PHYSICAL REVIEW A VOLUME 27, NUMBER 1 JANUARY 1983

Single-particle motion in liquids of charged particles

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(Received 28 April 1982)

We present a simple approximation for the velocity autocorrelation function of a tagged charged particle immersed in a liquid of charged particles. Application to a classical one-component plasma and a simple molten salt manifests the importance of the coupling between single-particle motion and charge-density excitations in *both* systems. The theory is also applied to molten sodium chloride with the result $D_{\mathrm{Na}^+}/D_{\mathrm{Cl}^-}=1.5$ for the diffusion coefficients of Na^+ and Cl^- ions.

I. INTRODUCTION

Recently computer-simulation studies have revealed some detailed features of single-particle motion in liquids of charged particles. In the classical one-component plasma (OCP)[1] it was found that the velocity autocorrelation function (VAF) for high densities shows marked oscillations with a frequency close to the plasma frequency ω_p. This oscillation indicates the strong coupling of single-particle motion to charge-density fluctuations which are dominated by plasma modes for small wave numbers. In a molten salt, a two-component liquid with both short-range repulsive and long-range Coulomb interactions, single-particle motion was also studied by molecular dynamics.[2,3] For a symmetric molten salt (SMS)[2] the VAF is found to be rather similar to that of liquid argon,[4] showing *no* pronounced oscillations. This result gave rise to speculations concerning the absence of coupling between the single-particle motion and the excitation of charge-density fluctuations in the molten salt.[3] At present there is no microscopic theory to explain the great difference between the VAF of the OCP and that of the SMS.

In this paper we suggest a simple mode-coupling approximation for the memory function of the VAF of a tagged charged particle in a liquid of charged particles. The theory provides an explanation for the different behavior of the single-particle motion when applied to OCP and SMS. Moreover, the general formulas are used to estimate the cation and anion diffusion coefficient of an unsymmetrical molten salt (UMS), in which cations and anions have different mass.

This paper is organized as follows. In Sec. II we give the necessary definitions of static correlation functions in a multicomponent system and we introduce the VAF and its memory function. In Sec. III we develop the approximation scheme which allows us to calculate the VAF from knowledge of all (coherent) density correlations in the liquid. In Secs. IV and V numerical results for OCP and SMS, respectively, are presented, while Sec. VI contains the application to an UMS.

II. FORMAL FRAMEWORK

Consider a system of N classical particles in a volume V at temperature T. Let the system consist of S different particle species $s=1,2,\ldots,S$ with mass m_s, charge e_s, and number of particles N_s implying $\sum_s N_s=N$ and $\sum_s e_sN_s=0$. Denoting the position of the jth particle of species s by $\vec{r}_j^{(s)}$ the Fourier-transformed partial number densities are

$$n_s(\vec{q})=\sum_{1\le j\le N_s}\exp(-i\vec{q}\cdot\vec{r}_j^{(s)})\ . \tag{1}$$

In the following, another set of density variables will be useful. For $\sigma=1,2,\ldots,S$ we define

$$\rho_\sigma(\vec{q})=\sum_{s=1}^{S}n_s(\vec{q})A_{s\sigma}(\vec{q})(N/N_s)^{1/2}\ , \tag{2}$$

where $A_{s\sigma}$ denotes the unitary matrix which diagonalizes the real symmetric matrix of partial structure factors $S_{ss'}(q)$,

$$\sum_{s,s'}A^\dagger_{\sigma s}S_{ss'}(q)A_{s'\sigma'}=\delta_{\sigma,\sigma'}S_\sigma(q) \tag{3}$$

with

$$S_{ss'}(q)=\langle \delta n_s(\vec{q})^*\delta n_{s'}(\vec{q})\rangle/(N_sN_{s'})^{1/2}$$
$$=\delta_{s,s'}+\frac{(N_sN_{s'})^{1/2}}{V}\int d^3r\, e^{-i\vec{q}\cdot\vec{r}}\,[g_{ss'}(r)-1] \tag{4a}$$

and

$$S_\sigma(q)=\langle \delta\rho_\sigma(\vec{q})^*\delta\rho_\sigma(\vec{q})\rangle/N\ . \tag{4b}$$

Here $\delta B=B-\langle B\rangle$, $\langle\cdots\rangle$ denotes the thermal average, and $g_{ss'}(r)$ is the pair-distribution function. In addition to the partial structure factors the corresponding direct correlation functions are defined by

$$\tilde{c}_{ss'}(q)\equiv\frac{(N_sN_{s'})^{1/2}}{V}\int d^3r\, e^{-i\vec{q}\cdot\vec{r}}c_{ss'}(r)$$
$$=\delta_{s,s'}-[S^{-1}(q)]_{ss'}\ , \tag{5a}$$

or

$$\tilde{c}_\sigma(q)=1-1/S_\sigma(q) \tag{5b}$$

for the diagonal elements in the representation of Eq. (2).

