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Electrolyte friction and the Langevin equation for charged Brownian particles

Magdaleno Medina-Noyola and Alejandro Vizcarra-Rendón
Departamento de Física, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional,
A.P. 14-740, 07000 México, D.F., México

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A Langevin equation for a charged spherical Brownian particle, diffusing in an ionic solution, is derived as a contraction of a description based on the fluctuating diffusion equation for the local concentrations of the electrolyte ions of the supporting solution. A fluctuation-dissipation relation is demonstrated between the electrostatic friction and its corresponding fluctuating force. Expressions are derived for the electrolyte contribution to the friction coefficient in terms of the equilibrium interionic correlation functions. The results previously found by Schurr are shown to follow in the Debye-Hückel limit.

I. INTRODUCTION

In a recent work, Gorti *et al.*[1] have measured the self-diffusion coefficient D_s of charged spherical macroparticles in an ionic solution as a function of electrolyte concentration. They find that D_s decreases from a "saturation" value as the ionic strength is diminished. In an attempt to establish a theoretical interpretation, they compare their experimental results with the expression for D_s given in terms of Einstein's relation, $D_s = k_B T/\zeta$, in which the friction coefficient ζ is supposed to be the combination of a "solvent" plus an "electrostatic" contribution, $\zeta = \zeta^s + \zeta^{el}$. For ζ^s, Gorti *et al.*[1] assume Stokes's expression, $\zeta^s = 6\pi\eta a$ (for a sphere of radius a in a medium of viscosity η), whereas for the electrostatic contribution ζ^{el} they consider the results of the theories developed by Schurr[2] and by Booth,[3] which provide expressions for ζ^{el} in terms of the ionic strength of the solution. Their conclusion is that the former theory provides a better fitting scheme for the experimental data.

In essence, Schurr's theory[2] is based on the calculation of the fluctuating electrostatic force on the macroparticle, due to the spontaneous equilibrium fluctuations in the local concentration of small ions in the neighborhood of the macroparticle. In this theory, the existence of a Langevin equation for charged macroparticles is implicitly assumed, and use is made of a fluctuation-dissipation relation[4] between the transport coefficient ζ^{el} and the correlation function of the fluctuating electrostatic force. In addition, a number of simplifying assumptions and approximations are introduced,[2] some of which could probably be dispensed with in a more general theoretical approach. One of the motivations of the present work is the need of a formal derivation of the Langevin equation and of the fluctuation-dissipation relation underlying Schurr's theory. As a consequence, a general scheme for calculation of ζ^{el} was produced, from which Schurr's results follow as a particular limit.

The Langevin equation has been the basis for the classical description[5,6] of Brownian motion. Several workers[7] have shown that the Langevin equation follows from the fundamental laws of classical mechanics, although only formal expressions are produced for the friction coefficient and the fluctuating force. The actual evaluation of the friction coefficient makes use of phenomenological, hydrodynamic arguments such as those leading to the Stokes expression, $\zeta = 6\pi\eta a$. It is then fair to say that a useful alternative derivation of the Langevin equation could originate from a fully hydrodynamic level of description. This point of view was taken by Fox and Uhlenbeck,[8] and others.[9,10] Starting from Newton's second law for an uncharged Brownian particle plus a fluctuating version of the hydrodynamic equations which describe the dynamics of the supporting fluid (i.e., the noncontracted description) it has been shown[9,10] that a Langevin equation with memory follows when the hydrodynamic variables are eliminated. The Markovian limit of this equation is the ordinary Langevin equation. This procedure is an example of what is generally referred to as the "contraction of a description." Berman[10] has demonstrated, under rather general conditions, that if the noncontracted description (i.e., that involving the fluctuating hydrodynamic equations in the example above) can be cast as a Gaussian, Markovian stochastic process, in which a fluctuation-dissipation theorem and the Onsager-Casimir relations hold, then a fluctuation-dissipation relation follows at the contracted level. This is a relation between the memory function occurring in the Langevin-type equation resulting from the contraction, and the time correlation function of the corresponding fluctuating force.

It would certainly be interesting to develop a formal derivation of the Langevin equation for a charged Brownian particle along these lines, i.e., as a contraction of a description involving the fluctuating hydrodynamic equations that describe the dynamics of the fluctuations in local composition and in local mass, energy, and momentum densities around the macroparticle. Such a derivation, however, would differ from the previous work on uncharged macroparticles[8,10] in only two essential respects: the presence of diffusive fluxes and of long-ranged (Coulomb) interactions. Thus, it may be more instructive to first carry out a somewhat simpler derivation in which the proper treatment of these two features is clearly exhibited. This is done in this paper under the following approximation: We shall neglect the dynamic coupling of the fluctuations in local mass, energy, and momentum densities with the fluctuations in local composition. The former are driven by hydrodynamic (mass, energy, and momentum) fluxes and have a faster dynamics than the latter, which are mainly driven by diffusive processes. Although the cross effects being neglected may be theoretically interesting by themselves, we do not expect them to contribute significantly to the total friction on the macroparticle. Thus, we can imagine that the process of contraction can be carried out in two independent stages. The hydrodynamic variables are first eliminated from the description, as done in previous work,[8,10] ignoring the electrostatic effects. This results in a "solvent" friction and its corresponding fluctuating term in the force on the macroparticle. The second stage of the contraction is carried out here, and consists of the elimination of the variables determining the local composition of the ionic solution, i.e., the local concentrations $n_i(\mathbf{x},t)$ $(i=1,2,\ldots,\nu)$ of electrolyte ions around the macroparticle. These variables will be assumed to obey a fluctuating version of the diffusion equation. From the fluctuation-dissipation relation between the fluctuating and the dissipative diffusive fluxes in this equation, we demonstrate the fluctuation-dissipation relation between the dissipative and the fluctuating electrostatic terms of the resulting Langevin equation for the macroparticle. This equation is not local in time, and expressions are derived for the memory function in terms of the equilibrium-concentration—concentration correlation functions for the small ions, and of the matrix $\mathscr{L}_{ij}$ of Onsager's phenomenologic coefficients appearing in the fluctuating diffusion equation. Schurr's results[2] follow when the simplest approximation (Debye-Hückel) for the interionic correlations, along with other simplifications, are employed in our general expressions for the electrostatic friction ζ^{el}.

