Statistical mechanics of dense ionized matter. VIII. Dynamical properties of binary ionic mixtures

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Molecular-dynamics calculations are reported for binary mixtures of ions of like charge in a uniform neutralizing background. For a system simulating the mixture H^+-He^{2+} the calculations show that the spectrum of charge fluctuations is dominated by a propagating plasmon mode with a lifetime which is finite even in the long-wavelength limit. At high charge densities there is an additional low-frequency contribution to the spectrum; this is shown to arise from a coupling between charge fluctuations and fluctuations in mass density. The results are in satisfactory agreement with a simple hydrodynamic calculation, though it appears that in practice the hydrodynamic limit is never fully attained; it is also found that a memory-function approach incorporating the coupling of mass and charge gives a good description of the collective dynamical modes at high charge densities.

I. INTRODUCTION

The work described in this paper is concerned with the dynamical properties of strongly coupled mixtures of classical point ions of like charge. Attention will be focused primarily on mixtures of protons (H^*) and α particles (He^{2*}) at temperatures and densities such that the electrons form a degenerate and rigid (i.e., weakly polarizable) Fermi gas. Under these conditions the ions may be regarded as moving in a uniform neutralizing background. The main body of the paper is concerned with presenting the results of molecular-dynamics calculations on such a system and with a phenomenological analysis of these "experimental" results in terms of linearized hydrodynamics and of the memory-function formalism.

There are two main reasons for undertaking the study. First, the static (thermodynamic and structural) properties of binary ionic fluids have recently received much attention. In particular, the possibility of demixing at low temperatures has attracted interest from astrophysicists.¹⁻⁴ Little is yet known, however, about the dynamical properties of such mixtures. Second, the work represents the last stage in a systematic investigation of the dynamics of Coulomb fluids in the intermediate and strong coupling regimes. In earlier papers we have discussed the properties of the one-component analog of the system studied here (the one-component plasma or OCP^5) and those of binary systems of particles of *opposite* charge: monovalent molten salts⁶ and the fully

ionized hydrogen plasma (the two-component plasma or TCP^7). A mixture of particles carrying different charges of the same sign is therefore the last in a list of simplest possible classical Coulomb systems.

Results obtained from computer simulations of the OCP, molten salts and the TCP have shown that the collective dynamics in strongly coupled Coulomb fluids differ quantitatively and even qualitatively from the predictions of mean-field theory and other weak coupling approximations. However, a number of exact results concerning the qualitative features of the collective modes in Coulomb systems have recently been established by Baus^{8,9} in the framework of kinetic theory. The most striking prediction for binary ionic mixtures concerns the optical (or plasmon) mode: this should have a temperature-dependent frequency and a finite lifetime in the long-wavelength limit, whereas the one-component case is characterized (in the same limit) by a unique plasma frequency and a lifetime which is infinite. A similar conclusion was reached on more phenomenological grounds in a preliminary version of the present work.10

Physically the binary mixtures considered here exist only at densities sufficiently high that both species are fully pressure-ionized. For the motion of the ions to be treated classically the temperature must also be sufficiently high that the thermal de Broglie wavelengths of the two species are much smaller than the mean interionic spacing. On the other hand the temperature must be

20

2590

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low compared to the Fermi temperature of the electrons in order to justify the assumption of complete degeneracy. The physical limitations of the uniform-background model have been discussed elsewhere,³ but it should be said that the extreme conditions of temperature and density under which the model can be considered as fully realistic are at present relevant only to certain astrophysical problems. Our primary concern here, however, is with building a more complete picture of the dynamical properties of Coulomb fluids and with discussing the theoretical treatment of such systems.

Section II of the paper contains the definitions and basic properties of the various correlation functions and their spectra. Section III summarizes briefly the molecular-dynamics procedure used in this work and the single-particle (or self-) motion of the ions is discussed in Sec. IV. Section V is concerned with collective modes describing fluctuations in charge and mass densities. The molecular-dynamics calculations lead to a quantitative estimate of the frequency shift and linewidth of the optical mode as a function of the coupling strength (or temperature). The most striking conclusion we reach is that in the strong coupling regime the characteristics (frequency and width) of the optical mode are independent of the coupling strength. In particular, the longwavelength limit of the characteristic optical frequency is temperature independent in that regime, and is slightly higher than the kinetic (or Vlasov) plasma frequency. The moleculardynamics results are analyzed in Sec. VI on the basis of phenomenological hydrodynamics and the memory-function approach of Mori and Zwanzig.¹¹ The latter proves to be successfuly only if proper account is taken of correlations between the fluctuating partial densities. When this is done the theory gives a fair description of the "experimental" facts, at least at strong coupling, without the introduction of any adjustable parameters. Some concluding remarks are contained in Sec. VII.

II. DEFINITIONS AND NOTATION

Consider a mixture of N_1 ions of charge Z_1e and mass M_1 with N_2 ions of charge Z_2e and mass M_2 , e being the elementary (proton) charge. Let V be the volume of the system and let $N=N_1$ $+N_2$ be the total number of ions. Then the number concentration of species α (=1,2) is x_{α} $=N_{\alpha}/N$ and the partial number density is ρ_{α} $=N_{\alpha}/V$. We may also define a dimensionless fractional charge z_{α} and mass m_{α} by the relations

$$z_{\alpha} = Z_{\alpha}/\overline{Z}, \quad m_{\alpha} = M_{\alpha}/\overline{M},$$
 (2.1)

where

$$\overline{Z} = x_1 Z_1 + x_2 Z_2, \quad \overline{M} = x_1 M_1 + x_2 M_2, \quad (2.2)$$

are, respectively, the mean charge and mean mass of the ions.