Now let us assume the presence of a further tagged particle of mass m_0 and charge e_0 with position $\vec{r}_0(t)$ and velocity $\vec{v}_0(t)$. The velocity autocorrelation function (VAF) is defined as[5]

$$\psi(t)=\frac{1}{3}\frac{\langle \vec{v}_0(t'+t)\cdot\vec{v}_0(t')\rangle}{\langle[\vec{v}_0(t')]^2\rangle}$$
$$=(\hat{v}_0^x\,|\,\exp(-it\mathscr{L})\,|\,\hat{v}_0^x)\ , \tag{6}$$

where the last expression results from the introduction of Mori's scalar product[6] in the space of dynamical variables $(A\,|\,B)\overset{\text{def}}{=}\langle\delta A^*\delta B\rangle/(k_BT)$, and $\mathscr{L}$ denotes the Liouville operator describing time evolution $A(t)=e^{it\mathscr{L}}A$. Normalized variables with respect to Mori's scalar product are denoted by a caret, $\hat{A}=A/(A\,|A)^{1/2}$. As derived earlier,[7] the VAF obeys a generalized Langevin equation

$$\dot{\psi}(t)=-\int_0^t d\tau K(t-\tau)\psi(\tau)\ ,\quad \psi(t=0)=1 \tag{7}$$

with the memory function

$$K(t)=\tfrac{1}{3}\Omega_{E0}^2\sum_{\alpha=1}^{3}(\hat{F}_0^\alpha\,|\,e^{-itQ\mathscr{L}Q}\,|\,\hat{F}_0^\alpha)$$
$$=\tfrac{1}{3}\Omega_{E0}^2\sum_{\alpha}\sum_{\sigma,\sigma'}\sum_{\vec{k},\vec{k}'}(\hat{F}_0^\alpha\,|\,\hat{B}_\sigma(\vec{k}))(\hat{B}_\sigma(\vec{k})\,|\,e^{-itQ\mathscr{L}Q}\,|\,\hat{B}_{\sigma'}(\vec{k}'))(\hat{B}_{\sigma'}(\vec{k}')\,|\,\hat{F}_0^\alpha)\ . \tag{8}$$

Here $Q=1-\sum_\alpha|\hat{v}_0^\alpha)(\hat{v}_0^\alpha)$ and $\vec{F}_0$ is the force on the tagged particle[8]

$$F_0^\alpha=im_0\mathscr{L}v_0^\alpha$$
$$=\frac{1}{iV}\sum_{\vec{k}}\sum_{s}u_{0s}(k)k^\alpha e^{i\vec{k}\cdot\vec{r}_0}n_s(\vec{k})$$
$$=\frac{1}{iV}\sum_{\vec{k}}\sum_{\sigma}v_{0\sigma}(k)k^\alpha e^{i\vec{k}\cdot\vec{r}_0}\rho_\sigma(\vec{k}) \tag{9}$$

with

$$v_{0\sigma}(k)=\sum_s u_{0s}(k)A^\dagger_{\sigma s}(k)(N_s/N)^{1/2}\ ,$$
$$u_{0s}(k)=\int d^3r\, e^{-i\vec{k}\cdot\vec{r}}u_{0s}(r)\ ,$$

and $u_{0s}(r)$ denoting the potential between a fluid particle of species s and the tagged particle. Finally, the Einstein frequency Ω_{E0} of the tagged particle is determined by

$$\Omega_{E0}^2\equiv\frac{1}{3m_0}\sum_\alpha(F_0^\alpha\,|\,F_0^\alpha)$$
$$=\frac{1}{3m_0V}\sum_{\vec{k},\sigma}(i\vec{k})^2v_{0\sigma}(k)\langle e^{i\vec{k}\cdot\vec{r}_0}\rho_\sigma(\vec{k})\rangle\ . \tag{10}$$

The latter expression in Eq. (8) takes account of the fact that the force F_0^α is a superposition of two-mode variables

$$B_\sigma(\vec{k})=e^{i\vec{k}\cdot\vec{r}_0}\rho_\sigma(\vec{k})\ . \tag{11}$$

That second form of $K(t)$ will serve as a starting point for our approximation.

