \right]^{-1/2} \ , \tag{2.42}$$

which can also be written in the form of Eq. (1.2) using Eqs. (2.25) and (2.40). In Appendix C we outline another derivation of Eq. (2.42) that does not involve the preaveraging approximation Eq. (2.39). It is based on a direct consideration of the left-hand side of Eq. (2.31) at finite concentrations. The present paper focuses on the long wavelength property D_c and thus does not consider the wave-vector dependency of $\Gamma_{\mathbf{k}}^{(0)}$ in a fashion similar to previous treatments of critical fluids [7,9] and polymer solutions [8,11]. If necessary, such dependence can be easily recovered from our discussion. In the next section we illustrate the validity of the generalized SE equation Eq. (2.42), by using available theoretical estimates and experimental data for suspensions at low concentrations.

III. COMPARISON OF THE GENERALIZED SE EQUATION WITH THEORY AND EXPERIMENT

The expansion for D_c in terms of volume fraction can be readily determined from Eq. (2.42) and well known virial expansions for the osmotic pressure Π and the viscosity η (we call all such volume fraction expansions "virial" expansions). Π has the expansion [13(b)]

$$\Pi v / k_B T = \phi[1 + 4\phi + O(\phi^2)] \tag{3.1}$$

and from this result we obtain, in leading order,

$$\frac{\partial \Pi}{\partial \bar{n}} = \frac{\partial \Pi}{\partial \phi} \frac{\partial \phi}{\partial \bar{n}} = k_B T[1 + 8\phi + O(\phi^2)] \ . \tag{3.2}$$

(Experiments by Newman *et al.* [2] indicate a leading osmotic virial 7.6±3.9 for a model suspension of compact DNA particles.) From Eq. (3.2) the compressibility-dependent contribution to D_c is given by

$$\begin{aligned} \left[\frac{S(\mathbf{0},0)}{S_0(\mathbf{0},0)} \right]^{-1/2} &= [1 + 8\phi + O(\phi^2)]^{1/2} \\ &= 1 + 4\phi + O(\phi^2) \ . \end{aligned} \tag{3.3}$$

The Einstein expansion for the velocity equals [6]

$$\eta/\eta_0 = 1 + 5\phi/2 + O(\phi^2) \ , \tag{3.4}$$

which compares well with dilute solution measurements [15]. Inserting Eqs. (3.3) and (3.4) into Eq. (2.42) yields

$$D_c/D_{c,0} = 1 + 3\phi/2 + O(\phi^2) \ . \tag{3.5}$$

The best theoretical estimates of the leading order D_c virial for repulsive hard spheres by Felderhof [16] and Bachelor [17] equal 1.56 and 1.45, respectively. Experimental data [2,3] on model suspensions also agree with Eqs. (3.3)–(3.5) to within experimental uncertainty. For example, Newman *et al.* [2] and Kops-Werkhoven and

Fignaut, and Russell [3] obtain 1.2±0.4 and 1.3±0.2, respectively.

We can also obtain the virial expansion of D_c for liquid droplets having viscosity η_{droplet} suspended in a solution of viscosity η_0 based on Taylor's expression [18] for the viscosity of dilute spherical droplet suspensions and Eq. (2.42),

$$D_c/D_{c,0}=1+k_D\phi+O(\phi^2)\ , \tag{3.6a}$$

$$k_D=3[1-\tfrac{1}{2}z_\eta/(1+z_\eta)],\quad z_\eta\equiv\eta_{\text{droplet}}/\eta_0\ , \tag{3.6b}$$

where z_η is the "relative fluidity." The friction on a liquid droplet of radius R at infinite dilution f_{droplet} is also a function of z_η [19,20],

$$f_{\text{droplet}}=4\pi\eta_0 R[1+\tfrac{1}{2}z_\eta/(1+z_\eta)]\ . \tag{3.6c}$$

Using Eq. (3.6) we find the apparently new result that the virial coefficient k_D for liquid drops is larger than that for hard spheres for any finite z_η. Felderhof [16] obtained the related result $k_D=3.5$ for spheres having a "slip" boundary condition which is comparable to Eq. (3.6a) for a "bubble" where $k_D(z_\eta\to 0+)=3$. The leading order η virial for a bubble is identical to a sphere having a slip boundary condition [18,20], so that a similar magnitude for k_D in the case of bubbles or slipping spheres should be expected. Our own calculations are limited, however, to the nonslip ("stick") boundary conditions for reasons explained in the Appendix B.