The molecular-dynamics calculations are made with periodic boundary conditions. We therefore restrict our attention to finite periodic systems and define the microscopic partial densities as

$$\rho_{\alpha}(\vec{\mathbf{k}},t) = \sum_{i=1}^{N_{\alpha}} \exp[i\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}_{i}(t)], \qquad (2.3)$$

where \vec{k} is a reciprocal-lattice vector of the periodic system, $\vec{r}_i(t)$ is the position of the *i*th ion of species α at time *t*, and the sum extends over all ions of that species. The Fourier components of the microscopic densities of mass and charge are given as linear combinations of the partial densities by

$$\rho_{m}(\mathbf{\bar{k}}, t) = m_{1}\rho_{1}(\mathbf{\bar{k}}, t) + m_{2}\rho_{2}(\mathbf{\bar{k}}, t) ,$$

$$\rho_{z}(\mathbf{\bar{k}}, t) = z_{1}\rho_{1}(\mathbf{\bar{k}}, t) + z_{2}\rho_{2}(\mathbf{\bar{k}}, t) .$$
(2.4)

The interaction Hamiltonian for the periodic system can be expressed in terms of the density $\rho_{g}(\vec{k}) \equiv \rho_{g}(\vec{k}, t=0)$ in the form

$$H = \frac{1}{2V} \sum_{\vec{k}\neq\vec{0}} \frac{4\pi \overline{Z}^2 e^2}{k^2} \left[\rho_z(\vec{k}) \rho_z(-\vec{k}) - N \langle Z^2 \rangle_{av} / \overline{Z}^2 \right], \quad (2.5)$$

where $\langle Z^2 \rangle_{av} = x_1 Z_1^2 + x_2 Z_2^2$; omission of the term $\vec{k} = \vec{0}$ takes account of the presence of the uniform background.

As a unit of length we shall use the ion-sphere radius as defined by

$$a^3 = 3/4\pi\rho$$
, (2.6)

where $\rho = \rho_1 + \rho_2$ is the total number density of ions. The static properties of a binary ionic mixture depend on only two variables, which are conveniently taken to be the concentration x_1 and the dimensionless parameter

$$\Gamma = e^2 / ak_B T \tag{2.7}$$

which, apart from a factor Z^2 , is the standard coupling parameter used to describe the thermodynamic state of the OCP. Since we are interested in dynamical properties, we must also introduce a scale of frequency and time. The natural choice of unit of frequency for a charged system is the plasma frequency. However, as we have already pointed out, the binary mixture cannot be characterized by a unique plasma frequency.^{9,10} We may instead define a "hydrodynamic" plasma frequency ω_p in terms of the macroscopic densities of charge, $\rho_Z = \overline{Z}e\rho$, and mass, $\rho_M = \overline{M}\rho$, as

$$\omega_{p}^{2} = 4\pi \rho_{Z}^{2} / \rho_{M} = 4\pi \rho (\overline{Z} e)^{2} / \overline{M} , \qquad (2.8)$$

and a "kinetic" plasma frequency Ω_p , which occurs naturally in mean-field (or Vlasov) theory, as

$$\Omega_{p}^{2} = \Omega_{p1}^{2} + \Omega_{p2}^{2} = 4\pi\rho_{1}(Z_{1}e)^{2}/M_{2} + 4\pi\rho_{2}(Z_{2}e)^{2}/M_{2}$$
$$= \frac{4\pi\rho(\overline{Z}e)^{2}}{\overline{M}} \left(x_{1}\frac{z_{1}^{2}}{m_{1}} + x_{2}\frac{z_{2}^{2}}{m_{2}} \right)$$
$$= \omega_{p}^{2} \left(x_{1}\frac{z_{1}^{2}}{m_{1}} + x_{2}\frac{z_{2}^{2}}{m_{2}} \right).$$
(2.9)

The difference $\Omega_p^2 - \omega_p^2$ may be cast in the form

$$\Omega_{p}^{2} - \omega_{p}^{2} = \Omega_{0}^{2} = \omega_{p}^{2} x_{1} x_{2} m_{1} m_{2} (z_{1}/m_{1} - z_{2}/m_{2})^{2} \ge 0,$$
(2.10)

so that $\Omega_p \ge \omega_p$. Note that $\Omega_p = \omega_p$ in the "symmetric" case, i.e., when $Z_1/Z_2 = M_1/M_2$; for H⁺ – He²⁺ mixtures the two plasma frequencies differ by only a few percent at any concentration. We have chosen ω_p to be our unit of frequency and ω_p^{-1} our unit of time.