III. MODE-COUPLING APPROXIMATION OF $K(t)$

A useful approximation suggested by the latter expression in Eq. (8) consists of the factorization of the normalized two-mode correlation functions

$$(\hat{B}_\sigma(\vec{k})\,|\,e^{-itQ\mathscr{L}Q}\,|\,\hat{B}_{\sigma'}(\vec{k}'))$$
$$\approx\delta_{\vec{k},\vec{k}'}\phi_0(k;t)\phi_\rho(\sigma,\sigma';k;t) \tag{12}$$

which leads to

$$K(t)=\frac{\Omega_{E0}^2}{6\pi^2N/V}\sum_{\sigma,\sigma'}\int_0^\infty dk\,k^2W(\sigma;k)^*W(\sigma';k)$$
$$\times\phi_0(k;t)\phi_\rho(\sigma,\sigma';k;t) \tag{13}$$

with the tagged particle density correlation function

$$\phi_0(k;t)=\langle e^{i\vec{k}\cdot[\vec{r}_0(t)-\vec{r}_0(0)]}\rangle \,, \qquad (14\text{a})$$

the liquid density correlation functions

$$\phi_\rho(\sigma,\sigma';k;t)=(\hat{\rho}_\sigma(\vec{k})\,|\,e^{-it\mathscr{L}}\,|\,\hat{\rho}_{\sigma'}(\vec{k}))=\frac{\langle\delta\rho_\sigma(\vec{k};t)^*\delta\rho_{\sigma'}(\vec{k};0)\rangle}{NS_\sigma(k)^{1/2}S_{\sigma'}(k)^{1/2}} \,, \qquad (14\text{b})$$

and the vertex functions

$$W(\sigma;k)=\widetilde{W}(\sigma;k)\Bigg/\left[\frac{1}{6\pi^2N/V}\sum_\mu\int_0^\infty dp\,p^2\,|\,\widetilde{W}(\mu;p)\,|^2\right]^{1/2} \qquad (15\text{a})$$

with

$$\widetilde{W}(\sigma;k)=(\hat{B}_\sigma(\vec{k})\,|\,\vec{F}_0\cdot\vec{k}/k)(N/m_0)^{1/2} \,. \qquad (15\text{b})$$

Note that Eq. (13) conserves the correct value $K(t=0)=\Omega_{E0}^2$.

The exact evaluation of the function $\widetilde{W}(\sigma;k)$ is difficult due to the normalization of the two-mode variables. We therefore introduce a second approximation by putting

$$\hat{B}_\sigma(\vec{k})\approx e^{i\vec{k}\cdot\vec{r}_0}\hat{\rho}_\sigma(\vec{k}) \qquad (16)$$

in Eq. (15b) which is equivalent to applying the diagonal-part approximation in the normalization matrix $(B_\sigma(\vec{k})\,|\,B_{\sigma'}(\vec{k}\,'))$. Inserting the approximate expression Eq. (16) into Eq. (15b) we find

$$\widetilde{W}(\sigma;k)=ik\left[\frac{k_BT}{m_0S_\sigma(k)}\right]^{1/2}\langle e^{i\vec{k}\cdot\vec{r}_0}\rho_\sigma(\vec{k})\rangle \,. \qquad (17)$$

Assuming the tagged particle to be a liquid particle of species $\tilde{s}$, i.e., $m_0\equiv m_{\tilde{s}}$, $e_0\equiv e_{\tilde{s}}$, $\vec{r}_0\equiv\vec{r}^{\,(\tilde{s})}_{N_{\tilde{s}}+1}$, the thermal average in Eqs. (10) and (17) may be further evaluated in terms of the static correlation function of the liquid leading to the final expressions dependent on $\tilde{s}$:

$$\widetilde{W}(\sigma;k)=ik\left[\frac{k_BTS_\sigma(k)N}{m_{\tilde{s}}N_{\tilde{s}}}\right]^{1/2}A_{\tilde{s}\sigma}(k)\tilde{c}_\sigma(k) \qquad (k>0) \quad (18\text{a})$$

$$\Omega_{E0}^2=\frac{4\pi}{3m_{\tilde{s}}}\sum_s\frac{N_s}{V}\int_0^\infty dr\,r^2g_{\tilde{s}s}(r)\Delta u_{\tilde{s}s}(r) \,. \qquad (18\text{b})$$