Having in mind applications to polymer solutions, it is also possible to introduce the attractive interparticle interaction into k_D through the osmotic compressibility. Following Batchelor [21(a)] we can incorporate an attractive ("sticky") contact interaction between the spheres so that for "sticky liquid droplets" we obtain

$$k_D=4\bar{\psi}-1-\tfrac{3}{2}z_\eta/(1+z_\eta)\ , \tag{3.7a}$$

where $\bar{\psi}$ is a dimensionless second osmotic virial coefficient normalized to vanish at the "theta point" ($T=\Theta$) and to equal 1 in a "good solvent" ($T\gg\Theta$). We compare Eq. (3.7a) to the estimate of k_D for hard spheres with a sticky interaction obtained using Batchelor's direct hydrodynamic method [21(c)],

$$k_D=4.48\bar{\psi}-3.03\ \text{(sticky hard spheres)}\ , \tag{3.7b}$$

which is quite similar to our estimate for sticky hard spheres from Eq. (3.7a),

$$k_D=4\bar{\psi}-\tfrac{5}{2},\quad z_\eta\to\infty\ . \tag{3.7c}$$

Equation (3.7a) further predicts that $k_D=-[\eta]$ at the Θ point ($\bar{\psi}=0$) for both hard spheres and liquid droplets. ($[\eta]$ is defined in Eq. (3.8).) Hard sphere suspensions and polymer solution are commonly observed to have k_D values which can be either positive or negative [21(c),22].

Douglas and Freed [23] introduced a simple model of polymers in dilute solutions in which the polymer is considered to be described by a droplet having a radius equal the chain radius of gyration and a fluidity similar to the surrounding solvent $z_\eta\approx 1$. The predicted variation of k_D from (3.7a) for such sticky liquid droplets equals

$$k_D\approx 4\bar{\psi}-\tfrac{7}{4},\quad z_\eta\approx 1\ . \tag{3.7d}$$

As in the case of hard spheres the diffusion coefficient, virial k_D for these droplets, is predicted to change sign for temperatures intermediate between Θ temperature and the good solvent regime. This variation is well established and universal for flexible polymer solutions and accurate data [22] indicate that k_D for polymer solutions monotonically increases with $\bar{\psi}$ from about -2 under Θ conditions to about 2 in good solvents. The corresponding range of k_D values for sticky droplets $-\frac{7}{4}<k_D<\frac{9}{4}$, predicted by (3.7d), is rather consistent with the polymer data. Theoretical estimates of k_D for polymer solutions are also consistent. For example, Freed [23(b)] obtained $k_D=-[\eta]$ for a dilute solution of flexible polymers under Θ conditions. Our main point for the present discussion is that qualitative observations on D_c for interacting particles can be rather well understood from the generalized SE equation (2.42).

It is also interesting to consider the second-order virial expansion for D_c. In this case we begin with viscosity expansion

$$\eta/\eta_0=1+[\eta]\phi+k_H([\eta]\phi)^2+O(\phi^3)\ , \tag{3.8}$$

where $[\eta]=\frac{5}{2}$ for hard spheres. Using the reasonable estimate $k_H=0.7$ from Refs. [15,24] and the well known [14] virial expansion for hard spheres

$$(S/S_0)^{-1/2}=1+4\phi+7\phi^2+O(\phi^3) \tag{3.9}$$

and then inserting Eqs. (3.8) and (3.9) into Eq. (2.42), we obtain the second-order expansion for D_c,