In the study of collective modes the quantities of primary interest are the three correlation functions

$$F_{ab}(k,t) = (1/N) \langle \rho_a(\vec{k},t) \rho_b(-\vec{k},0) \rangle$$
, (2.11)

where the indices a and b stand for m (mass density) or z (charge density). The three correlation functions are real functions of time and the cross correlation functions are equal, as a consequence of invariance to space reflection, time translation, and time reflection, i.e., $F_{mz}(k,t) \equiv F_{zm}(k,t)$. This reduces the number of independent correlation functions from four to three. The collective modes can also be discussed in terms of the three correlation functions of the microscopic partial densities

$$F_{\alpha\beta}(k,t) = \frac{1}{(N_{\alpha}N_{\beta})^{1/2}} \langle \rho_{\alpha}(\vec{k},t)\rho_{\beta}(-\vec{k},0) \rangle$$

$$(\alpha,\beta=1,2).$$

$$(2.12)$$

Since $\rho_{\alpha}(\vec{k}, t)$ and $\rho_{m}(\vec{k}, t)$ are linear combinations of the $\rho_{\alpha}(\vec{k}, t)$, the correlation function matrix $[F_{ab}(k, t)]$ is related to the matrix $[F_{\alpha\beta}(k, t)]$ by a linear transformation. If \vec{T} is the matrix

$$\hat{\mathbf{T}} = \begin{bmatrix} x_1^{1/2} m_1 x_2^{1/2} m_2 \\ \\ x_1^{1/2} z_1 x_2^{1/2} z_2 \end{bmatrix},$$
(2.13)

the transformation may be written

$$[F_{ab}(k,t)] = \widehat{\mathbf{T}}[F_{\alpha\beta}(k,t)]\widehat{\mathbf{T}}^{*}, \qquad (2.14)$$

where $\overline{\mathbf{T}}^*$ is the transpose of $\overline{\mathbf{T}}$; we use the symbol $[A_{ij}]$ to denote a matrix with components A_{ij} . The $t \to 0$ limits of the partial density correlation functions are the static partial structure factors

$$F_{\alpha\beta}(k,t=0) = S_{\alpha\beta}(k) \tag{2.15}$$

while in the same limit the functions $F_{ab}(k, t)$ reduce to the static mass-mass, mass-charge, and charge-charge structure factors

$$F_{ab}(k, t=0) = S_{ab}(k) . (2.16)$$

Note that $S_{zz}(k)$ differs by a factor $\langle Z^2 \rangle_{av} / \overline{Z}^2$ from the charge-density structure factor S'(k) introduced in Ref. 3.

The long-wavelength limits of the partial structure factors are related to certain thermodynamic derivatives in the form

$$\lim_{k \to 0} S_{\alpha\beta}(k) = [(-1)^{\alpha+\beta} Z_{\alpha'} Z_{\beta'} / D] (\rho_{\alpha} \rho_{\beta})^{-1/2}, \quad (2.17)$$

with

$$D = \frac{1}{k_B T} \left(Z_2^2 \frac{\partial \mu_1}{\partial \rho_1} \Big|_T, \rho_2 + Z_1^2 \frac{\partial \mu_2}{\partial \rho_2} \Big|_T, \rho_1 - 2Z_1 Z_2 \frac{\partial \mu_1}{\partial \rho_2} \Big|_T, \rho_1 \right), \qquad (2.18)$$

where μ_{α} is the chemical potential of species α , and $\alpha'(\beta')=1$ if $\alpha(\beta)=2$ and conversely. From Eqs. (2.14) and (2.16)–(2.18) we conclude that $S_{zz}(k=0)=S_{mz}(k=0)=0$, while $S_{mm}(k=0)$ has some nonzero value. The behavior of the three structure factors at small k can be deduced from fluctuation theory: the formulas turn out to be identical to those obtained for a binary system of ions of opposite charge (a molten salt or TCP) and are given explicitly elsewhere.¹² It follows from these expressions that $S_{mz}(k)$ and $S_{zz}(k)$ behave as k^2 for small k. In particular

$$S_{zz}(k) = a^2 k^2 / 3\Gamma \overline{Z}^2 + O(k^4)$$
, (2.19)

a relation which follows also from the usual charge neutrality and perfect screening conditions.¹³ Fluctuation theory also yields the conditions for thermodynamic stability. Apart from the positivity of the specific heat at constant volume these lead to the single inequality

$$\frac{\partial \mu_M}{\partial \rho_M}\Big|_{T,\rho_Z} = \frac{\partial^2 (F/V)}{\partial \rho_M^2}\Big|_{T,\rho_Z} > 0, \qquad (2.20)$$

where F/V is the Helmholtz free energy per unit volume. The quantity

$$\frac{\partial \mu_Z}{\partial \rho_Z}\Big|_{T,\rho_M}$$

can, however, be either positive or negative.