If now, as a third approximation, we employ the well-known Gaussian approximation[9] for the incoherent density correlation

$$\phi_0(k;t)\approx\exp\left[-k^2\left[\frac{k_BT}{m_{\tilde{s}}}\right]\int_0^t d\tau(t-\tau)\psi(\tau)\right] \,, \qquad (19)$$

the memory function $K(t)$ can be calculated from Eqs. (13), (15a), (18), and (19) provided one knows the potentials $u_{0s}(r)$, the pair-distribution functions $g_{ss'}(r)$, and the coherent density correlation functions $\phi_\rho(\sigma,\sigma';k;t)$. The latter have been calculated in our preceding work for the OCP[10] and the SMS.[11] Moreover, in Refs. 1 and 2 one finds, besides the required static correlation functions, excellent memory function fits to the "experimental" (computer simulated) spectral functions

$$\phi_\rho''(\sigma,\sigma';k;\omega)=\tfrac{1}{2}\int_{-\infty}^{+\infty}dt\,e^{it\omega}\phi_\rho(\sigma,\sigma';k;t)$$

which will be used in Secs. IV and V in order to check the validity of the above approximations.

Finally, we note that according to the exact relation

$$D_{\tilde{s}}=\frac{k_BT}{m_{\tilde{s}}}\Bigg/\int_0^\infty dt\,K(t) \qquad (20)$$

our approximation Eq. (13) allows for an estimate of the diffusion coefficient $D_{\tilde{s}}$ of a particle of species $\tilde{s}$ in the liquid. However, we do not expect very reliable results for $D_{\tilde{s}}$, since our simple approximation neglects any explicit coupling between the single-particle motion and shear excitations in the liquid. From experience on simple liquids[12,7] one might expect a contribution as large as 50% to $D_{\tilde{s}}$ which is due to the coupling to transverse current excitations. On the other hand, in pure Coulomb systems (OCP) one has evidence[13] that the transverse decay channel is not as effective as in liquids with short-range interactions.

IV. APPLICATION TO A ONE-COMPONENT PLASMA

For a one-component system ($S=1$), the memory function Eq. (13) reduces to

$$K(t)=\frac{\Omega_{\text{OCP}}^2}{nI_{\text{OCP}}}\int_0^\infty dk\,[k^2\tilde{c}(k)]^2\phi_0(k;t)S(k)\times\phi_\rho(k;t) \,, \qquad (21\text{a})$$

or, the corresponding spectral function,

$$K''(\omega)=\int_{-\infty}^{+\infty}\frac{dt}{2}e^{it\omega}K(t)$$
$$=\pi\frac{\Omega_{\text{OCP}}^{2}}{nI_{\text{OCP}}}\int_{0}^{\infty}dk\,[k^{2}\tilde{c}(k)]^{2}\times\int_{-\infty}^{+\infty}d\epsilon\,S_{0}(k;\epsilon)\times S(k;\omega-\epsilon)\tag{21b}$$

with the abbreviation ($n=N/V$)

$$I_{\text{OCP}}\equiv n^{-1}\int_{0}^{\infty}dk\,[k^{2}\tilde{c}(k)]^{2}S(k)\,,\tag{21c}$$

and the Einstein frequency[14]

$$\Omega_{\text{OCP}}^{2}=\tfrac{1}{3}\omega_{p}^{2},\quad \omega_{p}^{2}=4\pi e^{2}n/m\ .\tag{21d}$$

The functions

$$S_{0}(k;\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\,e^{it\omega}\phi_{0}(k;t)\,,\tag{22a}$$

$$S(k;\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\,e^{it\omega}\phi_{p}(k;t)S(k)\tag{22b}$$

are known as incoherent and coherent scattering laws,[15] respectively, and the other symbols are obvious specializations of the more general quantities defined in Secs. II and III.

It is interesting to note that the expression Eq. (21a) is closely connected to the result $K_{\text{GM}}(t)$ obtained by Gould and Mazenko.[16] One has

$$K(t)=\frac{\omega_{p}^{2}}{3}K_{\text{GM}}(t)/K_{\text{GM}}(t=0)\,,$$

i.e., our present approach—in contrast to the earlier result—conserves the correct value

$$K(t=0)=\pi^{-1}\int_{-\infty}^{+\infty}d\omega\,K''(\omega)=\omega_{p}^{2}/3\ .$$

There have been other attempts[17,18] to conserve this sum rule in the OCP. However, these authors manage to keep $K(t=0)$ correct at the expense of loosing the guarantee for positivity of the spectral function $K''(\omega)$.

