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A general formalism to study the dynamics of polyelectrolyte solutions is presented. We show in particular that the Berne–Pecora equations for charged pointlike particles are obtained by neglecting the memory function and using the Debye–Huckel potential with the linear approximation $\exp(-U/k_BT) \simeq 1 - U/k_BT$. We generalize Berne–Pecora results by introducing the effect of hydrodynamic interaction. Our calculations show a plasmon mode which corresponds to a nonzero frequency at zero scattering angle.

INTRODUCTION

A polyelectrolyte solution is a system that contains several species such as long chains of charged monomers (e.g., PSS⁻), small ions usually referred to as counter ions released during the ionization process of these monomers (e.g., TMA⁺), positively and negatively charged salt ions added to the solution to increase its ionic strength (e.g., Na⁺Cl⁻), and a solvent (e.g., water). The equilibrium properties of such systems show interesting behaviors that have been subject to active current research.[1,2] We have recently investigated the dependence on the wave vector q of the static structure factor using various simple models, in order to interpret the peak observed experimentally in scattering from polyelectrolyte solutions.[3] In the present work we study the dynamical behavior of such a solution by regarding it as a three-component system consisting of large polyions and small counter ions embedded in a solvent which acts as a continuous background. We first present a general formalism which does not rely on any particular model. In specific applications which we consider later, one needs explicit models for the internal structure of the polyions, the equilibrium distribution of all the particles in the solution, and their dynamic behavior.

GENERAL FORMALISM

Since our main concern in this work is a theoretical interpretation of dynamic scattering experiments on polyelectrolyte solutions, we focus our attention on the time evolution of the density of scattering centers. For simplicity we assume that all the monomers and counter ions scatter equally, and consider a solution of N_1 chains each having n_1 monomers that are all ionized (component 1), and N_2 counter ions each having the charge of a monomer with opposite sign (component 2). The counter ions will be treated as point particles. The densities of the two components are defined by

$$\rho_1 = \sum_{\alpha=1}^{N_1} \sum_{j=1}^{n_1} \exp(i\mathbf{q}\cdot\mathbf{R}_{\alpha j}), \qquad (1)$$

$$\rho_2 = \sum_{l=1}^{N_2} \exp(i\mathbf{q}\cdot\mathbf{R}_l), \qquad (2)$$

where $\mathbf{R}_{\alpha j}$ is the position vector of monomer j belonging to

the chain α, $\mathbf{R}_l$ is the position vector of counter ion l, and $\mathbf{q}$ is the wave vector.

In the following discussions, we use the matrix notation by introducing the column matrix:

$$\rho = \begin{bmatrix} \rho_1 \\ \rho_2 \end{bmatrix}. \qquad (3)$$

The time evolution of $\rho(t)$ is assumed to be governed by an equation of the form

$$\frac{\partial \rho}{\partial t} = -\mathscr{L}\,\rho \qquad (4)$$

where $\mathscr{L}$ is a Liouville-like operator which does not need to be specified in the general formalism in this section. Equation (4) can be transformed into a more appealing form by using a standard method in linear response theory based on the projection operator technique. We choose a projection operator P of Mori–Zwanzig[4–6] type, which produces, when it acts on a dynamical variable G, a vector PG defined by

$$PG = \langle G\rho^+\rangle\cdot\langle \rho\rho^+\rangle^{-1}\rho. \qquad (5)$$

Here ρ denotes $\rho(0)$ and $\langle\cdots\rangle$ represents an ensemble average with respect to the equilibrium distribution function ψ_0 which depends on particle coordinates of both components. The ρ^+ is the row vector adjoint to ρ, $\langle \rho\rho^+\rangle^{-1}$ is the inverse of the static structure matrix $S(\mathbf{q}) = \langle \rho\rho^+\rangle$. Combining Eqs. (4) and (5) one finds, with standard manipulations, an exact equation for $\rho(t)$:

$$\frac{\partial \rho(t)}{\partial t} + \bar{\varOmega}\cdot\rho(t) - \int_0^t du\, \bar{\bar{\varPhi}}(t-u)\cdot\rho(u) = \mathbf{f}(t) \qquad (6)$$

which is often referred to as the generalized Langevin equation. The quantities $\bar{\varOmega}$ and $\bar{\bar{\varPhi}}(t)$ are, respectively, the frequency matrix

$$\bar{\varOmega} = \langle \rho\mathscr{L}\rho^+\rangle\cdot\langle \rho\rho^+\rangle^{-1} \qquad (7)$$

and the memory matrix

$$\bar{\bar{\varPhi}}(t) = \langle \mathbf{f}(t)\mathbf{f}^+\rangle\cdot\langle \rho\rho^+\rangle^{-1}, \qquad (8a)$$

where the random force $\mathbf{f}(t)$ is defined by

$$\mathbf{f}(t) = \exp[-t(1-P)\mathscr{L}](1-P)\mathscr{L}\rho. \qquad (8b)$$

Equation (6) can be used to study either the time correlation functions between the components of the vector $\rho(t)$, or to obtain an equation of motion for the ensemble average of $\rho(t)$ itself. In the former case one uses the causality property of

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f(t):

$$\langle \mathbf{f}(t)\mathbf{\rho}^{+} \rangle = 0, \quad t > 0. \tag{9}$$

Multiplying Eq. (6) from the right by $\mathbf{\rho}$ and taking the ensemble average with respect to the equilibrium distribution ψ_0, one obtains an equation for the dynamic correlation matrix:

$$\overline{S}(q,t) = \langle \mathbf{\rho}(t)\mathbf{\rho}^{+} \rangle \tag{10}$$

in the following form:

$$\frac{\partial \overline{S}(q,t)}{\partial t} + \overline{\Omega}\cdot\overline{S}(q,t) - \int_0^t du \, \overline{\Phi}(t-u)\cdot\overline{S}(q,u) = 0. \tag{11}$$

The Laplace transform of Eq. (11) yields

$$\overline{S}(q,s) = [s\overline{I} + \overline{\Omega} - \overline{\Phi}(s)]^{-1}\langle \mathbf{\rho}\mathbf{\rho}^{+} \rangle, \tag{12}$$

where s is the transform variable and $\overline{I}$ is the identity matrix. The usual dynamic structure factor $\overline{S}(q,\omega)$ is obtained from $\overline{S}(q,s)$ as

$$\overline{S}(q,\omega) = (2/\pi)\text{Re}[i\omega\overline{I} + \overline{\Omega} - \overline{\Phi}(i\omega)]^{-1}\langle \mathbf{\rho}\mathbf{\rho}^{+} \rangle, \tag{13}$$

where ω denotes the frequency, and Re means taking the real part. The exact formalism presented here is of course well known and has been used extensively in recent years in the interpretation of dynamic scattering experiments in one component solutions. More recently it has also been applied, in its matrix form, to the study of dynamic scattering from bimodal solutions,[7] and the concentration dependence of the apparent diffusion coefficient.[7] The formalism is exact in the sense that it can be applied to Brownian particles interacting via an arbitrary potential with or without hydrodynamic interaction. In particular it can be used to study the dynamics of polyelectrolyte solutions. In the following section we use this formalism to obtain tractable equations for the time evolution of the average density and formulas for the intermediate scattering function in such solutions.

HYDRODYNAMIC EQUATIONS FOR THE AVERAGE DENSITY

The ensemble average of both sides of Eq. (6) with respect to the intitial distribution $\psi(t = 0)$ yields an exact equation for the average density $\mathbf{C}(\mathbf{q},t)$ defined by

$$\mathbf{C}(\mathbf{q},t) = \overline{\mathbf{\rho}(t)}, \tag{14}$$

where the overbar is introduced to distinguish the average with respect to the initial distribution from the equilibrium average

$$\frac{\partial \mathbf{C}(\mathbf{q},t)}{\partial t} + \overline{\Omega}\cdot\mathbf{C}(\mathbf{q},t) - \int_0^t du \, \overline{\Phi}(t-u)\cdot\mathbf{C}(\mathbf{q},u) = \overline{\mathbf{f}(t)}. \tag{15}$$