This paper is organized as follows. In Sec. II, the fluctuating diffusion equations are set up to describe the local fluctuations in the concentration of the various species of ions around the macroparticle. These equations, along with Newton's second law for the macroparticle, are the dynamic equations on which we base our developments. The force on the macroparticle is the addition of the solvent friction with its corresponding fluctuating force, as in the Langevin equation for an uncharged particle, plus the electrostatic force on the macroparticle derived from its interaction with the small ions. Although the resulting equations are nonlinear, the description of the diffusion processes from a reference frame fixed to the macroparticle allows its linearization around the equilibrium values of the macroparticle velocity $\mathbf{V}$ and the local concentrations $\langle n_i(\mathbf{r})\rangle_{\text{eq. av.}}$. This linearization is carried out in Sec. III where the properties of the equilibrium solution are discussed. In Sec. IV we show that the linearized equations can be cast as a multivariate Langevin-type equation for the stochastic vector whose components are the components of the macroparticle velocity $\mathbf{V}(t)$ and the fluctuations in the local concentration $\delta n_i(\mathbf{r},t)$. The fluctuation-disspation relation is established between the relaxation matrix of this equation and the correlation function of its fluctuating, purely random, Gaussian stationary term. In addition, the ("local"[10]) Onsager-Casimir relations are also shown to hold at this noncontracted level. According to Berman's contraction theorem,[10] it is not difficult to show that then the fluctuation-dissipation theorem at the contracted level follows. We have chosen to give an alternative demonstration based on the explicit construction of the time correlation function of the fluctuating electrostatic force on the macroparticle. The formal steps in this derivation are summarized in a contraction theorem in the Appendix, which, although more restrictive than Berman's contraction theorem[10] is still general enough to be useful in other applications. The resulting Langevin equation is discussed in Sec. V, where the approximations needed to reproduce Schurr particular results are indicated.

II. THE NONCONTRACTED DESCRIPTION

Our starting point is the following time-evolution equations for the macroparticle velocity $\mathbf{V}(t)$ and for the local concentrations $n_i(\mathbf{x},t)$ $(i=1,2,\ldots,\nu)$ of electrolyte ions:

$$\frac{dV_\alpha(t)}{dt}=-\frac{\zeta^s}{M}V_\alpha(t)+f^s_\alpha(t)-\frac{Q}{M}\int d\mathbf{x}\frac{\sum_{i=1}^{\nu}q_i n_i(\mathbf{x},t)}{\epsilon\,|\mathbf{x}-\mathbf{R}(t)|^3}[\mathbf{x}_\alpha-\mathbf{R}_\alpha(t)]\;, \quad (\alpha=1,2,3) \tag{1}$$

and

$$\frac{\partial n_i(\mathbf{x},t)}{\partial t}=-\nabla\cdot\mathbf{J}_i(\mathbf{x},t)\quad(i=1,2,\ldots,\nu)\;. \tag{2}$$

The first term on the right-hand side of Eq. (1) is the friction of the solvent (M is the mass of the macroparticle) and $\mathbf{f}^s(t)$ the corresponding fluctuating force, which we shall assume to have the same properties as for uncharged macroparticles, so that ζ^s can be approximated by its Stokes expression

$$\zeta^s=6\pi\eta a\;, \tag{3}$$

with η being the viscosity of the solvent, and a the radius of the macroparticle. The fluctuating force $f^s_\alpha(t)$ will be modeled by a Gaussian, stationary, and purely random process,[5,6] with zero mean and correlation function given by

$$\langle f^s_\alpha(t)f^s_\beta(t')\rangle=\gamma^s_{\alpha\beta}\delta(t-t')\quad(\alpha,\beta=1,2,3)\;, \tag{4}$$

where $\gamma^s_{\alpha\beta}$ is related with ζ^s by the following fluctuation-dissipation relation:

$$\gamma^s_{\alpha\beta}=\delta_{\alpha\beta}\frac{2\zeta^s k_B T}{M^2}\;. \tag{5}$$

The third term in Eq. (1) corresponds to the electrostatic force on the macroparticle of charge Q and radius a. q_i is the charge of ions of type i, whose local number concentration is $n_i(\mathbf{x},t)$, and ϵ is the dielectric constant of the solvent. The domain of integration V is defined as $|\mathbf{x}-\mathbf{R}(t)|>a$, and it changes with time, as the macroparticle moves according to

$$\frac{d\mathbf{R}(t)}{dt}=\mathbf{V}(t)\ . \tag{6}$$

The continuity equations for $n_i(\mathbf{x},t)$ in Eq. (2) will be complemented with the pertinent constitutive relations (Fick's Law). Let us notice first that the boundary conditions on $n_i(\mathbf{x},t)$ at the moving surface of the macroparticle lead to an implicit dependence of $n_i(\mathbf{x},t)$ and $\mathbf{J}_i(\mathbf{x},t)$ on $\mathbf{R}(t)$. All this dependence on $\mathbf{R}(t)$ can be eliminated by describing the diffusion equation in a reference frame fixed to the macroparticle, i.e., by using the linear, but time-dependent, transformation, $\mathbf{x}=\mathbf{R}(t)+\mathbf{r}$, in Eq. (2). This equation would then read

$$\frac{\partial n_i^*(\mathbf{r},t)}{\partial t}=\mathbf{V}(t)\cdot\nabla_r n_i^*(\mathbf{r},t)-\nabla_r\cdot\mathbf{J}_i^*(\mathbf{r},t)\ , \tag{7}$$

where

$$n_i^*(\mathbf{r},t)\equiv n_i(\mathbf{R}(t)+\mathbf{r},t) \tag{8}$$

and

$$\mathbf{J}_i^*(\mathbf{r},t)\equiv\mathbf{J}_i(\mathbf{R}(t)+\mathbf{r},t)\ . \tag{9}$$

The fluxes $\mathbf{J}_i^*(\mathbf{r},t)$ have two contributions,

$$\mathbf{J}_i^*(\mathbf{r},t)=\mathbf{J}_i^d(\mathbf{r},t)+\tilde{\mathbf{J}}_i(\mathbf{r},t)\ , \tag{10}$$

where $\tilde{\mathbf{J}}_i$ is a fluctuating flux originating in the thermal fluctuations of the eliminated hydrodynamic variables, and $\mathbf{J}_i^d(\mathbf{r},t)$ are the corresponding "systematic" diffusive fluxes, given by Fick's Law,[4]

$$\mathbf{J}_i^d(\mathbf{r},t)=-\mathscr{L}_{ij}\nabla_r\beta\mu_j(\mathbf{r},t)\quad(i=1,2,\dots,\nu)\ , \tag{11}$$

where summation over repeated indices $(j=1,2,\dots,\nu)$ is implied, $\beta=1/k_BT$, T being the temperature, and $\mu_j(\mathbf{r},t)$ is the electrochemical potential of ions of species j at $\mathbf{r}$. $\mathscr{L}_{ij}$ is a matrix of Onsager phenomenological coefficients,[4] such that $\mathscr{L}_{ij}=\mathscr{L}_{ji}$.

The electrochemical potential is a functional,[11] rather than an ordinary function of the local ionic concentrations $n_1,n_2,\dots,n_\nu$. This is indicated as

$$\beta\mu_j(\mathbf{r},t)=\beta\mu_j^{\text{in}}[\mathbf{r};n(t)]+\beta q_jQ/\epsilon r\ , \tag{12}$$

where the functional dependence is denoted by the square brackets around the argument of $\beta\mu_j^{\text{in}}$, which is the actual ("intrinsic") chemical potential and can be written in general as[12]

$$\beta\mu_j^{\text{in}}[\mathbf{r};n]=\beta\mu_j^0+\ln[n_j(\mathbf{r})]-c_j^{(1)}[\mathbf{r};n]\ . \tag{13}$$

In this equation, $c_j^{(1)}[\mathbf{r};n]$ is a functional of n, such that its functional derivative,

$$\frac{\delta c_j^{(1)}[\mathbf{r};n]}{\delta n_k(\mathbf{r}')}\equiv c_{jk}^{(2)}[\mathbf{r},\mathbf{r}';n] \tag{14}$$

is the two-particle direct correlation function appearing in the Ornstein-Zernike integral equation of the theory of liquids.[13] The simplest expression for $c_{jk}^{(2)}$ is the so-called Debye-Hückel approximation, which in our case reads

$$c_{jk}^{(2)}[\mathbf{r},\mathbf{r}';n]=-\beta q_jq_k/\epsilon\,|\mathbf{r}-\mathbf{r}'|\ . \tag{15}$$

This, however, is only one of several possible approximations,[11] and we shall not commit ourselves to any of them at this stage.