$$D_c/D_{c,0}=1+3\phi/2-7.375\phi^2+O(\phi^3)\ . \tag{3.10}$$

(There are other estimates of k_H differing somewhat from the present estimate [3], so that the precise value of the second-order virial for D_c is not emphasized.) The observed value of the second-order virial coefficient has been estimated as -12 ± 5 in Ref. [3]. Given the roughness of the second-order virial coefficient estimates we can claim only qualitative agreement with (3.10). Perhaps future experiments, which more precisely determine the second-order virial coefficient, will allow for a more meaningful consistency check of Eq. (2.42) [or Eq. (3.10)].

There is another basic nonperturbative equation relating D_c to the sedimentation coefficient $\Lambda(\phi)$ ("mobility") and the osmotic compressibility [25]

$$D_c(\phi)/D_{c,0}=[\Lambda(\phi)/\Lambda_0](S/S_0)^{-1}\ . \tag{3.11}$$

The infinite dilution calculation of sedimentation coefficient Λ_0 was first given by Svedberg [10a] and, accordingly, we term Eq. (3.11) the generalized Svedberg equation. A comparison of Eq. (3.11) to Eq. (1.2) gives some important qualitative insight into Λ. Since the fluidity $[(\eta/\eta_0)^{-1}]$ is generally rather insensitive to the osmotic compressibility, then Λ must depend rather strongly on osmotic compressibility. From Eqs. (3.5) and (3.11) we obtain the sedimentation coefficient Λ virial expansion for hard spheres [See Ref. [10b]),

$$\Lambda/\Lambda_0=1-6.5\phi+O(\phi^2)\ . \tag{3.12}$$

Newman *et al.* [2] and Kops-Werkhoven and Fignaut [3] measure the leading sedimentation virial as -6 ± 1 and -6.7 ± 0.8, respectively, which again is rather consistent with the theoretical virial expansions obtainable from Eqs. (2.42) and (3.11).

The sensitivity of Λ to the osmotic forces is illustrated in the case of interacting liquid drops where we obtain, using Eqs. (3.7) and (3.11),

$$\Lambda/\Lambda_0=(S/S_0)^{1/2}/(\eta/\eta_0)\equiv1-k_f\phi+O(\phi^2)\ , \tag{3.13a}$$

$$k_f=4\bar{\psi}+[\eta(z_\eta)],\quad k_f=k_D+2[\eta(z_\eta)]\ , \tag{3.13b}$$

where $[\eta(z_\eta)]$ is Taylor's results for the intrinsic viscosity of a spherical droplet solution [18],

$$[\eta(z_\eta)]=1+\tfrac{3}{2}z_\eta/(1+z_\eta)\ . \tag{3.13c}$$

Equation (3.13a) reduces to Eq. (3.12) for the hard sphere limit $(z_\eta\rightarrow\infty)$ and good solvents $(\bar{\psi}\rightarrow1)$, but the friction virial coefficient k_f is apparently much smaller under Θ conditions, reflecting the decreased contribution of osmotic forces to Λ. From Eqs. (2.40) and (3.13a) we also see that the sedimentation coefficient Λ *diverges* $(\Lambda\sim\xi_s)$ below the Θ point as the critical point for phase separation is approached $T\rightarrow T_c$. Such a divergence has been observed in critical fluid mixtures [26] and can perhaps be exploited to separate fluid suspended matter efficiently.

IV. DISCUSSION

The cooperative diffusion coefficient D_c of a suspension of interacting particles at nonvanishing concentrations reflects the changing particle fluidity with increasing concentration and particle interaction through the osmotic compressibility. Generalized Stokes-Einstein equations (1.1) and (1.2) are derived which prescribe the dependence of D_c on these factors.