When small deviations from the equilibrium state are considered, the average value of the random force $\overline{\mathbf{f}(t)}$ can be approximated by zero. This approximation implies linearization of Eq. (15). It is important to note that although the resulting equation for $\mathbf{C}(\mathbf{q},t)$ is approximate, Eq. (11) for $\overline{S}(q,t)$, which has the same form as Eq. (15) is exact.

In the Markov limit where $q \to 0$ and $t \to \infty$ such that $q^2 t$ remains finite the solution of Eq. (15) is exponential:

$$\mathbf{C}(\mathbf{q},t) = \exp(-\overline{\Gamma}t)\cdot\mathbf{C}(\mathbf{q},0), \tag{16}$$

where $\overline{\Gamma}$ is given by

$$\overline{\Gamma} = \overline{\Omega} - \int_0^{\infty} du \, \overline{\Phi}(u). \tag{17}$$

In the short time limit, however, the effect of the memory function tends to vanish and $\mathbf{C}(\mathbf{q},t)$ decays again exponentially but with a decay rate $\overline{\Omega}$, i.e.,

$$\mathbf{C}(\mathbf{q},t) = \exp(-\overline{\Omega}t)\cdot\mathbf{C}(\mathbf{q},0). \tag{18}$$

In many cases of practical interest $\overline{\Omega}$ can be calculated explicitly as opposed to the memory function $\overline{\Phi}$ which is far more difficult to handle. Fortunately, $\overline{\Phi}$ usually contains enough information about the dynamics of the system so that the memory term can be approximately treated or, in some applications even completely neglected. Since $\overline{\Omega}$ can be measured by neutron[8,9] and light[10] scattering experiments with sufficient accuracy through cumulant analysis, it has been used extensively to interpret such experiments on neutral polymer solutions. In this paper we calculate $\overline{\Omega}$ in the case of polyelectrolytes. The definition of $\overline{\Omega}$ given by Eq. (7) can be written as

$$\overline{\Omega} = k_B T q^2 \overline{\mu}(q)\cdot\overline{S}^{-1}(q), \tag{19}$$

where we have introduced the generalized mobility[11] matrix $\overline{\mu}(q)$:

$$\overline{\mu}(q) = q^{-2}(k_B T)^{-1}\langle \mathbf{\rho}\mathcal{L}\mathbf{\rho}^{+} \rangle \tag{20}$$

and $\overline{S}(q) = \langle \mathbf{\rho}\mathbf{\rho}^{+} \rangle$, $k_B T$ is the temperature in units of Boltzmann factor k_B. More explicitly, $\overline{\Omega}(q)$ can be expressed in terms of the matrix elements of $\overline{\mu}(q)$ and $\overline{S}(q)$ as

$$\overline{\Omega}(q) = \frac{q^2 k_B T}{S_{11}S_{22} - S_{12}S_{21}} \\ \times \begin{bmatrix} \mu_{11}S_{22} - \mu_{12}S_{21} & \mu_{12}S_{11} - \mu_{11}S_{12} \\ \mu_{21}S_{22} - \mu_{22}S_{21} & \mu_{22}S_{11} - \mu_{21}S_{12} \end{bmatrix}. \tag{21}$$