2592

This result should be contrasted with the case of mixtures of neutral particles, where thermodynamic stability leads to two inequalities.¹⁴ The situation here is more reminiscent of the OCP, a system which is thermodynamically stable even when the compressibility is negative.¹⁵

The spectra of fluctuations in mass and charge densities are described by the dynamic structure factors defined as

$$S_{ab}(k,\,\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\,\omega\,t} F_{ab}(k,\,t)\,dt$$
 (2.21)

with analogous definitions of the partial dynamic structure factors $S_{\alpha\beta}(k,\omega)$. The even moments of the spectra $S_{\alphab}(k,\omega)$, given by

$$\langle \omega_{ab}^{2n} \rangle_{av} = \int_{-\infty}^{+\infty} \omega^{2n} S_{ab}(k, \omega) \, d\omega \,, \qquad (2.22)$$

are linked in the usual fashion to the short-time expansion of the functions $F_{ab}(k, t)$. Introducing the dimensionless wave number q = ak and separation x = r/a, we obtain for n = 0, 1, and 2 the expressions

$$\langle \omega_{ab}^{0} \rangle_{av}(q) = S_{ab}(q), \qquad (2.23)$$

$$\langle \omega_{mm}^2 \rangle_{av}(q) = \langle \omega_{mz}^2 \rangle_{av}(q) = \omega_p^2 q^2 / 3\Gamma \overline{Z}^2 \equiv \omega_0^2(q),$$
 (2.24)

$$\langle \omega_{zz}^2 \rangle_{\mathrm{av}}(q) = \omega_0^2(q) \xi^2$$
, (2.25)

$$\langle \omega_{mm}^{4} \rangle_{av}(q) = \omega_{p}^{2} \omega_{0}^{2}(q) \left(1 + \frac{3 \omega_{0}^{2}(q)}{\omega_{p}^{2}} - 2 \sum_{\alpha=1}^{2} \sum_{\beta=1}^{2} x_{\alpha} x_{\beta} z_{\alpha} z_{\beta} I_{\alpha\beta}(q) \right),$$
(2.26)

$$\langle \omega_{mz}^{4} \rangle_{av}(q) = \omega_{p}^{2} \omega_{0}^{2}(q) \Big(\xi^{2} + 3 \frac{\omega_{0} \langle q \rangle}{\omega_{p}^{2}} \sum_{\alpha=1}^{\infty} \frac{x_{\alpha} x_{\alpha}}{m_{\alpha}} - 2 \sum_{\alpha=1}^{2} \sum_{\beta=1}^{2} x_{\alpha} x_{\beta} \frac{z_{\alpha}^{2} z_{\beta}}{m_{\alpha}} I_{\alpha\beta}(q) \Big),$$
(2.27)

$$\begin{split} \langle \omega_{zz}^{4} \rangle_{av}(q) &= \omega_{p}^{2} \omega_{0}^{2}(q) \bigg[\xi^{4} + \frac{3\xi^{2} \omega_{0}^{2}(q)}{\omega_{p}^{2}} \\ &+ \frac{1}{3} x_{1} x_{2} z_{1} z_{2} \bigg(\frac{z_{1}}{m_{1}} - \frac{z_{2}}{m_{2}} \bigg)^{2} \\ &- 2 \sum_{\alpha=1}^{2} \sum_{\beta=1}^{2} x_{\alpha} x_{\beta} \frac{z_{\alpha} z_{\beta}}{m_{\alpha} m_{\beta}} I_{\alpha\beta}(q) \bigg], \end{split}$$

with

$$\xi^2 = \sum_{\alpha=1}^2 \frac{x_{\alpha} z_{\alpha}^2}{m_{\alpha}} = \frac{\Omega_p^2}{\omega_p^2}, \qquad (2.29)$$

(2.28)

$$I_{\alpha\beta}(q) = -\int_0^\infty [g_{\alpha\beta}(x) - 1] x^{-1} j_2(qx) \, dx \,, \qquad (2.30)$$

where $g_{\alpha\beta}(x)$ is the radial distribution function for ions of species α and β , and $j_2(qx)$ is the spherical Bessel function of second order. The frequency moments can therefore be computed from the known³ static pair structure of the mixture. They serve as a convenient check on the molecular-dynamics results and prove to be of major importance in the theoretical analysis presented in Sec. VI. The small-q expansion of the fourth moments is given in Ref. 10. When x_1 $\rightarrow 0$ or 1, the expressions (2.23)-(2.30) reduce correctly to the corresponding frequency moments of the OCP.⁵ The frequency moments of the partial dynamical structure factors $S_{\alpha\beta}(q,\omega)$ can be obtained by forming the appropriate linear combinations of the moments of the functions $S_{ab}(q, \omega)$.

III. MOLECULAR-DYNAMICS CALCULATIONS

The details of the molecular -dynamics calculations are almost identical to those described in our earlier work on the OCP.⁵ In each simulation the classical equations of motion of the ions were solved by stepwise numerical integration for a total of N_t steps with a time step Δt . In all cases the system consisted of 250 ions, 125 of each species (i.e., $x_1 = \frac{1}{2}$), contained within a periodically repeating cube. A total of five runs were carried out, four for the mixture $H^+ + He^{2+}$ and one for the symmetric mixture $D^+ + He^{2+}$; the results for the symmetric mixture are discussed only in the concluding sentences of Sec. V. Some technical details of the calculations are summarized in Table I; the quoted values of Γ are time averages over the run.

The main problem in any simulation of an ionic system lies in taking proper account of the long range of the Coulomb potential. In the calculations reported here the interionic forces were calculated by the Ewald method. The alternative sometimes used is to compute the force on a given ion by summing only on those neighboring ions lying within the periodic cube centered on the ion in question. It has been known since the pioneer-

TABLE I. Details of the molecular-dynamics calculations.