We calculated $K''(\omega)$ according to Eqs. (21) and (19) for the plasma parameter $\Gamma=140$ taking all input information from Ref. 1. The resulting velocity autocorrelation spectrum

$$\psi''(\omega)=\int_{-\infty}^{+\infty}\frac{dt}{2}e^{it\omega}\psi(t)$$
$$=\frac{K''(\omega)}{[\omega+K'(\omega)]^{2}+[K''(\omega)]^{2}}\,,\tag{23}$$

where

$$K'(\omega)=\frac{2\omega}{\pi}P\int_{0}^{\infty}d\epsilon\frac{K''(\epsilon)}{\epsilon^{2}-\omega^{2}}\tag{24}$$

(where P is the principle part integral), is plotted in Fig. 1(a) in comparison to the computer simulation result of Ref. 1. For the self-diffusion coefficient we find, from Eq. (20),

$$D^{*}\equiv D(\tfrac{4}{3}\pi n)^{2/3}/\omega_{p}=0.0027=0.7D_{\text{expt}}^{*}\ .$$

These results show that the main features of the VAF in the OCP at high densities are reproduced well by the present theory.

V. APPLICATION TO A SYMMETRIC MOLTEN SALT

For a two-component system ($S=2$) in which the particle species differ only in the sign of their charge, one has $N_{s}=N/2$, $m_{s}=m$, $e_{1}=-e_{2}=e$, and $A_{11}=A_{12}=A_{21}=-A_{22}=1/\sqrt{2}$; i.e.,

$$\rho_{1}(\vec{q})=n_{1}(\vec{q})+n_{2}(\vec{q})=\rho_{m}(\vec{q})/m\ ,\tag{25a}$$

$$\rho_{2}(\vec{q})=n_{1}(\vec{q})-n_{2}(\vec{q})=\rho_{Q}(\vec{q})/e\ ,\tag{25b}$$

denote mass- and charge-density variables, respectively. Owing to the charge-conjugation symmetry of the SMS, mixed mass-charge correlations vanish, and Eq. (13) reduces to

$$K(t)=\frac{\Omega_{\text{SMS}}^{2}}{nI_{\text{SMS}}}\sum_{\sigma=1,2}\int_{0}^{\infty}dk\,[k^{2}\tilde{c}_{\sigma}(k)]^{2}\phi_{0}(k;t)\times S_{\sigma}(k)\phi_{p}(\sigma,\sigma;k;t)\tag{26a}$$

or, for the corresponding spectral function

$$K''(\omega)=\pi\frac{\Omega_{\text{SMS}}^{2}}{nI_{\text{SMS}}}\sum_{\sigma=1,2}\int_{0}^{\infty}dk\,[k^{2}\tilde{c}_{0}(k)]^{2}\times\int_{-\infty}^{+\infty}d\epsilon\,S_{0}(k;\epsilon)\times S_{\sigma}(k;\omega-\epsilon)\tag{26b}$$

with the abbreviation ($n\equiv N/V$)

$$I_{\text{SMS}}=n^{-1}\sum_{\sigma=1,2}\int_{0}^{\infty}dk\,[k^{2}\tilde{c}_{\sigma}(k)]^{2}S_{\sigma}(k)\,,\tag{27}$$

and the mass- and charge-density van Hove functions

$$S_{\sigma}(k;\omega)$$
$$=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\,e^{it\omega}\phi_{p}(\sigma,\sigma;k;t)S_{\sigma}(k)\ .\tag{28}$$