Point particles in the free draining limit

Here we assume that all the molecules including polyions appear as pointlike particles. This is the case when the wave vector q is sufficiently small so that the scattered radiation cannot resolve any detailed internal structure of these molecules. In this special case the matrix elements S_{ij} are given by

$$S_{11} = N_1 \left\{ 1 + 4\pi \frac{N_1}{V} \int_0^{\infty} dR \, R^2 [g_{11}(R) - 1] \frac{\sin qR}{qR} \right\}, \tag{22a}$$

$$S_{12} = N_1 N_2 \frac{4\pi}{V} \int_0^{\infty} dR \, R^2 [g_{21}(R) - 1] \frac{\sin qR}{qR}, \tag{22b}$$

and similar equations hold for S_{22} and S_{21}. Here V is the volume of the solution and $g_{ij}(R)$ is the radial distribution function for a pair of particles of type i and j, i.e.,

$$g_{ij}(R) = \exp[-U_{ij}(R)/k_B T], \tag{}$$

$U_{ij}(R)$ being the potential for the mean force between two particles of type i and j. The radial distribution functions depend on concentrations of both polyions and counter ions. In this application, however, we need their infinite dilution limit, in which $U_{ij}(R)$ reduces to the interaction potential for an isolated pair. When combined with the linearization approximation $g_{ij}(R)$ reduces to

$$g_{ij}(R) = 1 - U_{ij}(R)/k_B T. \tag{23a}$$

In polyelectrolytes $U_{ij}(R)$ can be chosen as the screened Debye–Huckel model:

$$U_{ij}(R) = Z_i Z_j \frac{e^2}{\epsilon_0 R} \exp(-KR), \tag{23b}$$

where $Z_i e$ is the charge of particle i, ϵ_0 the dielectric permittivity, and K^{-1} is the Debye screening length:

$$K^2 = K_1^2 + K_2^2 \tag{23c}$$

or

$$K^2 = \frac{4\pi}{\epsilon_0 k_B T}\left[\frac{N_1}{V}(Z_1 e)^2 + \frac{N_2}{V}(Z_2 e)^2\right]. \tag{23d}$$

Substitution of Eqs. (23) into Eq. (22) yields

$$S_{11} = N_1\left[1 - \frac{K_1^2}{(q^2 + K^2)}\right], \tag{24a}$$

$$S_{22} = N_2\left[1 - \frac{K_2^2}{(q^2 + K^2)}\right], \tag{24b}$$

$$S_{12} = S_{21} = (N_1 N_2)^{1/2}\frac{K_1 K_2}{(q^2 + K^2)}. \tag{24c}$$

The calculation of the matrix elements of the mobility tensor requires a model for the time evolution operator $\mathscr{L}$. In the absence of hydrodynamic interaction (i.e., Rouse or free draining limit) one can use the familiar Kirkwood–Riseman[12] model, which in the case of point particles is given by

$$\mathscr{L} = -\sum_j D_j[\nabla_j + \nabla_j(\ln \psi_0)]\cdot\nabla_j, \tag{25}$$

where D_j is the diffusion coefficient of a single particle, i.e., $D_{1,2} = k_B T/\xi_{1,2}$ in which $\xi_{1,2}$ is the friction constant of either a monomer (1) or a counter ion (2), $\nabla_j = \partial/\partial \mathbf{R}_j$. Substitution of Eq. (25) into Eq. (20) yields

$$\mu_{11} = N_1 D_1/k_B T, \tag{26a}$$

$$\mu_{22} = N_2 D_2/k_B T, \tag{26b}$$

$$\mu_{12} = \mu_{21} = 0. \tag{26c}$$

The matrix elements of $\overline{\overline{\Omega}}$ [cf. Eq. (21)] can be readily obtained in the Rouse limit using the point particle description. When the results are inserted into

$$\frac{\partial \mathbf{C}(\mathbf{q},t)}{\partial t} = -\overline{\overline{\Omega}}\cdot\mathbf{C}(\mathbf{q},t), \tag{27a}$$

one obtains explicitly

$$\frac{\partial C_1(\mathbf{q},t)}{\partial t} = -D_1(q^2 + K_1^2)C_1(\mathbf{q},t) - D_1 K_2^2 C_2(\mathbf{q},t), \tag{27b}$$

$$\frac{\partial C_2(\mathbf{q},t)}{\partial t} = -D_2 K_1^2 C_1(\mathbf{q},t) - D_2(q^2 + K_2^2)C_2(\mathbf{q},t). \tag{27c}$$