System	Г	N _t	Δt	
$H^+ + He^{2+}$	0.4	$4.0 imes 10^4$	0.02	
	24.5	$8.0 imes10^3$	0.20	
	40.0	$4.5 imes10^4$	0.20	
	61.5	$8.0 imes10^3$	0.20	
$D^* + He^{2+}$	0.4	$2.5 imes10^4$	0.03	

2593



FIG. 1. Velocity autocorrelation functions for Γ = 40.0. Circles: H⁺; dots: He²⁺. The unit of time is ω_{ρ}^{-1} .

ing work of Brush *et al.*¹⁶ that use of this so-called minimum-image method leads to serious systematic errors in static properties for $\Gamma>10,\ but$ yields staisfactory results at lower charge densities. Since the minimum-image summation is computationally more economic, we adopted this in place of the Ewald sum in our earlier calculations⁵ on the OCP at low Γ . We now believe, however, that the fact that static properties are satisifactorily reproduced can be misleading and that the study of cooperative dynamical effects requires the use of an Ewald or related method at much lower charge densities than had previously been thought. We should add finally that since the neutralizing background is assumed to be rigid, it has no effect on the motion of the ions.

IV. SINGLE-PARTICLE MOTION

The self-motion of the ions can be described in terms of the velocity autocorrelation functions, defined as

$$Z_{\alpha}(t) = \langle \vec{\mathbf{v}}_{i\alpha}(t) \cdot \vec{\mathbf{v}}_{i\alpha}(0) \rangle / \langle |\vec{\mathbf{v}}_{i\alpha}|^2 \rangle, \qquad (4.1)$$

where $\overline{\mathbf{v}}_{i\alpha}(t)$ is the velocity of an ion *i* of species α and $\langle |\overline{\mathbf{v}}_{i\alpha}|^2 \rangle = 3k_B T/M_{\alpha}$. The self-diffusion coefficient D_{α} is related to the corresponding velocity autocorrelation function by the well-known formula

TABLE II. Diffusion coefficients for $H^+ + He^{2+}$.

Γ	$D_{ m H}$	D _{He}	
0.4	4.89	1.54	
24.5	0.0228	0.0135	
40.0	0.0112	0.0064	
61.5	0.0051	0.0029	



FIG. 2. Function $\sigma_{zz}(q, \omega)$ for q = 0.619. Circles: $\Gamma = 0.4$; squares: $\Gamma = 24.5$; dots: $\Gamma = 40.0$; crosses: $\Gamma = 61.5$. The unit of frequency is ω_p .

$$D_{\alpha} = (k_B T / M_{\alpha}) \int_0^\infty Z_{\alpha}(t) dt . \qquad (4.2)$$

At $\Gamma = 0.4$ the two velocity autocorrelation functions are found to decay monotonically to zero in the manner characteristic of a dilute gas, the lifetime of the correlations being greater for the lighter ion. At $\Gamma = 40.0$, however, the most prominent feature of the curves is a strong oscillation at a frequency close to ω_p , the oscillations being more pronounced for H⁺ than for He²⁺; the results are plotted in Fig. 1. The onset of these oscillations shows that at high charge densities the motion of single ions cannot be considered separately from the plasma oscillations and confirms the overwhelmingly collective character of the dynamics of strongly coupled plasmas. Qualitatively similar behavior is seen in the OCP.



FIG. 3. As Fig. 2, but for q = 1.384.



FIG. 4. As Fig. 2, but for q = 1.857.

The main effect of increasing Γ in the strongcoupling regime is to decrease slightly the damping of the oscillations. The calculated diffusion coefficients are listed in Table II. Both coefficients are strongly varying functions of Γ , but for large Γ the ratio $D_{\rm H}/D_{\rm He}$ is almost independent of Γ and equal to 1.72 ± 0.04 .

V. DENSITY FLUCTUATIONS

The main computational effort has been directed at the calculation of the spectrum of charge-density fluctuations, i.e., the function $S_{zz}(q, \omega)$ introduced in Sec. II. Restricting our attention for the present to the system $H^* + He^{2*}$, we show in Figs. 2-5 the way in which the normalized spectrum

$$\sigma_{zz}(q, \omega) = S_{zz}(q, \omega) / S_{zz}(q)$$
(5.1)



FIG. 5. As Fig. 2, but for q = 2.316.



FIG. 6. Characteristic frequency of the optical mode (in units of ω_p) as a function of q. Squares: $\Gamma = 24.5$; dots: $\Gamma = 40.0$; crosses: $\Gamma = 61.5$. The curve is the approximate dispersion relation (5.2).

varies with Γ at four different values of the reduced wave number q. (Note that the value q=0.619 corresponds to the smallest wave number compatible with the periodic boundary conditions used in the molecular-dynamics calculations.) It is immediately clear that there is a marked



FIG. 7. $\sigma_{zz}(q, \omega=0)$ as a function of q. Reading from top to bottom: $\Gamma=61.5$, 40.0, 24.5, and 0.4.



FIG. 8. Time correlation functions for $\Gamma = 40.0$, q = 0.619. Circles: $F_{mm}(q,t)$; dots $F_{zz}(q,t)$. The unit of time is ω_{b}^{-1} .

difference in the behavior at the three higher charge densities ($\Gamma = 24.5$, 40.0, and 61.5) compared with that seen at $\Gamma = 0.4$.