In Eqs. (12)—(15) we have omitted the asterisk that indicates the reference frame to which the position vectors $\mathbf{r}$ and $\mathbf{r}'$ are referred. This is due to the fact that these equations express the functional relationship between the electrochemical potential and the local ionic concentrations, which is independent of the reference frame employed in its description. Similarly, Fick's law in Eq. (11), involving only spatial derivatives, has the same form as in the laboratory-fixed reference frame. From now on we shall drop the asterisk on n_i^* and J_i^*, with the understanding that the position variable in $n_i(\mathbf{r},t)$ and $\mathbf{j}_i(\mathbf{r},t)$ is referred to the center of the macroparticle. In summary, our dynamic equations now read

$$\frac{dV_\alpha(t)}{dt}=-\frac{\zeta^s}{M}V_\alpha(t)+f_\alpha^s(t)-\frac{Q}{\epsilon M}\int_V d\mathbf{r}\sum_i\frac{r_\alpha}{r^3}q_in_i(\mathbf{r},t)\qquad(\alpha=1,2,3) \tag{16}$$

and

$$\frac{\partial n_i(\mathbf{r},t)}{\partial t}=\mathbf{V}(t)\cdot\nabla n_i(\mathbf{r},t)+\sum_j\mathscr{L}_{ij}\nabla^2[\beta\mu_j(\mathbf{r},t)]+f_i^d(\mathbf{r},t)\quad(i,j=1,2,\dots,\nu)\ , \tag{17}$$

where the fluctuating terms $f_i^d(\mathbf{r},t)=-\nabla\cdot\tilde{\mathbf{J}}_i(\mathbf{r},t)$ will be modeled by a Gaussian, stationary, purely random process, with zero mean and correlation function given by

$$\langle f_i^d(\mathbf{r},t)f_j^d(\mathbf{r}',t')\rangle=\gamma_{ij}^d(\mathbf{r},\mathbf{r}')\delta(t-t')\quad(i,j=1,2,\dots,\nu)\ . \tag{18}$$

III. EQUILIBRIUM SOLUTION AND LINEARIZED EQUATIONS

At equilibrium, the average value of $V_\alpha(t)$ is zero, whereas the equilibrium average of $n_i(\mathbf{r},t)$, denoted as $\langle n_i(\mathbf{r})\rangle_{\text{eq. av.}}$ is such that

$$\langle\mathbf{J}_i^d(r,t)\rangle_{\text{eq. av.}}=0\ . \tag{19}$$

From Eqs. (11)—(14), we see that $\langle n_i(r)\rangle_{\text{eq. av.}}$ must be such that

$$\nabla\langle\beta\mu_i(\mathbf{r})\rangle_{\text{eq. av.}}=\sum_j\int_V E_{ij}(\mathbf{r},\mathbf{r}')\nabla'\langle n_j(\mathbf{r}')\rangle_{\text{eq. av.}}d\mathbf{r}'+\beta\nabla\left[\frac{q_iQ}{\epsilon r}\right]=0\ , \tag{20}$$

where

$$E_{ij}(\mathbf{r},\mathbf{r}')\equiv\left[\frac{\delta\mu_i^{\text{in}}[\mathbf{r};n]}{\delta n_j(\mathbf{r}')}\right]_{n=\langle n\rangle_{\text{eq. av.}}}=\frac{\delta_{ij}\delta(\mathbf{r}-\mathbf{r}')}{\langle n_i(\mathbf{r})\rangle_{\text{eq. av.}}}-c_{ij}^{(2)}[\mathbf{r},\mathbf{r}';\langle n\rangle_{\text{eq. av.}}]\ . \tag{21}$$

The inverse of this matrix $E_{ij}(\mathbf{r},\mathbf{r}')$, defined by the equation

$$\sum_j \int E_{ij}(\mathbf{r},\mathbf{r}')\sigma_{jk}(\mathbf{r}',\mathbf{r}'')d\mathbf{r}'=\delta_{ik}\delta(\mathbf{r}-\mathbf{r}'') \ , \tag{22}$$

is the matrix of static correlation functions. These are defined as

$$\sigma_{ij}(\mathbf{r},\mathbf{r}')\equiv\langle[n_i(\mathbf{r})-\langle n_i(\mathbf{r})\rangle_{\text{eq. av.}}]\times[n_j(\mathbf{r}')-\langle n_j(\mathbf{r}')\rangle_{\text{eq. av.}}]\rangle_{\text{eq. av.}} \ . \tag{23}$$

An alternative notation for $\sigma_{ij}(\mathbf{r},\mathbf{r}')$ is

$$\sigma_{ij}(\mathbf{r},\mathbf{r}')=\langle n_i(\mathbf{r})\rangle_{\text{eq. av.}}\delta_{ij}\delta(\mathbf{r}-\mathbf{r}')+\langle n_i(\mathbf{r})\rangle_{\text{eq. av.}}\langle n_j(\mathbf{r}')\rangle_{\text{eq. av.}}h_{ij}(\mathbf{r},\mathbf{r}') \ , \tag{24}$$

which, when inserted in Eq. (22), along with Eq. (21), shows that Eq. (22) is another form of writing the Ornstein-Zernike equation for inhomogeneous fluids,[12]

$$h_{ij}(\mathbf{r},\mathbf{r}')=c_{ij}(\mathbf{r},\mathbf{r}')+\sum_{k=1}^{\nu}\int h_{ik}(\mathbf{r},\mathbf{r}'')\langle n_k(\mathbf{r})\rangle_{\text{eq. av.}}c_{kj}(\mathbf{r}'',\mathbf{r}')d\mathbf{r}'' \ , \tag{25}$$

where $c_{ij}(\mathbf{r},\mathbf{r}')$ abbreviates $c_{ij}^{(2)}[\mathbf{r},\mathbf{r}';n]$. This equation requires an additional "closure" relation between $c(\mathbf{r},\mathbf{r}')$ and $h(\mathbf{r},\mathbf{r}')$, which, along with Eqs. (12)—(14) and (20)—(25) leads to the simultaneous solution for $\langle n_i(\mathbf{r})\rangle_{\text{eq. av.}}$ and $\sigma_{ij}(\mathbf{r},\mathbf{r}')$ and all other quantities involved in those equations. Although this is in general a rather complicated problem, it can be shown,[11(a)] for example, that the nonlinear Poisson-Boltzmann equation for the electrical double layer around the macroparticles results from these equations when the Debye-Hückel approximation, Eq. (15), is employed as the closure relation.