Owing to the symmetry of the SMS the Einstein

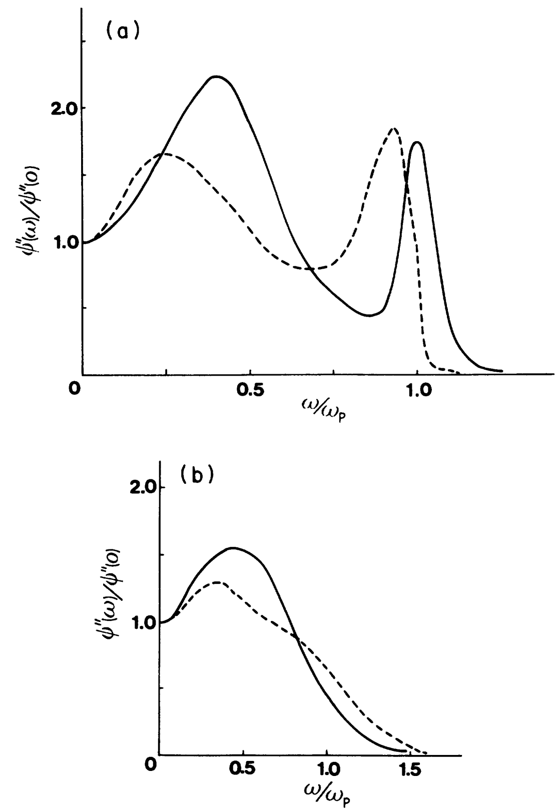

FIG. 1. Normalized velocity autocorrelation spectra of (a) the one-component plasma and (b) the simple molten salt. Full line, present theory ($\Gamma=140$); dashed line, computer simulation ($\Gamma=152.4$) from Ref. 1. Diffusion constants are $D^*_{\text{theor}}=0.0027$ ($D^*_{\text{expt}}=0.00393$) for the OCP and $D^*_{\text{theor}}=0.0046$ ($D^*_{\text{expt}}=0.0049$) for the SMS, where $D^*=\omega_p^{-1}(4\pi n/3)^{2/3}\psi''(\omega=0)$.

frequency of a tagged cation does not differ from that of an anion. From Eq. (18b) one finds

$$\Omega^2_{\text{SMS}}=\frac{\omega_p^2}{3}\int_0^\infty dr\, r^2 \tfrac{1}{2}[g_l(r)+g_u(r)] \times \Delta u(r)/e^2\,, \qquad (29)$$

where $g_l(r)=g_{11}(r)=g_{22}(r)$ and $g_u(r)=g_{12}(r)$, denote the pair-distribution functions of like and unlike particles, respectively, $u(r)=u_{11}(r)-e^2/r$ is the (non-Coulombic) short-range part of the two-particle potential, and $\omega_p^2=4\pi ne^2/m$ is the plasma frequency.

We calculated $K''(\omega)$ according to Eqs. (26) and (19) with the model potential[2]

$$u(r)=\frac{e^2}{9\lambda}\left[\frac{\lambda}{r}\right]^9$$

[λ is the separation at which the cation-anion potential $u_{12}(r)=u(r)-e^2/r$ has a minimum]. All necessary input information was taken from computer simulation work.[2] The resulting velocity autocorrelation spectrum is plotted in Fig. 1(b) in comparison with molecular dynamics (MD) results (we Fourier transformed the VAF given in Ref. 2 for this purpose). For the diffusion coefficient, which is identical for cations and anions of the SMS, we find

$$D^*\equiv D/(\lambda^2\omega_p)=0.0046=0.94D^*_{\text{expt}}\,.$$

Again, our approximation for the memory spectrum $K''(\omega)$ reproduces the main features of the velocity autocorrelation spectrum of the SMS which shows a broad maximum at about $0.4\omega_p$ with *no* additional sharp resonance close to ω_p which was the case for the OCP [Fig. 1(a)].

The properties of the VAF can be traced back directly to the behavior of $K''(\omega)$ which is plotted in Figs. 2 and 3 for the OCP and SMS, respectively. While the memory spectrum of the OCP shows a sharp maximum close to the plasma frequency (Fig. 2), the spectrum of the SMS does not; it is a monotonously decreasing function of ω (Fig. 3). This qualitative difference in the memory spectra has the following reasons: (a) While the OCP has a sharply defined plasma mode for small k, this excitation is strongly damped in the SMS expressing the finite conductivity of the melt,[1,2] (b) the dispersion of the plasma mode is much stronger in the SMS[2] than in the OCP; and (c) the diffusion constant D^* is larger in the SMS than in the OCP, i.e., for small k $S_0(k;\omega)$ is narrower in the one-component system. From these three facts the difference in the memory

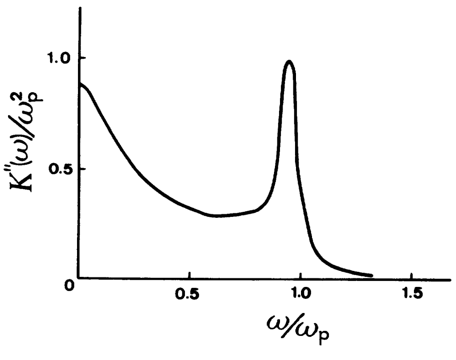

FIG. 2. Spectrum of the memory function for OCP.

spectra is easily understood. Any residual influence of the plasma peak is washed out in the k and ϵ integrations in Eq. (26b) in the case of the SMS, while for the OCP the small-k contribution to the integral in Eq. (21b) is responsible for the pronounced peak in $K''(\omega)$ close to ω_p.