FIG. 9. Function $\sigma_{gg}(q,\omega)$ for $\Gamma=0.4$. Below: q = 0.619; above: q = 1.857. Dots: $H^+ + He^{2+}$; crosses: $D^+ + He^{2+}$. The unit of frequency is ω_p .

The long-wavelength spectra at large values of Γ appear to separate into two rather well-defined components: a sharp peak around $\omega = 0$, representing a diffusive-type mode, and a broader peak centered close to the plasma frequency, corresponding to a propagating optical-type or plasmon mode. As q increases, the optical peak shifts to lower frequencies in the manner shown in Fig. 6, i.e., the dispersion is negative, in agreement with results obtained previously⁵ for the OCP. It is also striking that the dispersion, intensity and shape of the optical peak are almost independent of Γ . By contrast, the height of the central peak is a rapidly increasing function of Γ , as shown in Fig. 7. Furthermore the intensity plotted as a function of q shows a maximum in the neighborhood of q = 1.5, again almost independent of Γ . Both the central and optical peaks broaden with increasing q and this behavior, coupled with the frequency shift of the optical peak, eventually causes the two peaks to merge into a single, featureless curve. At still larger values of q the spectrum takes on the Gaussian shape characteristic of free-particle behavior. The shift with q of the characteristic optical frequency at maximum intensity is in qualitative agreement with a simple dispersion law^{10} based on the moments (2.23) and (2.28), i.e.,

$$\omega_m^2(q) = \langle \omega_{zz}^4 \rangle_{av}(q) / \langle \omega_{zz}^2 \rangle_{av}(q)$$
(5.2)

though the theoretical curve is somewhat flatter that the "experimental" one. Extrapolation of the molecular-dynamics results reveals that at long wavelength (q=0) the frequency of the optical mode is shifted positively with respect to ω_p by approximately 10%, in fair agreement with the estimate obtained from Eq. (5.2), i.e., $\omega_m(q=0)$ = 1.076. This last result is again independent of Γ .

The situation for $\Gamma = 0.4$ is rather different. We see in particular that there is no clearly defined central peak, even at the smallest accessible value of q; the optical peak is much broader than at high charge densities; and there is a pronounced high-frequency wing, a feature which is entirely lacking at larger values of Γ . The optical peak now broadens so rapidly that little significance can be attached to the way in which the peak position varies with q. This is marked contract to results obtained⁵ for the OCP at a comparable value of Γ , where the dispersion is well defined and strongly positive. No evidence for such behavior is seen in the present calculations. The approximate relation (5.2) does predict a strong positive dispersion, a result which illustrates the danger of relying on arguments based on moments when the spectrum is broad and, in particular, when there is an appreciable high-frequency contribution to the intensity. Calculations for smaller values of q are required before it can be established how close the limiting value of the optic frequency lies to the kinetic plasma frequency Ω_{b} . We should add here that a similar moleculardynamics calculation at $\Gamma = 0.4$ based on the minimum-image convention gave broadly similar results for $\sigma_{xx}(q, \omega)$, but the optical peak at small q was shifted to lower frequencies by almost 10%. This calculation was abandoned when it was found that the low-order moments were in poor agreement with results based on the hypernetted-chain approximation, which in this range of Γ is very nearly exact. No such discrepancy appears when the Ewald method is used.

It can be shown on rather general theoretical grounds, as we shall see in Sec. VI, that the physical effect giving rise to the two-peak structure in $\sigma_{zz}(q, \omega)$ at small q and large Γ is the coupling of fluctuations in charge and mass densities. The same conclusion can be reached in a more direct way by examining the form of the time correlation functions $F_{zz}(q, t)$, $F_{mm}(q, t)$, and $F_{mz}(q, t)$, examples of which are plotted in Fig. 8. For the particular choice made here for q and Γ we see that $F_{zz}(q, t)$ is dominated by a weakly damped oscillation at a frequency close to (but somewhat above) ω_{p} . At the same time it is clear that $F_{zz}(q, t)$ is oscillating not about zero but about a small and positive level which itself is slowly approaching zero. In other words the plasma oscillation appears as a relatively short-lived modulation of a much lower frequency motion. At the other extreme the function $F_{mm}(q, t)$ is dominated by a slow and almost monotonic relaxation towards zero, except that at short times there is a superimposed small amplitude "ripple" at a frequency close to ω_p . Finally, the cross correlation function $F_{ms}(q, t)$ combines the main features of the charge and mass fluctuations in roughly equal measure, changing from a strongly oscillatory behavior at short times to a slow relaxation at large times.

The extent to which charge fluctuations are coupled to fluctuations in mass is a function not only of q and Γ but also of the charge ratio Z_1/Z_2 and the mass ratio M_1/M_2 . In the special case when these two ratios are equal, the three correlation functions $F_{zz}(q, t)$, $F_{mm}(q, t)$, and $F_{mz}(q, t)$ become identical. Thus for the system D⁺ + He²⁺ we find the behavior shown in Fig. 9, where results on $\sigma_{zz}(q, \omega)$ at $\Gamma=0.4$ are given for two values of q. At small q the spectra differ in striking fashion from those obtained for H⁺ + He²⁺ at the same value of Γ . The high-frequency wing is absent, and the optical peak is much sharper and shows a *positive* dispersion, tending with decreasing q towards the value ω_p . In fact the curves resemble in all essential respects the spectra obtained⁵ for the OCP at a comparable charge density. As q increases the differences rapidly disappear, and at q = 1.384 (see Fig. 9) have almost completely disappeared.