These equations were also obtained before by Berne and Pecora[13] using a phenomenological approach. In the appendix we present the derivation of these equations using yet another method. This simple example involving point particles in the absence of hydrodynamic interactions elucidates the various approximations one has to introduce to obtain Berne–Pecora equations from the exact equations (15), namely (i) the linearization of Eq. (15) and the neglect of the memory effects, (ii) the infinite dilution limit for $g_{ij}(R)$, (iii)

the linearization of $\exp(-U_{ij}/k_B T)$ as $1 - U_{ij}/k_B T$ and (iv) the use of the Debye–Huckel form for the pair interaction potential. We shall return to these points once more in a later section.

The present formalism enables one to immediately generalize these results by introducing the effect of hydrodynamic interaction.

Point particles with hydrodynamic interaction

In this case the operator $\mathscr{L}$ becomes

$$\mathscr{L} = -\sum_{j,l}[\nabla_j + \nabla_j(\ln \psi_0)]\cdot\overline{\overline{D}}_{jl}\cdot\nabla_l. \tag{28}$$

Moreover, since we are considering point particles in this example also, the effect of hydrodynamic interaction appears only in the interparticle generalized mobilities μ_{12} and μ_{21}:

$$\mu_{12} = \mu_{21} = \sum_{j=1}^{N_1}\sum_{l=1}^{N_2}\langle T_{33}(\mathbf{R}_{jl})\exp(i\mathbf{q}\cdot\mathbf{R}_{jl})\rangle \tag{29a}$$

which can be written as

$$\mu_{12} = \mu_{21} = N_1 N_2\langle T_{33}(\mathbf{R})\exp(i\mathbf{q}\cdot\mathbf{R})\rangle, \tag{29b}$$

where $T_{33}(\mathbf{R})$ is the component of the Oseen tensor along the direction of the wave vector $\mathbf{q}$:

$$T_{33}(\mathbf{R}) = (1 + \alpha^2)/8\pi\eta_0 R \tag{30}$$

in which η_0 is the viscosity of the solvent, α is the cosine of the angle between $\mathbf{R}$ and $\mathbf{q}$, and $\mathbf{R}$ is the vector distance between two particles of different kinds. Substituting Eq. (30) into Eq. (29b), and using the approximations for the pair distribution function which are described by Eqs. (23) one obtains

$$\mu_{12} = \mu_{21} = \frac{\sqrt{N_1 N_2}}{8\pi\eta_0}\frac{K_1 K_2}{q}\mathscr{F}(q/K), \tag{31a}$$

where the function $\mathscr{F}(x)$ is defined by

$$\mathscr{F}(x) = x^{-1} - (x^{-2} - 1)\tan^{-1}x. \tag{31b}$$

We note that μ_{11} and μ_{22} remain unchanged when hydrodynamic interaction is included, and are still given by Eqs. (26). Hence, the components of $\overline{\overline{\Omega}}$ in the presence of hydrodynamic interactions become

$$\Omega_{11} = D_1(q^2 + K_1^2) + \frac{k_B T}{8\pi\eta_0}\frac{K_1^2 K_2^2}{q}\mathscr{F}(q/K). \tag{32a}$$

$$\Omega_{12} = D_1 K_2^2 + \frac{k_B T}{8\pi\eta_0}\frac{K_1^2(q^2 + K_2^2)}{q}\mathscr{F}(q/K), \tag{32b}$$

and analogous equations for Ω_{22} and Ω_{21}.