In Fig. 3 we separately indicated the contribution $K_Q''(\omega)$ to $K''(\omega)$ which is due to the coupling between single-particle motion and charge-density fluctuation. Roughly speaking, $K_Q'' \approx \frac{3}{4}K''$, manifesting the great importance of this decay channel also for the molten salt and disproving earlier assumptions[3] concerning the effectiveness of this coupling.

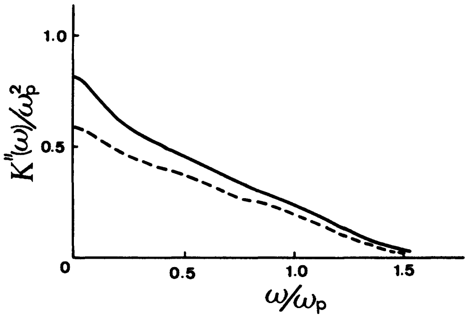

FIG. 3. Spectrum of the memory function for SMS (full line). Dashed line: Contribution $K_Q''(\omega)$ to $K''(\omega)$ from the term $\sigma=2$ in Eq. (26b).

VI. APPLICATION TO AN UNSYMMETRIC MOLTEN SALT

For a two-component system ($S=2$), in which particles differ not only in the sign of their charge but also have different masses ($m_1 \neq m_2$) and interactions $[u_{11}(r) \neq u_{22}(r)]$, the partial structure factors $S_{11}(q)$ and $S_{22}(q)$ are no longer equal and the matrix elements $A_{s\sigma}(q)$, eigenvectors $\rho_\sigma(\vec{q})$, and Eq. (3) are quite different from those of the SMS. However, we obtain from Eqs. (13), (15), and (18), after lengthy calculations,

$$K(t)=\frac{\Omega_{\mathrm{UMS}}^2}{nI_{\mathrm{UMS}}}\int_0^\infty dk\,k^4\left[\sum_{D=N,Q} c_D^{\tilde{s}}(k)^2 S(D,D;k,t)+(2-4\delta_{\tilde{s},2})c_N^{\tilde{s}}(k)c_Q^{\tilde{s}}(k)S(N,Q;k,t)\right]\phi_0(k,t) \tag{30}$$

with the Einstein frequency

$$\Omega_{\mathrm{UMS}}^2=\frac{m}{m_{\tilde{s}}}\frac{\omega_p^2}{3}\sum_{s=1,2}\int_0^\infty dr\,r^2\tfrac{1}{2}[g_{\tilde{s}s}(r)\Delta u_{\tilde{s}s}(r)]/e^2 , \tag{31}$$

where $\omega_p^2=4\pi ne^2/m$, $m^{-1}=(m_1^{-1}+m_2^{-1})/2$, and

$$I_{\mathrm{UMS}}=n^{-1}\int_0^\infty dk\,k^4\left[\sum_{D=N,Q} c_D^{\tilde{s}}(k)^2 S(D,D;k,t=0)+(2-4\delta_{\tilde{s},2})c_N^{\tilde{s}}(k)c_Q^{\tilde{s}}S(N,Q;k,t=0)\right] . \tag{32}$$

The c function $c_D^s(k)$ is expressed as

$$c_D^s(k)=\tilde{c}_{ss}(k)+\mathrm{sgn}(D)\tilde{c}_{s\bar{s}}(k) \tag{33}$$

with the direct correlation function $\tilde{c}_{ss'}(k)$ defined by Eq. (5a), $\bar{s}=1(2)$ for $s=2(1)$ and $\mathrm{sgn}(D)=1$ for $D=N$ and -1 for $D=Q$. The van Hove function $S(D,D';k,t)$ is defined by

$$S(D,D';k,t)=N^{-1}\langle\rho_D(\vec{k};t)^*\rho_{D'}(\vec{k};0)\rangle \tag{34}$$