Assuming that the equilibrium solutions $\langle n_i(r)\rangle_{\text{eq. av.}}$ are available, we now linearize the time-evolution equations [Eqs. (16) and (17)] around $\langle \mathbf{V}\rangle_{\text{eq. av.}}$ (which vanishes) and $\langle n_i(\mathbf{r})\rangle_{\text{eq. av.}}$. Substituting

$$n_i(\mathbf{r},t)=\langle n_i(\mathbf{r})\rangle_{\text{eq. av.}}+\delta n_i(\mathbf{r},t) \tag{26}$$

in these equations, and keeping only linear terms in $\delta n_i(\mathbf{r},t)$ and $\mathbf{V}(t)$, we get

$$\frac{dV_\alpha(t)}{dt}=-\frac{\zeta^s}{M}V_\alpha(t)+f_\alpha^s(t)-\frac{Q}{M\epsilon}\int_V d\mathbf{r}\sum_i\frac{r_\alpha q_i\delta n_i(\mathbf{r},t)}{r^3} \tag{27}$$

and

$$\frac{\partial\delta n_i(\mathbf{r},t)}{\partial t}=[\nabla\langle n_i(\mathbf{r})\rangle_{\text{eq. av.}}]\cdot\mathbf{V}(t)+\sum_k\mathscr{L}_{ik}\nabla_r^2\int_V\sum_j E_{kj}(\mathbf{r},\mathbf{r}')\delta n_j(\mathbf{r}',t)d\mathbf{r}'+f_i^d(\mathbf{r},t) \ , \tag{28}$$

where use has been made of the following relationship:

$$\delta\beta\mu_i(\mathbf{r},t)=\sum_j\int E_{ij}(\mathbf{r},\mathbf{r}')\delta n_j(\mathbf{r},t)d\mathbf{r}' \tag{29}$$

between the fluctuations in the local chemical potential and the fluctuations in local concentration. This is an expression of the local equilibrium assumption implicit in our theory.[11] In addition, we have used the fact that the average electrostatic force on the macroparticle is zero at equilibrium.

To conclude this section, we notice that the third term in Eq. (27), being of a mechanical nature, does not have associated an additional fluctuating force, as opposed to the "solvent" friction term in that equation, which is related with the fluctuating force $\mathbf{f}^s(t)$ by the fluctuation-dissipation relation in Eqs. (4) and (5). In a similar manner, the first term in Eq. (28) has also a purely mechanical origin, and is not associated with any fluctuating term in that equation. However, the second term, describing diffusion, is related with the fluctuating "forces" $f_i^d(\mathbf{r},t)$ via a fluctuation-dissipation relation, which completes the definition of the stochastic properties of this fluctuating term in Eq. (18). Such a fluctuation-dissipation relation reads[14]

$$\gamma_{ij}^d(\mathbf{r},\mathbf{r}')=-2\mathscr{L}_{ij}\nabla_r^2\delta(\mathbf{r}-\mathbf{r}') \ . \tag{30}$$

Finally, we should point out that our equations for $\langle n_i(\mathbf{r})\rangle_{\text{eq. av.}}$ and $\delta n_i(\mathbf{r},t)$ should be complemented with corresponding boundary conditions which reflect the impenetrability of the macroparticle for the small ions, and pertinent electrostatic boundary conditions. However, within the particular approximations that we shall introduce later the explicit consideration of these conditions will be unnecessary.

IV. FLUCTUATION DISSIPATION AND ONSAGER-CASIMIR RELATIONS AT THE NONCONTRACTED LEVEL

The derivation of the Langevin equation for the charged spherical macroparticle starts from the time-evolution equations for $\mathbf{V}(t)$ and $\delta n_i(\mathbf{r},t)$ in Eqs. (27) and (28). In essence, we want to solve Eq. (28) for $\delta n_i(\mathbf{r},t)$ and insert it in Eq. (27). An interesting procedure to achieve this makes use of the linear irreversible thermodynamic theory of fluctuations.[4,6] We first notice that Eqs. (27) and (28) can be written in terms of the stochastic vector

$$a\equiv(V^1,V^2,V^3,\delta n_1(\mathbf{r}),\delta n_2(\mathbf{r}),\ldots,\delta n_\nu(\mathbf{r})) \tag{31}$$

as the following stochastic differential equation:

$$\frac{da(t)}{dt}=-Ga(t)+f(t) \ , \tag{32}$$

where the fluctuating force $f(t)$ has components

$$f\equiv(f_1^s,f_2^s,f_3^s,f_1^d(\mathbf{r}),f_2^d(\mathbf{r}),\ldots,f_\nu^d(\mathbf{r})) \ . \tag{33}$$

From Eqs. (27) and (28), we can see that the relaxation matrix G can be written as

$$G\equiv\begin{bmatrix}G_{11} & G_{12}\\ G_{21} & G_{22}\end{bmatrix} \ , \tag{34}$$

where the submatrices G_{ij} are defined as

$$(G_{11})_{\alpha\beta}\equiv\frac{\zeta_s}{M}\delta_{\alpha\beta} \quad (\alpha,\beta=1,2,3) \ , \tag{35}$$

$$(G_{12})_{\alpha,i\mathbf{r}} \equiv \frac{Qq_i r_\alpha}{M\epsilon r^3}$$

$$(\alpha=1,2,3;\ i=1,2,\ldots,\nu;\ \mathbf{r}\in V)\ , \tag{36}$$

$$(G_{21})_{i\mathbf{r},\beta} \equiv -[\nabla_\beta \langle n_i(\mathbf{r})\rangle_{\text{eq. av.}}]$$

$$(i=1,2,\ldots,\nu;\ \mathbf{r}\in V;\ \beta=1,2,3)\ , \tag{37}$$

$$(G_{22})_{i\mathbf{r},j\mathbf{r}'} \equiv -\sum_k \mathscr{L}_{ik}\nabla_r^2 E_{kj}(\mathbf{r},\mathbf{r}')$$

$$(i,j=1,2,\ldots,\nu;\ \mathbf{r},\mathbf{r}'\in V)\ . \tag{38}$$

The matrix product in Eq. (32) involves summation on common discrete indices $\alpha=1,2,3$, $i=1,2,\ldots,\nu$, and integration over the volume $V(|\mathbf{r}|>a)$ for the common continuous indices $\mathbf{r}$ or $\mathbf{r}'$. The properties of the fluctuating forces $\mathbf{f}^s(t)$ and $f_i^d(\mathbf{r},t)$ assumed before can now be enunciated in terms of the composite fluctuating vector $f(t)$ defined in Eq. (33). Thus, $f(t)$ is a vector of stochastic Gaussian, stationary, purely random variables, with zero mean and correlation function given by

$$\langle f(t)f^\dagger(t')\rangle = \Gamma\delta(t-t')\ , \tag{39}$$

where the transpose of f has been indicated as $f^\dagger$. The matrix Γ can be written as

$$\Gamma = \begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} = \begin{bmatrix} \gamma^s & 0 \\ 0 & \gamma^d \end{bmatrix}\ , \tag{40}$$

where the partitioning of Γ is similar to that of G in Eq. (34), and γ^s and γ^d are the matrices appearing in Eqs. (4) and (18). In addition, we have assumed that the correlations between $\mathbf{f}^s(t)$ and $f_i^d(\mathbf{r},t')$ $(i=1,2,\ldots,s)$ are zero for all times t and t'.