A comment is in order here, concerning the equilibrium distribution for the point charged particles and the approximations in Eqs. (23). One observes that U_{ij} is positive when the particles i and j are of the same kind, and hence $g_{ij}(R)$ increases from zero to one as R varies from zero to infinity. However, U_{ij} is negative when the particles i and j are of opposite charge, and consequently $g_{ij}(R)$ increases to infinity as R approaches zero. This implies that the integral in Eq. (22b) diverges and the definition of S_{12} becomes ambiguous. In fact, by allowing R to tend to zero one includes the possibility of recombination of oppositely charged particles to

form either a new charged particle with a charge $Z_1 - Z_2$, or a neutral particle, and thereby changing the composition of the system. This problem is encountered in computer simulation of fully ionized plasmas by Baus and Hansen.[15] They replaced the bare Coulomb potential for ion–electron pairs by $[1 - \exp(-KR)]/R$ with an appropriate value for K, to prevent recombination. The situation bears a certain resemblance to the condensation phenomenon[16] encountered in polyelectrolyte solutions in the case of macroions with internal structure. It is interesting to note that this difficulty was avoided in the present case by virtue of linearization of the pair distribution function and the use of the Debye–Huckel potential which leads to a mathematically well-behaved and integrable quantity in Eq. (22b). Although we have considered only pointlike molecules in the present application, the general formalism described earlier is also useful in cases where the internal structure of these molecules has to be taken into account, as in neutron scattering in which q^{-1} may be of the order of the size of a monomer.

INTERMEDIATE SCATTERING FUNCTION $\overline{S}(q,t)$

In this section we obtain an approximate expression for the intermediate scattering function $S(q,t)$ in polyelectrolyte solutions starting from the exact generalized Langevin equation in matrix form. In the Markov limit Eq. (10) reduces to

$$\overline{S}(q,t) = \exp(-\overline{\Gamma}t)\cdot\overline{S}(q), \tag{33}$$

where the relaxation matrix $\overline{\Gamma}$ is given by

$$\overline{\Gamma} = \overline{\Omega} - \int_0^\infty du\, \overline{\Phi}(q,u). \tag{34}$$

In the three-component description considered in this work, the intermediate scattering function $S(q,t)$, actually measured in dynamic scattering experiments, is related to the components of $\overline{S}(q,t)$ by

$$S(q,t) = \sum_{i,j=1}^{2} S_{ij}(q,t), \tag{35}$$

where $S_{ij}(q,t)$ are defined by

$$S_{ij}(q,t) = \langle \rho_i(t)\rho_j^* \rangle. \tag{36}$$

One can show that[7]

$$\frac{S(q,t)}{S(q)} = \frac{\Gamma_1 + AS^{-1}(q)}{\Gamma_1 - \Gamma_2}\exp(-\Gamma_1 t)$$

$$\quad - \frac{\Gamma_2 + AS^{-1}(q)}{\Gamma_1 - \Gamma_2}\exp(-\Gamma_2 t), \tag{37a}$$

where $S(q) = S(q,t=0)$ is the total static structure factor and the quantity A denotes

$$A = (S_{11} + S_{12})(\Gamma_{21} - \Gamma_{22}) + (S_{22} + S_{21})(\Gamma_{12} - \Gamma_{11}). \tag{37b}$$

Here, S_{ij} are the elements of the matrix $\overline{S}(q)$, and Γ_{ij} are those of $\overline{\Gamma}$. We have suppressed the arguments showing the explicit q dependence to ease the notation. The relaxation frequencies Γ_1 and Γ_2 are given by

$$\Gamma_{1,2} = \Gamma_{\mathrm{av}} \pm \sqrt{\Gamma_{\mathrm{av}}^2 - \Delta}, \tag{38a}$$

$$\Gamma_{\mathrm{av}} = \frac{\Gamma_{11} + \Gamma_{22}}{2}, \tag{38b}$$

$$\Delta = \Gamma_{11}\Gamma_{22} - \Gamma_{12}\Gamma_{21}. \tag{38c}$$

In the absence of memory effects, Γ_{ij} coincides with Ω_{ij} which we have calculated explicitly for pointlike charged particles in the previous section. We present the expressions of the relaxation frequencies in two extreme limits:

(i) Small q limit ($q \to 0$)

Assuming $D_1 = D_2$, one has in this limit $\Delta = 0$, $\Gamma_2 = 0$, and

$$\Gamma_1 = D_1 K_1^2 + D_2 K_2^2 + \frac{k_B T}{\pi\eta_0}\frac{K_1^2 K_2^2}{3K}, \tag{39}$$

where we have used Eq. (32a). This constant relaxation frequency when $q = 0$ is referred to as the "plasmon mode" by analogy with the total plasma frequency.[11] We note that Γ_1 depends on the properties of both components indicating a strong coupling.