The generalized Stokes-Einstein equation (1.1) apparently arises in many physical contexts other than particle suspensions. We mentioned the case of D_c for critical binary mixtures and semidilute polymer solutions. In each case Eq. (1.1) has been verified to remarkable accuracy [27,28]. It is also known that Eq. (1.1) describes the thermal diffusivity of condensing fluids [28]. Tanaka and co-workers [29] have shown that the temperature dependence of the diffusion coefficient D_c, associated with concentration fluctuations in swollen gels, is accurately described by an expression similar to Eq. (1.1) and this has important implications for the swelling of gels [30].

There is also evidence that this type of dynamic sum rule applies to a wide range of conductivity problems. For example, the electrophoretic contribution to the conductivity σ_c (ion) of a univalent pointlike ion in a dilute electrolyte solution equals [31]

$$\sigma_e=k_BT/6\pi\eta_0\xi_{\rm DH}\ , \tag{4.1}$$

where $\xi_{\rm DH}$ is the Debye-Hückel electrostatic screening length. This effect arises from a coupling between local charge density fluctuations and velocity fluctuations [31] in much the same fashion as a critical fluid where local velocity and concentration fluctuations couple. Indeed, the original mode-coupling theory of critical dynamics of Fixman drew upon this analogy between critical fluid fluctuations and ion "solvation" fluctuations [32]. Another interesting example of this type of mode-coupling effect arises in the Hubbard-Onsager calculation [33] of the "dielectric friction" f_ϵ of a pointlike ion in a dilute solution which also obeys a Stokes-Einstein-type relation

$$f_\epsilon\sim\eta_0R_{\rm HO}\ , \tag{4.2}$$

where $R_{\rm HO}$ is the "electrohydrodynamic ion radius." A diffusing solvated ion experiences dielectric friction since the ion polarizes the fluid locally and the fluid is unable to adjust its polarization fast enough to stay in equilibrium with the moving ion. The Hubbard-Onsager theory [33] treats the mode coupling between velocity and local polarization fluctuations. It is easy to imagine that mode coupling between solvent velocity and charge and polarization fluctuations could arise at higher electrolyte concentrations leading to general dynamic sum rules relating the conductivity, viscosity, and osmotic compressibility. This possibility deserves examination.

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APPENDIX A: CALCULATIONS OF $\Gamma_{\mathbf{k}}^{(0)}$ FOR NONINTERACTING SUSPENSION OF BROWNIAN SPHERES

Let D be the diffusion coefficient for the individual particle; then the diffusion equation can be written as

$$\partial n(\mathbf{r},t)/\partial t=D\nabla^2n(\mathbf{r},t)\ , \tag{A1}$$

where $n(\mathbf{r},t)$ is the microscopic particle density defined by Eq. (2.1). Multiplying both sides of Eq. (A1) by $n(\mathbf{r}',t')$, taking into account Eqs. (2.3) and (2.5), and volume averaging we obtain, after Fourier transforming,

$$\frac{\partial S(\mathbf{k},t)}{\partial t}+k^2DS(\mathbf{k},t)=0\ . \tag{A2}$$

The above equation should be supplemented with an initial condition. Following Ref. [13(a)] we write

$$S(\mathbf{R},0)=[\bar{n}(\partial\bar{n}/\partial\Pi)_T\delta(|\mathbf{R}|)]k_BT\ , \tag{A3}$$

where $(\partial\Pi/\partial\bar{n})_T$ is the osmotic compressibility. Combining Eqs. (A2) and (A3) and remembering that $\tau=|t-t'|$ we obtain

$$S(\mathbf{k},\tau)=\bar{n}[(\partial\bar{n}/\partial\Pi)_Te^{-k^2D\tau}]k_BT\ . \tag{A4}$$

For an ideal solution we have $(\partial\Pi/\partial\bar{n})_T=k_BT$, so that $\bar{n}(\partial\bar{n}/\partial\Pi)k_BT=\bar{n}$. The combined use of Eqs. (2.7) and (A4) produces

$$S(\mathbf{k},\omega)=\left[\frac{2nk^2D}{\omega^2+(k^2D)^2}\right] . \tag{A5}$$

Equation (2.8) and (A4) imply

$$\Gamma_{\mathbf{k}}^{(0)}=k^2D , \tag{A6}$$

so that

$$D=\frac{\partial}{\partial k^2}\Gamma_{\mathbf{k}}^{(0)}|_{\mathbf{k}=0} . \tag{A7}$$

Although this result is obtained in the limit of infinite dilution, we expect it to hold as well for finite concentrations by the principles of continuity and complementary.