with

$$\rho_D(\vec{k})=n_+(k)+\mathrm{sgn}(D)n_-(k) . \tag{35}$$

Thus, as in the case of SMS, the memory function $K(t)$ is expressed with the direct correlation functions $\tilde{c}_{ss'}(k)$, Eq. (5a), and the van Hove functions for number- and charge-density fluctuations. Note that now $K(t)$ or $K''(\omega)$ depends on the species $\tilde{s}$ to which the tagged particle belongs (a) explicitly via the prefactor $m/\tilde{m}$ in the Einstein frequency and the functions $g_{\tilde{s}\tilde{s}}(r)$, $u_{\tilde{s}\tilde{s}}(r)$, and $c_D^{\tilde{s}}(k)$, and (b) implicitly via the single-particle density correlation $\phi_0(k,t)$. Finally, according to Eq. (20) the diffusion coefficients of cations and anions were determined for the case of molten sodium chloride by evaluating $K''(\omega=0)=\int_0^\infty dt\,K(t)$ for Na^+ and Cl^-. The necessary input data to calculate $K''(\omega=0)$ were taken from Ref. 19. Since the mixed correlation function $S(N,Q;k,t)$ of number and charge is usually small[3] compared with the autocorrelation functions $S(N,N;k,t)$ and $S(Q,Q;k,t)$, we neglect it in Eq. (30). We find $D_{\mathrm{Na}^+}=0.0041a^2\omega_p$ and $D_{\mathrm{Cl}^-}=0.0027a^2\omega_p$ resulting in $D_{\mathrm{Na}^+}/D_{\mathrm{Cl}^-}=1.5$. This must be compared to the experimental values[20] $D_{\mathrm{Na}^+}(\mathrm{expt})=0.0058a^2\omega_p$ and $D_{\mathrm{Cl}^-}(\mathrm{expt})$

$=0.0042a^2\omega_p$ with $(D_{\mathrm{Na}^+}/D_{\mathrm{Cl}^-})_{\mathrm{expt}}=1.38$. While the ratio of the diffusion coefficients agrees well with the experiment, the calculated absolute values are small by about 30%. As discussed at the end of Sec. III, such discrepancies are not surprising within the present simple approximation.

ACKNOWLEDGMENTS

This work is part of the research program of the Sonderforschungsbereich 161 supported by the Deutsche Forschungsgemeinschaft. One of us (T.M.) acknowledges hospitality at the Freie Universität Berlin during his stay in Berlin.

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[1] J. P. Hansen, I. R. McDonald, and E. L. Pollock, Phys. Rev. A 11, 1025 (1975).

[2] J. P. Hansen and I. R. McDonald, Phys. Rev. A 11, 2111 (1975).

[3] G. Cicotti, G. Jacucci, and I. R. McDonald, Phys. Rev. A 13, 426 (1976).

[4] A. Rahman, Phys. Rev. 136, 405 (1964).

[5] Strictly speaking, the thermal average in Eq. (6) is different from the one in Eqs. (4) and (5) since there is the additional particle now. However, this difference becomes negligible in our applications when the tagged particle is identical to a liquid particle.

[6] H. Mori, Prog. Theor. Phys. 33, 429 (1965); 34, 399 (1965).

[7] J. Bosse, W. Götze, and Anette Zippelius, Phys. Rev. A 18, 1214 (1978).

[8] Equation (9) generalizes Eq. (10b) of Ref. 7 to a multicomponent system.

[9] G. H. Vineyard, Phys. Rev. 110, 999 (1958).

[10] J. Bosse and K. Kubo, Phys. Rev. A 18, 2337 (1978).

[11] J. Bosse and T. Munakata, Phys. Rev. A 25, 2763 (1982).

[12] J. Bosse, W. Götze, and M. Lücke, Phys. Rev. A 20, 1603 (1979).

[13] M. Baus and J. Bosse, Phys. Rev. A 22, 2284 (1980).

[14] If one looks at the OCF as a one-component system $(S=1)$ he must remember that there is a contribution to the force F_0^α from the homogenous neutralizing background which is *not* included in Eq. (9) and which is responsible for the contribution $\omega_p^2/3$ to Ω_{E0}^2 (see, e.g., Ref. 10). Another way of getting to Eq. (21) is to treat the OCP as an SMS with $2N$ particles and set $g_{12}(r)=1$ reflecting the homogenously smeared out background charges. Then $A_{s\sigma}\equiv\delta_{s\sigma}$ and straightforward application of the general formulas leads to our result for $K(t)$.

[15] L. van Hove, Phys. Rev. 95, 249 (1954).

[16] H. Gould and G. F. Mazenko, Phys. Rev. Lett. 35, 1455 (1975); Phys. Rev. A 15, 1274 (1977).

[17] T. Gaskell and O. Chiakwelu, J. Phys. C 10, 2021 (1977).

[18] M. Baus and J. Wallenborn, Phys. Lett. 55A, 90 (1975); J. Stat. Phys. 16, 91 (1977).

[19] E. M. Adams, I. R. McDonald, and K. Singer, Proc. R. Soc. London Ser. A 357, 37 (1977).

[20] R. E. Young and J. P. O'Connell, Ind. Eng. Chem. Fundam. 10, 418 (1971).