(ii) Large q limit

Combining Eqs. (32) and (38), and replacing $\overline{\Gamma}$ by $\overline{\Omega}$, one finds in this limit $\Gamma_1 = D_1 q^2$ and $\Gamma_2 = D_2 q^2$ which indicates, as expected a decoupling between the two components.

CONCLUSIONS

In this paper we have summarized a general formalism, based on the linear response theory, for the interpretation of dynamic scattering experiments in neutral polymer solution developed by Akcasu et al.,[7] and demonstrated its application to the dynamics of pointlike charged molecules in solution. We have shown that the linearized version of Berne–Pecora equations for the mean particle densities are obtained in this formalism by neglecting the memory effects. The latter approximation is sometimes referred to as the mean field theory.[17] We have extended these equations to include hydrodynamic interactions among the charged particles. The alternative derivation of Berne–Pecora equations in their nonlinear form presented in the appendix elucidates further the approximations inherent in these equations and suggests ways for improvement within the framework of the above formalism. We have pointed out that, although the equations for the mean concentrations are approximate, the generalized Langevin equation satisfied by the dynamic structure factor is exact. We solved this equation in the case of pointlike charged particles including hydrodynamic interactions ignoring memory effects. The main difficulty in this approach, as is well known in statistical mechanics, is the calculation of the memory functions. Several methods[18] have been attempted either to calculate these functions directly, or to study indirectly their effects on the time evolution of $S(q,t)$. Any direct calculation using Eq. (8) is complicated by the presence of the modified propagator $\exp[-t(1-P)\mathscr{L}]$. There are, however, several indirect methods which seem to be promising, in particular in applications in polyelectrolyte solutions.

ACKNOWLEDGMENTS

APPENDIX: AN ALTERNATIVE DERIVATION OF BERNE–PECORA EQUATIONS

Here we follow a procedure similar to that used by Klimontovich[19] in plasma physics. We start with the density of one of the components in the configuration space:

$$\rho_A = \sum_{j=1}^{N_A} \delta(\mathbf{R} - \mathbf{R}_j), \tag{A1}$$

where $\mathbf{R}$ is a field point in space. ρ_A satisfies $\partial\rho_A/\partial t = -\mathscr{L}\rho_A$. In the case of pointlike particle description and in the absence of hydrodynamic interaction the operator $\mathscr{L}$ is given by Eq. (25). Taking advantage of Dirac δ functions, one can verify that

$$\mathscr{L}\rho_A = -D_A \nabla_\mathbf{R}^2 \rho_A + \frac{D_A}{k_B T} \nabla_\mathbf{R} \cdot \sum_{j=1}^{N_A} \delta(\mathbf{R} - \mathbf{R}_j)\mathbf{F}_j(\mathbf{R}^N), \tag{A2}$$

where

$$\nabla_\mathbf{R}^2 = \nabla_\mathbf{R} \cdot \nabla_\mathbf{R}, \nabla_\mathbf{R} = \partial/\partial\mathbf{R}, \text{ and } \mathbf{R}^N = \mathbf{R}_1,...,\mathbf{R}_N.$$