APPENDIX B: CONSEQUENCES OF GALILEAN INVARIANCE

From Eq. (2.12) we have

$$\frac{d\mathbf{r}_i(t)}{dt}=v(\mathbf{r}_i,t) . \tag{B1}$$

Consider now an infinitesimal ($|\epsilon|\to 0+$) Galilean transformation

$$\mathbf{r}'=\mathbf{r}-\epsilon t, \quad t'=t . \tag{B2}$$

Suppressing the i subscript we then require

$$\frac{d\mathbf{r}'}{dt}=\mathbf{v}'(\mathbf{r}',t) \tag{B3}$$

if (B1) holds. This requirement implies

$$v'(\mathbf{r}',t)=\frac{d\mathbf{r}'}{dt}=v(\mathbf{r},t)-\epsilon \tag{B4a}$$

or

$$v(\mathbf{r},t)=\epsilon+v'(\mathbf{r}'t) . \tag{B4b}$$

On the other hand, we also have the relations

$$\frac{d}{dt}(\mathbf{r}'-\mathbf{r})=v'(\mathbf{r}',t)-v(\mathbf{r},t) \tag{B5}$$

or

$$v'(\mathbf{r}',t)-v(\mathbf{r},t)=-\epsilon . \tag{B6}$$

Using (B2) again we obtain:

$$\begin{aligned}-\epsilon&=v'(\mathbf{r}',t)-v(\mathbf{r}'+\epsilon t,t)\\&=v'(\mathbf{r}',t)-v(\mathbf{r}',t)-t\epsilon\cdot\left.\frac{\partial v}{\partial \mathbf{r}}\right|_{\mathbf{r}=\mathbf{r}'} .\end{aligned} \tag{B7}$$

The matrix $\partial v_i/\partial r_j$ can evidently be brought to the diagonal form. Then, using the incompressibility condition Eq. (2.20) we obtain

$$-\epsilon=v'(\mathbf{r}',t)-v(\mathbf{r}',t) . \tag{B8}$$

Combining this result with Eq. (B4b) we have

$$v(\mathbf{r},t)=v(\mathbf{r}',t) . \tag{B9}$$

Finally, using Eq. (B2) we arrive at the relation

$$v(\mathbf{r},t)=v(\mathbf{r}-\epsilon t,t)=v(\mathbf{r},t)-t\epsilon\cdot\partial v/\partial\mathbf{r} . \tag{B10}$$

The last equation becomes an identity if the fluid is incompressible, whence the imposition of the nonslip boundary condition is equivalent to the requirement of fluid incompressibility . If the fluid is compressible, then the nonslip condition Eq. (B1) should be modified in order to preserve Galilean invariance.

The above derivation is applicable, strictly speaking, only for spheres. In the more general case of bodies of arbitrary shape the boundary condition Eq. (B1) should be changed.