VI. DISCUSSION

We want now to show how the spectra discussed in the previous section can be described in terms of the memory-function formalism of Mori and Zwanzig.¹¹ This approach is strongly phenomenological in character, but has the merit of yielding quantitative results which can be compared in detail with data obtained in the course of the molecular-dynamics calculations. A rigorous but more qualitiative analysis of the collective modes in a binary ionic mixutre has been given recently by Baus.^{8,9} Baus distinguishes between two types of modes: genuine hydrodynamic modes, characterized by a vanishing frequency and infinite lifetime in the limit $k \rightarrow 0$; and so-called relaxation modes, for which either the frequency or lifetime, possibly both, display nonhydrodynamic behavoir in the same limit. Only two longitudinal modes are hydrodynamic: these are diffusion modes, mixing heat conduction with mutual diffusion of the two species. The remaining longitudinal modes are of the relaxation type, included among which are the two charge relaxation modes associated with plasma oscillations. Baus's analysis also shows that the plasma frequency itself is a function of Γ , reducing to Ω_{ρ} in the $\Gamma \rightarrow 0$ limit and to the lower "hydrodynamic" frequency ω_{b} in the strong coupling limit. Since these results are exact, they serve as useful constraints on approximate treatments of the problem.

A. Linearized hydrodynamics

Before passing to the analysis in terms of memory functions it is worthwhile looking briefly at the results obtained from a calculation based on the linearized equations of hydrodynamics. The basic equations for an ionic mixture of the type of interest here (expressing conservation of charge, mass, momentum, and energy) are in fact nearly identical to those appropriate to molten salts (mixtures of oppositely charged ions) and are given explicitly in Refs. 12 and 17. The only difference is in the definition of the stress tensor [Eq. (13) of Ref. 12], since in the present case there is an additional first-order term stemming from the electrostatic potential of the background. The stress tensor now has components 2598

$$\pi_{\nu\mu} = \rho^{(M)} v_{\nu} v_{\mu} + P \delta_{\nu\mu} + e \rho_{z} \phi \delta_{\nu\mu} - \frac{1}{4\pi} (E_{\nu} E_{\mu} - \frac{1}{2} E_{\nu}^{2} \delta_{\nu\mu}) - \sigma_{\nu\mu}' (\nu, \mu = x, y, z), \quad (6.1)$$

where $\rho^{(M)}$ is the macroscopic local mass density; ρ_z is the charge density of the uniform background; $\mathbf{\vec{v}}$ is the local velocity field; P is the pressure; ϕ is the local electrostatic potential; $\vec{E} = -e\vec{\nabla}\phi$ is the local electric field, related to the macroscopic local charge density by Poisson's equation; and the quantities $\sigma'_{\nu\mu}$ are the components of the dissipative (viscous) part of the stress tensor [cf. Eq. (16) of Ref. 12]. On linearization of the hydrodynamic equations the terms quadratic in the local electric field vanish, which explains why linearized hydrodynamics does not predict an optical mode in molten salts, but the background electrostatic term remains. It is this last term which is responsible for the plasmon modes.

The determinant of the hydrodynamic matrix has four frequency roots. The first two are purely imaginary and correspond to diffusive hydrodynamic modes involving thermal conduction and interdiffusion of the two species; this is is good accord with Baus's results. The two remaining roots are complex conjugate and correspond to damped, propagating plasmon modes. In the $k \rightarrow 0$ limit they are given by

$$\omega = \pm (\omega_p^2 - \frac{1}{4}\omega_d^2)^{1/2} - \frac{1}{2}i\omega_d, \qquad (6.2)$$

where $\omega_d = 4\pi e^2 \alpha$ and α , the interdiffusion coefficient, is a phenomenological transport coefficient apeearing in the dissipative part of the electric current [see Eq. (17) of Ref. 12]. The main conclusion to be drawn from Eq. (6.2) is that the optical mode is damped (i.e., it has a finite lifetime) even in the long-wavelength limit. This arises as a consequence of interdiffusion and therefore has no analog in the one-component case (the OCP). Comparison with Baus's exact results shows that the behavior predicted by Eq. (6.2) is qualitatively correct, but the fact that the shift of the optical frequency from ω_{p} and the width of the plasmon mode are determined solely by the coefficient α is an oversimplification. The disagreement with Baus's work stems from the

fact that the plasmon mode is not a genuine hydrodynamic mode, but rather a relaxation mode, and hence cannot be described rigorously by the phenomenological hydrodynamic equations, even in the $k \rightarrow 0$ limit.

The four modes discussed above contribute in different fashion to each of the three normalized spectra $\sigma_{ab}(k, \omega)$, defined as in Eq. (5.1) (a, b =m, z). The diffusive hydrodynamic modes give rise to a central peak and the plasmon modes contribute symmetric optical peaks centered approximately on $\pm \omega_{p}$. In Table III we list the amplitudes and widths of the peaks to dominate order in k, together with the location (at positive frequency) of the maximum in the optic peak. It is clear from the table that the central peak should be the main feature of $\sigma_{mm}(k, \omega)$, the optical peaks should dominate $\sigma_{zz}(k, \omega)$, and the two types of peak should be of similar strength (area) in $\sigma_{mz}(k, \omega)$. These predictions are in good accord with the moelcular-dynamics results at small k and large г.