With these assumptions for the fluctuating force $f(t)$, and from the stochastic differential equation for $a(t)$ in Eq. (32), we can conclude that $a(t)$ is a multivariate Gaussian, stationary, Markov stochastic process[12] (i.e., an Ornstein-Uhlenbeck stochastic process), whose various probability distribution functions can be written in terms of the matrices G and Γ. In particular, one can calculate $P(at\,|\,a_0)$, the conditional probability that the stochastic variable $a(t)$ has values a at time t, given the values a_0 at time zero. For very large values of t, this function must approach the equilibrium distribution $W^{\text{eq}}(a)$, which is given by the Boltzmann-Planck distribution

$$W^{\text{eq}}(a) = (\text{const})\exp(-a^\dagger E a)\ , \tag{41}$$

with the matrix E being the matrix of second derivatives of the entropy. The equilibrium correlation matrix

$$\sigma = \langle aa^\dagger\rangle_{\text{eq. av.}} \equiv \int W^{\text{eq}}(a)aa^\dagger da \tag{42}$$

can be calculated from Eq. (41), yielding

$$\sigma E = \mathbb{1}\ . \tag{43}$$

In our application, the equilibrium correlations are given by

$$\sigma = \begin{bmatrix} \sigma_{11} & \sigma_{12} \\ \sigma_{21} & \sigma_{22} \end{bmatrix}\ , \tag{44}$$

with

$$(\sigma_{11})_{\alpha\beta} = \langle V_\alpha V_\beta\rangle_{\text{eq. av.}} = \delta_{\alpha\beta}\frac{k_\beta T}{M}\ , \tag{45}$$

$$(\sigma_{12})_{\alpha,i\mathbf{r}} = (\sigma_{21})_{i\mathbf{r},\alpha} = \langle V_\alpha \delta n_i(\mathbf{r})\rangle_{\text{eq. av.}} = 0\ , \tag{46}$$

and

$$(\sigma_{22})_{i\mathbf{r},j\mathbf{r}'} = \sigma_{ij}(\mathbf{r},\mathbf{r}')\ , \tag{47}$$

where the equipartition theorem has been used in Eq. (45), and the lack of correlation between V^α and $\delta n_i(\mathbf{r})$ in Eq. (46) is a consequence of the fact that $\delta n_i(\mathbf{r})$ depends only on position variables which are statistically uncorrelated with momentum variables at equilibrium. In Eq. (47), $\sigma_{ij}(\mathbf{r},\mathbf{r}')$ refers to the definition in Eq. (22) above. In a similar manner, and using Eq. (43), we can write the matrix E as

$$E = \begin{bmatrix} E_{11} & E_{12} \\ E_{21} & E_{22} \end{bmatrix}\ , \tag{48}$$

with

$$(E_{11})_{\alpha\beta} = \frac{M}{k_B T}\delta_{\alpha\beta}\ , \tag{49}$$

$$(E_{12})_{\alpha,i\mathbf{r}} = (E_{21})_{i\mathbf{r},\alpha} = 0\ , \tag{50}$$

and

$$(E_{22})_{i\mathbf{r},j\mathbf{r}'} = E_{ij}(\mathbf{r},\mathbf{r}')\ , \tag{51}$$

where $E_{ij}(\mathbf{r},\mathbf{r}')$ was defined in Eq. (21).

The requirement that $P(at\,|\,a_0)$ approaches $W^{\text{eq}}(a)$ as $t\to\infty$ leads to the generalized fluctuation-dissipation theorem,[6] which reads

$$G\sigma + \sigma G^\dagger = \Gamma\ . \tag{52}$$

Alternatively, writing the relaxation matrix G as

$$G = k_B L E\ , \tag{53}$$

the fluctuation-dissipation relation in Eq. (52) can also be written as

$$\Gamma = k_B(L + L^\dagger)\ . \tag{54}$$

In Onsager's theory of irreversible thermodynamics,[14] L is the matrix of transport coefficients whose symmetry constitutes his celebrated reciprocity relations. In general, however, the relaxation matrix may have contributions due to streaming or mechanical terms in the evolution equations for a [like the first terms of Eq. (28), and the third in Eq. (27)]. These contributions destroy the symmetry of L. In a correct application of the theory, however, these nondissipative terms should only contribute to the antisymmetric part of L, so that if we split L in its symmetric and antisymmetric parts,

$$L = L^s + L^a\ , \tag{55}$$

Eq. (54) reads

$$\Gamma = 2k_B L^s\ . \tag{56}$$

We now demonstrate that in our particular application the fluctuation-dissipation relation in Eq. (56) is consistent, and in fact, equivalent to the fluctuation-dissipation relations, previously assumed in Eqs. (5) and (30) above. In addition, we demonstrate that, indeed, the mechanical and streaming terms in Eqs. (27) and (28) contribute only to the antisymmetric part of L. Let us first identify the matrix L of our problem. Using Eqs. (53), (43), (34), and (44), we find that

$$L=\begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix}, \tag{57}$$

where

$$(L_{11})_{\alpha\beta}=\frac{\zeta^s T}{M^2}\delta_{\alpha\beta}, \tag{58}$$

$$(L_{12})_{\alpha,i\mathbf{r}}=\sum_j \int_V \frac{Qq_i r'_\alpha}{k_B M \epsilon r'^3}\sigma_{ij}(\mathbf{r},\mathbf{r}')dr', \tag{59}$$

$$(L_{21})_{i\mathbf{r},\beta}=-\frac{T}{M}\nabla_\beta \langle n_i(\mathbf{r})\rangle_{\text{eq. av.}}, \tag{60}$$

$$(L_{22})_{i\mathbf{r},j\mathbf{r}'}=-\frac{1}{k_B}\mathscr{L}_{ij}\nabla_r^2\delta(\mathbf{r}-\mathbf{r}') . \tag{61}$$

Now, let us see that the following property of the above submatrices L_{12} and L_{21} holds:

$$L_{21}^{\dagger}=-L_{12} . \tag{62}$$

From Eq. (20) of Sec. III, which defines $\langle n_i(\mathbf{r})\rangle_{\text{eq. av.}}$ we have that

$$\sum_j \int_V d\mathbf{r}' E_{kj}(\mathbf{r}'',\mathbf{r}')\nabla'\langle n_j(\mathbf{r}')\rangle_{\text{eq. av.}}=\frac{\beta q_k Q\mathbf{r}''}{\epsilon(r'')^3} . \tag{63}$$

Multiplying by $\sigma_{ik}(\mathbf{r},\mathbf{r}'')$ and integrating over $\mathbf{r}''$, summing on k, and using Eq. (22), we have

$$\nabla\langle n_i(\mathbf{r})\rangle_{\text{eq. av.}}=\sum_k \int_V \frac{q_k Q\mathbf{r}'}{\epsilon k_B T(r')^3}\sigma_{ik}(\mathbf{r}',\mathbf{r})d\mathbf{r}' . \tag{64}$$