Let $\mathbf{R}(t)$ denote the position of the center of mass of the arbitrarily shaped body. Assuming that our body rotates with angular velocity $\boldsymbol{\Omega}(t)$, for some point $\mathbf{r}$ at its surface, we obtain

$$\frac{d\mathbf{r}}{dt}=\boldsymbol{\upsilon}+\boldsymbol{\Omega}\times[\mathbf{r}-\mathbf{R}(t)]\equiv v^{(t)}+v^{(r)} , \tag{B11}$$

where $\boldsymbol{\upsilon}$ is the velocity of the center of mass, i.e., $\boldsymbol{\upsilon}=d\mathbf{R}/dt$. In the case of a sphere we obtain $\mathbf{r}-\mathbf{R}(t)=R\mathbf{e}$, where R is radius of the sphere and $\mathbf{e}$ is the unit outward normal to the surface of the sphere. In this case we have

$$d[\mathbf{r}(t)-\mathbf{R}]/dt=Rd\mathbf{e}/dt , \tag{B12}$$

so that Eq. (B12), in view of Eq. (B11), acquires the form

$$d\mathbf{e}/dt=\boldsymbol{\Omega}\times\mathbf{e} . \tag{B13}$$

Equation (B13) describes a pure rotation and it is analogous to Eq. (5.9) of Ref. [34]. Finally, for the sphere, let

$$v^{(t)}+v^{(r)}=v^{(t)}(\mathbf{r},t)+v^{(r)}(\mathbf{r},t)\equiv v(\mathbf{r},t) , \tag{B14}$$

where $v(\mathbf{r},t)$ is fluid velocity. Because of Eqs. (B11) and (B13), we conclude that the rotational and translational motions are completely decoupled. This fact was used implicitly by Einstein [5] in his treatment of Brownian motion and a more sophisticated consideration of this decoupling problem is given in Ref. [35]. For suspensions of spheres, the analysis of Galilean invariance presented above is complete. In the more general situation of a body of arbitrary shape there is coupling between rotational and translational motion [35] so that the arguments presented in the main text as well as in this appendix should be modified accordingly.

APPENDIX C: VELOCITY CORRELATOR FOR A SUSPENSION OF BROWNIAN SPHERES AT FINITE CONCENTRATIONS

In Eq. (2.34) we introduced an angular averaging $\langle\ \rangle_s$. This averaging is appropriate only for spheres and the case of infinite dilution. To generalize this result to finite concentrations, we need to consider instead of Eq. (2.34) the expression

$$\langle \cdots \rangle_S=\sum_{i\le j}\frac{1}{A_iA_j}\int dS_i\int dS_j \cdots , \tag{C1}$$

where A_i is the area of ith surface. For surfaces of arbitrary shape we obtain

$$W=\langle 1/|\mathbf{r}-\mathbf{r}'|\rangle_s =\sum_{i\le j}\frac{1}{A_iA_j}\int d^2\xi_i\sqrt{g_i}\,\frac{1}{|\mathbf{r}(\xi_i)-\mathbf{r}(\xi_j)|}\int d^2\xi_j\sqrt{g_j}\ , \tag{C2}$$

where g_i is the determinant of the induced metric of the surface. Expressions of this sort were considered in our previous work (Ref. [36]). Equation (C2) could be viewed as a total electrostatic energy of the collection of extended objects. Unlike the case of usual electrostatics, where there are charges of opposite signs to ensure the electrical neutrality, all the surface "charges" $(1/A_i)$ have the same sign in the present case. The statistical mechanics of such systems is rather peculiar because they cannot undergo any kind of phase transition, contradicting the experimental facts [37]. This leads us to conclude that the hydrodynamic ("Coulomb-like") interactions present in Eq. (C2) should be *screened* at finite concentrations. The extent of this screening cannot be arbitrary because of the consistency condition Eq. (2.31). It is well known [9] that the preaveraging approximation leading to Eq. (2.27) works rather well even in the critical regime. In this regime Eq. (2.27) produces the formal result Eq. (2.40), where ξ is the correlation length which also enters the general relationship Eq. (2.41). We may be able to obtain the result Eq. (2.27) with the help of Eq. (C2) only if the electrostatic energy W is additionally averaged in accordance with the rules of statistical mechanics, e.g., as they are outlined in our previous work [36]. Even without doing the explicit calculations, it is clear that the extent of the hydrodynamic screening should be compatible with the length ξ_s. This follows from the consistency condition Eq. (2.31).

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