The force acting on the jth particle is denoted by $\mathbf{F}_j = -\nabla_j U(\mathbf{R}^N)$, where U is the potential energy of the system. In the case of pure Coulomb interaction between particles, $\mathbf{F}_j = Z_A e_A \widetilde{\mathbf{E}}_j$ where $\widetilde{\mathbf{E}}_j$ is the electric field at the position $\mathbf{R}_j$ of the jth particle, produced by the other particles in the system. We shall use $\widetilde{\mathbf{E}}_j$ instead of F_j for convenience even in the case of nonCoulombic interaction by treating $e_A Z_A$ as a property of a particle of kind A. By virtue of the Dirac δ function in Eq. (A2), $\mathbf{R}_j$ in $\widetilde{\mathbf{E}}_j$ can be replaced by $\mathbf{R}$ so that $\widetilde{\mathbf{E}}_j$ becomes $\widetilde{\mathbf{E}}(\mathbf{R}_1,...,\mathbf{R}_j = \mathbf{R},...,\mathbf{R}_N)$. In the Klimontovich theory one includes the self-energy of particles in the potential energy of the system. This allows us to replace $\widetilde{\mathbf{E}}_j$ in Eq. (A2) by $\widetilde{\mathbf{E}}(\mathbf{R},\mathbf{R}^N)$, which is the field at a point $\mathbf{R}$ produced by all the particles including the jth one. The inclusion of the self-energy term enables one to perform the summation of $\delta(\mathbf{R} - \mathbf{R}_j)$ over j, and to introduce ρ_A. Taking the average of the resulting equation with respect to the initial distribution $\psi(0,\mathbf{R}^N)$, one can obtain an equation for the mean density $C_A(\mathbf{R},t) = \overline{\rho_A(\mathbf{R},t)}$ as

$$\frac{\partial C_A(\mathbf{R},t)}{\partial t} = -D_A \nabla^2 C_A + \frac{Z_A e_A}{k_B T} D_A \nabla \cdot \overline{(\rho_A \mathbf{E})}. \tag{A3}$$

If one uses the mean field approximation

$$\overline{\rho_A \widetilde{\mathbf{E}}} \simeq C_A \mathbf{E}, \tag{A4}$$

where $\mathbf{E}$ is the mean field, and substitutes Eq. (A4) into Eq. (A3), one recaptures the Berne–Pecora equation [Eq. (9.2.7) in Ref. 13]. In general, the mean field $\mathbf{E}(\mathbf{R},t)$ does not satisfy the Poisson equation. Assuming a pairwise additive interaction potential, we can obtain an equation for $\mathbf{E}(\mathbf{R},t)$ starting

from

$$\mathbf{E}(\mathbf{R},\mathbf{R}^N) = -\nabla_\mathbf{R} \sum_B \int d^3R' \, \phi_B(\mathbf{R} - \mathbf{R}')\rho_B(\mathbf{R}'), \tag{A5}$$

where $\Phi_B(\mathbf{R} - \mathbf{R}')$ is the potential at $\mathbf{R}$ due to a particle of kind B at $\mathbf{R}'$, and the summation is over the kinds. By taking the average of Eq. (A5) over the initial distribution, we find

$$\nabla \cdot \mathbf{E} = -\sum_B \int d^3R' \, \nabla_\mathbf{R}^2 \, \phi_B(\mathbf{R} - \mathbf{R}')C_B(\mathbf{R}',t). \tag{A6}$$

This, of course, reduces to the Poisson equation in the case of Coulomb interaction for which $\phi_B(\mathbf{R}) = Z_B e_B/R$ and $\nabla^2 \phi_B = -4\pi Z_B e_B \delta(\mathbf{R})$.

If the mean field approximation in Eq. (A4) is not introduced, Eq. (3) becomes

$$\frac{\partial C_A(\mathbf{R},t)}{\partial t} = -D_A \nabla^2 C_A$$
$$+ \frac{Z_A e_A D_A}{k_B T} \sum_B \int d^3R' \, \nabla_\mathbf{R}^2 \, \phi(\mathbf{R} - \mathbf{R}') \overline{\rho_A(\mathbf{R},t)\rho_B(\mathbf{R}',t)} \tag{A7}$$

which involves the doublet density $\overline{\rho_A \rho_B}$. The mean field approximation corresponds to replacing this product by $C_A C_B$. It is of course possible to generate a hierarchy of equations by treating the doublet density as a new dynamical variable as is done in the kinetic theory. Since it is a well known procedure we do not pursue this path any further.

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