The comparison of this equation with the definitions in Eq. (59) and (60) demonstrates that

$$\begin{aligned}(L_{21}^{\dagger})_{\alpha,i\mathbf{r}}=(L_{21})_{i\mathbf{r},\alpha}&=-\frac{T}{M}\nabla_\alpha\langle n_i(\mathbf{r})\rangle_{\text{eq. av.}}\\ &=-(L_{12})_{\alpha,i\mathbf{r}} .\end{aligned} \tag{65}$$

On the other hand, it is clear from Eqs. (58) and (61) that both L_{11} and L_{22} are symmetric. Thus,

$$L^s=\begin{bmatrix} L_{11} & 0 \\ 0 & L_{22} \end{bmatrix} \text{ and } L^a=\begin{bmatrix} 0 & L_{12} \\ L_{21} & 0 \end{bmatrix} \tag{66}$$

and now it is trivial to see that the fluctuation-dissipation theorem in Eq. (56) is equivalent to the fluctuation-dissipation relations assumed in Eqs. (5) and (30). In addition, the lack of correlation between $\mathbf{f}^s(t)$ and $f_i(\mathbf{r},t)$, assumed in Eq. (40), is actually a consequence of the antisymmetric relationship between L_{12} and L_{21}. This relationship, in its turn, is a consequence of the nondissipative nature of the mechanical and streaming terms of the relaxation equations. Its very demonstration indicates the self-consistency of the linearization procedure carried out in the previous section. These symmetry properties of the matrix L are called Onsager-Casimir relations. According to Berman's contraction theorem,[10] they are essential to demonstrate the fluctuation-dissipation relation at the contracted level.

V. THE CONTRACTED DESCRIPTION AND THE RESULTING LANGEVIN EQUATION

In the previous section we showed that the time evolution equations that govern the dynamics of the Brownian motion of a charged macroparticle can be written, within well-defined approximations, as a multivariate stochastic differential equation of the Langevin type for a vector of random variables $a(t)$. In general, the elimination of some of the components of $a(t)$ leads to a Langevin equation with memory for the vector whose components are the remaining variables (V_1, V_2, and V_3 in our case). The memory function involved in this equation is proportional to the time correlation function of the resulting fluctuating force. Such fluctuation-dissipation relation can be shown to follow as a direct consequence of the fluctuation-dissipation relation holding at the uncontracted level. In the Appendix, these statements are formally enunciated as a rather general theorem. Considering the content of the last section, it is easy to see that the hypothesis of such theorem are fully satisfied in our particular application. Thus, we now quote the most relevant consequences of that theorem as they apply to our problem. Taking $a=(V_1,V_2,V_3,\delta n_i(\mathbf{r}),\ldots,\delta n_\nu(\mathbf{r}))$ and $a_1=(V_1,V_2,V_3)$, we see from Eqs. (A9) and (A10) that the Langevin equation resulting from the process of contraction is

$$\begin{aligned}\frac{dV_\alpha(t)}{dt}=&-\frac{\zeta^s}{m}V_\alpha(t)+f_\alpha^s(t)\\ &-\sum_\beta \int_0^t K_{\alpha\beta}(t-t')V_\beta(t')dt'+F_\alpha(t) ,\end{aligned} \tag{67}$$

where the matrix $K(t)$ is defined as

$$K(t)=-G_{12}e^{-G_{22}|t|}G_{21} \tag{68}$$

and $F_\alpha(t)$ is the fluctuating force originated by the spontaneous, thermal distortion of the ionic atmosphere around the macroparticle. According to the contraction theorem, and to the assumptions summarized in the preceding section, this force is a Gaussian, stationary process with zero mean and correlation function given by the following fluctuation-dissipation relation [see Eqs. (A11) and (45)]

$$\langle F_\alpha(t)F_\beta(t')\rangle=\frac{k_B T}{M}K_{\alpha\beta}(t-t') . \tag{69}$$

Due to the spherical symmetry, $K_{\alpha\beta}$ is expected to be diagonal and isotropic, i.e.,

$$K_{\alpha\beta}(t)=k(t)\delta_{\alpha\beta} . \tag{70}$$

Using Eqs. (35)—(38) and (61), we have that

$$k(t)=\int_V d\mathbf{r}\int_V d\mathbf{r}'\sum_{i,j}\frac{Qq_i}{M\epsilon}\frac{z}{r^3}(e^{-G_{22}|t|})_{i\mathbf{r},j\mathbf{r}'}\times\frac{\partial}{\partial z'}\langle n_j(\mathbf{r}')\rangle_{\text{eq. av.}}\,, \tag{71}$$

with

$$(G_{22})_{i\mathbf{r},j\mathbf{r}'}=-\sum_k \mathscr{L}_{ik}\nabla_r^2 E_{kj}(\mathbf{r},\mathbf{r}')\,. \tag{72}$$

The statistical properties of the random motion generated by the Langevin equation of the type above have been studied.[15] Thus, it is known that $\mathbf{V}(t)$ is a Gaussian, but non-Markovian stochastic process. Nevertheless, because of its Gaussian nature, all its statistical properties are determined by its time correlation function,

$$c(t)=\langle \mathbf{V}(t)\cdot\mathbf{V}(0)\rangle\,. \tag{73}$$

The Laplace transform of this function can be obtained from the Langevin equation above:

$$\hat{c}(z)\equiv\int_0^\infty e^{-zt}c(t)dt=\left[z+\frac{\zeta^s}{M}+\hat{k}(z)\right]^{-1}\langle\mathbf{V}(0)\cdot\mathbf{V}(0)\rangle\,, \tag{74}$$

where

$$\hat{k}(z)=\int_0^\infty e^{-zt}k(t)dt=-[G_{12}(z\mathbb{1}+G_{22})^{-1}G_{21}]_{z,z}\,. \tag{75}$$

The self-diffusion constant D_s can be defined in terms of $\hat{c}(z)$ as

$$D_s=\tfrac{1}{3}\int_0^\infty\langle\mathbf{V}(t)\cdot\mathbf{V}(0)\rangle dt=\tfrac{1}{3}\hat{c}(0) \tag{76}$$

and, using Eq. (74) with $\langle\mathbf{V}(0)\cdot\mathbf{V}(0)\rangle=3k_BT/M$, as

$$D_s=k_BT/\zeta\equiv k_BT/(\zeta^s+\zeta^{\text{el}})\,, \tag{77}$$

with

$$\zeta^{\text{el}}\equiv M\hat{k}(z=0)=-M(G_{12}G_{22}^{-1}G_{21})_{z,z}\,, \tag{78}$$

where Eq. (75) was also used.

The actual evaluation of the memory function $k(t)$, the velocity autocorrelation function, and the electrostatic friction ζ^{el} requires the solution of the equilibrium properties $\langle n_i(\mathbf{r})\rangle_{\text{eq. av.}}$ and $E_{ij}(r,r')$. This is in general a rather complicated problem, but well-defined models and approximations, nowadays standard in the statistical thermodynamic theory of liquids, render this aspect of the problem perfectly manageable, and a detailed account of calculations of this type will be reported later. For the time being, and to conclude this paper, we shall indicate that one of the simplest calculations that can be done starting from the general expression for ζ^{el} above leads to the result of the theory of Schurr[2] for the electrostatic friction. The simplifications needed to reproduce Schurr's results are the following: (a) two species of small ions; (b) $q_2=-q_1=q$; (c) same mobility, such that $\mathscr{L}_{ij}=D^0n\delta_{ij}$ (D^0 is the diffusion constant of small ions, n the bulk number concentration of ions of either type); (d) Debye-Hückel interionic correlations, disregarding the presence of the macroparticle, i.e.,

$$E_{ij}(\mathbf{r},\mathbf{r}')=\frac{\delta_{ij}\delta(\mathbf{r}-\mathbf{r}')}{n}+\frac{\beta q^2(-1)^{i+j}}{\epsilon|\mathbf{r}-\mathbf{r}'|} \tag{79}$$

[compare with Eq. (21)], and

$$\sigma_{ij}(\mathbf{r},\mathbf{r}')=n\delta_{ij}\delta(\mathbf{r}-\mathbf{r}')-\frac{\beta q^2(-1)^{i+j}}{\epsilon|\mathbf{r}-\mathbf{r}'|}e^{-\kappa|\mathbf{r}-\mathbf{r}'|}\,, \tag{80}$$

with

$$\kappa^2=8\pi\beta nq^2/\epsilon\,;$$

and (e) use of these approximations in the following expression for ζ^{el},

$$\zeta^{\text{el}}=\frac{M^2}{k_B^2T}[G_{12}(\sigma_{22}L_{22}^{-1}\sigma_{22})G_{12}^\dagger]_{z,z}\,. \tag{81}$$

This is formally equivalent to Eq. (78). Carrying out the integrals involved in the matrix operations in Eq. (81), we arrive at Schurr's result:

$$\zeta^{\text{el}}=\left[\frac{Q^2}{12\epsilon D^0\kappa a^2}\right][1-e^{-2\kappa a}(1+2\kappa a)]\,. \tag{82}$$

The comparison of this result with experimental measurements seems to indicate that even though there is some qualitative agreement, a somewhat reduced value of Q has to be used in order to fit the experimental data. It would be interesting to see if the use of a more accurate approximation than the Debye-Hückel could lead to a better agreement between theory and experiment. The use of our results render such calculations perfectly feasible.

VI. CONCLUDING REMARKS

In this paper we have presented a derivation of the electrostatic terms of the Langevin equation for a charged macroparticle diffusing in an electrolyte solution. In this derivation we have calculated the fluctuating electrostatic force on the macroparticle produced by the spontaneous distortion of its ionic atmosphere. As the source of the latter, we considered the fluctuations in the local charge density around the macroparticle driven by diffusion, and have neglected any correlation with the local fluctuations of total density driven by hydrodynamic fluxes. In this manner, the treatment of the electrostatic interactions were left as the main complication. Concepts borrowed from the equilibrium theory of inhomogeneous fluids provided a useful formal tool to describe these interactions. As a result, expressions were derived for the memory function appearing in the Langevin equation in terms of the equilibrium distribution of the small ions around the macroparticle and their static spatial correlations. As a simple illustration, we have evaluated the electrostatic contribution to the friction coefficient ζ^{el} within the Debye-Hückel approximation, and have found that this corresponds to the results of Schurr's theory. Our derivation, however, seems more straightforward (once the Langevin equation has been derived), and more economical in the assumptions and simplifications involved. In addition, the consideration of more realistic models (e.g., charged hard spheres) and more accurate approximations for the description of interionic correlations is immediate from our results. Simplifications such as the symmetry of the charge of the small ions ($q_1=-q_2$) and the lack of dynamic coupling between the diffusion of small ions of different type ($L_{12}=0$) can also be lifted with the use of our results. A report on this type of calculation will be given latter.

APPENDIX: THE CONTRACTION THEOREM

In this appendix we state, and outline the demonstration of, the following.

Theorem. Let $a(t)$ be a vector of N random components, satisfying the stochastic differential equation

$$\frac{\partial a(t)}{\partial t}=-Ga(t)+f(t) \tag{A1}$$

in which G is a positive-definite relaxation matrix and $f(t)$ is an N-dimensional vector of Gaussian, stationary, and purely random "forces," with zero mean and correlation function given by

$$\langle f(t)f^{\dagger}(t')\rangle=\Gamma\delta(t-t') \,. \tag{A2}$$

Let a fluctuation-dissipation relation hold between G and Γ, such that

$$G\sigma+\sigma G^{\dagger}=\Gamma \tag{A3}$$

in which

$$\sigma\equiv\lim_{t\to\infty}\langle a(t)a^{\dagger}(t)\rangle \,. \tag{A4}$$

Let us call $a_1(t)$ the n-dimensional vector whose components are the first n components of a, and similarly for f. Let us partition the matrix G as

$$G=\begin{bmatrix} G_{11} & G_{12} \\ G_{21} & G_{22}\end{bmatrix} , \tag{A5}$$

in which G_{11} is $n\times n$ dimensional, G_{12} is $n\times(N-n)$ dimensional, etc., and similarly for the other $N\times N$-dimensional matrices. For simplicity, let us assume that there are no static correlations between the components of $a_1(t)$ and the other variables in a, i.e., that

$$\sigma_{12}=\sigma_{21}^{\dagger}=0 \,. \tag{A6}$$

Finally, let the matrix L, defined as

$$L=\frac{1}{k_B}G\sigma , \tag{A7}$$

be such that

$$L_{12}=-L_{21}^{\dagger},\; L_{11}=L_{11}^{\dagger},\; L_{22}=L_{22}^{\dagger} \,. \tag{A8}$$

Then, the random vector $a_1(t)$ satisfies the following stochastic differential equation:

$$\frac{\partial a_1(t)}{\partial t}=-G_{11}a_1(t)+f_1(t)-\int_0^t K(t-t')a_1(t')+F(t) , \tag{A9}$$

where K is an $n\times n$-dimensional matrix given by

$$K(t)=-G_{12}e^{-G_{22}|t|}G_{21} \tag{A10}$$

and $F(t)$ is a Gaussian, stationary, random vector, uncorrelated with $f_1(t)$, with zero mean and correlation function given by

$$\langle F(t)F^{\dagger}(t')\rangle=K(t-t')\sigma_{11} \,. \tag{A11}$$

Demonstration. Let us define the projection operators

$$P\equiv\begin{bmatrix} \mathbb{1}_{11} & 0 \\ 0 & 0\end{bmatrix} \text{ and } Q=\mathbb{1}-P \tag{A12}$$

in which $\mathbb{1}$ and $\mathbb{1}_{11}$ are the $N\times N$ and $n\times n$-dimensional identity matrices, and the 0's are matrices with all its elements being zero. Let us also define

$$a^{(1)}\equiv Pa \text{ and } a^{(2)}\equiv Qa \tag{A13}$$

and similarly for f. Thus,

$$(a^{(1)})^{\dagger}=(a_1^{\dagger},0^{\dagger}) \text{ and } (a^{(2)})^{\dagger}=(0^{\dagger},a_2^{\dagger}) , \tag{A14}$$

where the 0's are vectors whose components are zero. Multiplying Eq. (A1) by Q, we can write

$$\frac{\partial a^{(2)}(t)}{\partial t}=-QGa^{(1)}(t)-QGa^{(2)}(t)+f^{(2)}(t) , \tag{A15}$$

whose solution, inserted in the corresponding equation for $a^{(1)}(t)$, leads to the following equation for $a^{(1)}(t)$:

$$\begin{aligned}\frac{\partial a^{(1)}(t)}{\partial t}&=-PGa^{(1)}(t)+\int_0^t PGe^{-QG(t-\tau)}QGa^{(1)}(\tau)d\tau\\ &\quad+\left[-PGe^{-QGt}a^{(2)}(0)+f^{(1)}(t)-\int_0^t PGe^{-QG(t-\tau)}f^{(2)}(\tau)d\tau\right] .\end{aligned} \tag{A16}$$

This is an equation for the N components of $a^{(1)}(t)$, $(N-n)$ of which are zero. Using the properties of P, we can write the equation for the first n components of $a^{(1)}(t)$, i.e., for the vector $a_1(t)$, as

$$\frac{\partial a_1(t)}{\partial t}=-G_{11}a_1(t)+f_1(t)+\int_0^t G_{12}e^{-G_{22}(t-\tau)}G_{21}A_1(\tau)d\tau+\left[-G_{12}e^{-G_{22}t}a_2(0)-\int_0^t G_{12}e^{-G_{22}(t-\tau)}f_2(\tau)d\tau\right] \tag{A17}$$

from which Eqs. (A9) and (A10) follow, with

$$F(t)=-G_{12}e^{-G_{22}t}a_2(0)-\int_0^t G_{12}e^{-G_{22}(t-\tau)}f_2(\tau)d\tau \ . \tag{A18}$$

Thus, $F(t)$ is a linear combination of the random variables $a_2(0)$ and $f_2(\tau)$ $(0\leq\tau\leq t)$. From Eqs. (A2), (A3), and (A7), we have that

$$\langle f(t)f(t')^\dagger\rangle=k_B(L+L^\dagger)\delta(t-t') \ , \tag{A19}$$

so that, because of Eq. (A8), $f_1(t)$ and $f_2(t')$ are uncorrelated. For $a_2(0)$ we take its equilibrium distribution, i.e., $a_2(0)$ is uncorrelated with $f(t)$, and has a Gaussian distribution with zero mean and covariance given by

$$\langle a_2(0)a_2^\dagger(0)\rangle=\sigma_{22} \ . \tag{A20}$$

Thus, we conclude that $F(t)$ is such that

$$\langle F(t)f_1(t')\rangle=0 \tag{A21}$$

and that $F(t)$ is a Gaussian stochastic processes with zero mean. We now evaluate its correlation function $\langle F(t)F(t')^\dagger\rangle$. Using Eq. (A18), we have that

$$\langle F(t)F^\dagger(t')\rangle=G_{12}e^{-G_{22}t}\langle a_2(0)a_2^\dagger(0)\rangle e^{-(G_{22})^\dagger t'}(G_{12})^\dagger+\int_0^t d\tau\int_0^{t'}d\tau' G_{12}e^{-G_{22}(t-\tau)}\langle f_2(\tau)f_2^\dagger(\tau')\rangle e^{-(G_{22})^\dagger(t'-\tau')}(G_{12})^\dagger \ . \tag{A22}$$

The second term in the right-hand side of this equation can also be written, using Eq. (A19) and (A8), as

$$\int_0^t d\tau\int_0^{t'}d\tau' G_{12}e^{-G_{22}(t-\tau)}2k_BL_{22}e^{-(G_{22})^\dagger(t'-\tau')}(G_{12})^\dagger\delta(t-\tau') \tag{A23}$$

and since

$$\begin{aligned}L_{22}e^{-(G_{22})^\dagger(t'-\tau')}&=L_{22}e^{-(k_BL_{22}\sigma_{22}^{-1})^\dagger(t'-\tau')}\\&=e^{-(k_BL_{22}\sigma_{22}^{-1})(t'-\tau')}L_{22} \ ,\end{aligned} \tag{A24}$$

as

$$\begin{aligned}&G_{12}e^{-G_{22}(t+t')}\left[\int_0^t d\tau\int_0^{t'}d\tau' e^{G_{22}(\tau+\tau')}\delta(\tau-\tau')\right]2k_BL_{22}(G_{12})^\dagger\\&=G_{12}e^{-G_{22}(t+t')}(e^{2G_{22}t_<}-1)(2G_{22})^{-1}2k_BL_{22}(G_{12})^\dagger\\&=G_{12}e^{-G_{22}|t-t'|}(2G_{22})^{-1}2k_BL_{22}(G_{12})^\dagger-G_{12}e^{-G_{22}(t+t')}(2G_{22})^{-1}2k_BL_{22}(G_{12})^\dagger\\&=G_{12}e^{-G_{22}|t-t'|}\sigma_{22}(G_{12})^\dagger-G_{12}e^{-G_{22}(t+t')}\sigma_{22}(G_{12})^\dagger \ ,\end{aligned} \tag{A25}$$

where we have used the fact that

$$(2G_{22})^{-1}2k_BL_{22}=(2k_BL_{22}\sigma_{22}^{-1})^{-1}2k_BL_{22}=\sigma_{22} \ . \tag{A26}$$

Similarly, using Eq. (A20), we see that the first term on the right-hand side of Eq. (A22) can also be written as

$$G_{12}e^{-G_{22}t}\sigma_{22}e^{-(G_{22})^\dagger t'}(G_{12})^\dagger=G_{12}e^{-G_{22}(t+t')}\sigma_{22}(G_{12})^\dagger \ , \tag{A27}$$

where we have used the fact that

$$\begin{aligned}\sigma_{22}e^{-(G_{22})^\dagger t'}&=\sigma_{22}e^{-(k_BL_{22}\sigma_{22}^{-1})^\dagger t'}\\&=\sigma_{22}e^{-k_B\sigma_{22}^{-1}L_{22}t'}\\&=e^{-k_BL_{22}\sigma_{22}^{-1}t'}\sigma_{22} \ .\end{aligned} \tag{A28}$$

Thus, using the results in Eqs. (A25) and (A26), Eq. (A22) reads

$$\langle F(t)F(t')^\dagger\rangle=-G_{12}e^{-G_{22}|t-t'|}G_{21}\sigma_{11} \ , \tag{A29}$$

where we also used the relation

$$\begin{aligned}\sigma_{22}(G_{12})^\dagger&=\sigma_{22}(k_BL_{12}\sigma_{22}^{-1})^\dagger\\&=k_BL_{12}^\dagger\\&=-k_BL_{21}\\&=-G_{21}\sigma_{11} \ .\end{aligned} \tag{A30}$$

Comparing Eq. (A29) with the expression for the memory in Eq. (A10), we are led to Eq. (A11). Since the correlation function $\langle F(t)F^\dagger(t')\rangle$ only depends on $|t-t'|$ we conclude that $F(t)$ is also a stationary (and, in fact, even) process. Thus, the theorem has been demonstrated.

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