B. Memory-function analysis

From the discussion just given it is clear that at large values of Γ fluctuations in the densities of charge and mass are strongly correlated. Any successful microscopic theory must therefore treat the two densities on an equal footing. This can be achieved within the context of the Mori-Zwanzig theory by working in terms of a two-component vector of dynamical variables defined, in the notation of Ref. 11, as

$$\left|\vec{\mathbf{A}}(t)\right\rangle = \begin{bmatrix} (1/\sqrt{N_1})\rho_1(\vec{\mathbf{q}}, t)\\ (1/\sqrt{N_2})\rho_2(\vec{\mathbf{q}}, t) \end{bmatrix},\tag{6.3}$$

with a correlation function matrix $\dot{\mathbf{Y}}(t)$ given (in unnormalized form) by

$$\begin{aligned} \mathbf{\hat{Y}}(t) &= \langle \mathbf{\vec{A}}(t) \cdot \mathbf{\vec{A}}^* \rangle \\ &= \left[F_{\alpha\beta}(q, t) \right], \end{aligned}$$
(6.4)

From Eq. (2.15) it follows that

$$\mathbf{Y}(0) = \left[S_{\alpha\beta}(q)\right]. \tag{6.5}$$

The standard calculation based on a suitable choice of projection operator leads to an exact equation

TABLE III. Predictions of hydrodynamics for the position, height, and width of the central and optical peaks in the normalized dynamic structure factors.

 \leftrightarrow

	σ _{mm}		σ_{mz}		σ_{zz}	
	Central	Optical	Central	Optical	Central	Optical
Position	0	ω	0	$(\omega_p^2 - \frac{1}{2}\omega_d^2)^{1/2}$	0	ω
Height Width	k^{-2} k^2	k^2 k^0	k^{-2} k^2	k^0 k^0	k^0 k^2	k^0 k^0

of motion for the Laplace transform $\vec{\bar{Y}}(\omega)$ of the correlation function matrix in the form¹¹

$$\mathbf{\tilde{\breve{Y}}}(\omega) = [\mathbf{\tilde{\breve{M}}}(\omega) - i\omega \mathbf{\hat{I}}]^{-1} \mathbf{\hat{\breve{Y}}}(0), \qquad (6.6)$$

where \hat{I} is the 2×2 unit matrix and $\mathbf{\tilde{M}}(\omega)$ is the Laplace transform of a memory-function matrix $\mathbf{\tilde{M}}(t)$. The latter may be written

$$\vec{\mathbf{M}}(t) = \vec{\mathbf{m}}(t) \vec{\mathbf{Y}}^{-1}(0)$$
(6.7)

with

$$m(0) = \langle \vec{A} \cdot \vec{A}^* \rangle = \omega_0^2(q) \begin{bmatrix} m_1^{-1} & 0 \\ 0 & m_2^{-1} \end{bmatrix},$$
(6.8)

where the dots denote time derivatives and $\omega_0^2(q)$ is defined by Eq. (2.24). The time dependence of the matrix $\vec{m}(t)$ is determined by a time-evolution operator acting in the subspace orthogonal to the vector $|\vec{A}(t)\rangle$.

At this stage it is necessary to introduce some approximations. We therefore suppose that the variation of $\vec{m}(t)$ may be characterized by a single *q*-dependent relaxation time $\tau(q)$ and write

$$\widehat{\mathbf{m}}(t) = \widehat{\mathbf{m}}(0) f(t/\tau(q)) \tag{6.9}$$

and further assume that the function f has the Gaussian form given by

$$f(t/\tau(q)) = \exp[-(t/\tau(q))^2].$$
(6.10)

The real and imaginary parts of the Laplace transform of (6.10) are

$$\tilde{f}'(\omega) = \tau(q)\phi_1(s), \quad \tilde{f}''(\omega) = \tau(q)\phi_2(s),$$
 (6.11)

where $s = \omega \tau$ and

$$\phi_1(s) = \frac{1}{2}\sqrt{\pi} \exp(-\frac{1}{4}s^2),$$
 (6.12)

~ / 0

$$\phi_2(s) = \exp(-\frac{1}{4}s^2) \int_0^{s/2} \exp(x^2) \, dx = \mathfrak{D}(\frac{1}{2}s) \,, \quad (6.13)$$

where D denotes Dawson's integral.

An explicit expression for $\bar{\Upsilon}(\omega)$ can now be obtained by substitution in Eq. (6.6); the matrix of partial dynamical structure factors, $[S_{\alpha\beta}(q,\omega)]$, is then given (apart from a factor π^{-1}) by the real part of $\bar{\Upsilon}(\omega)$. After some lengthy algebra we find that

$$S_{\alpha\beta}(q,\omega) = (1/\pi) \tilde{Y}_{\alpha\beta}(q,\omega)$$

$$= \tau^{3}(q) \omega_{0}^{2}(q) \phi_{1}(s) \frac{\theta_{\alpha\beta}(q,s)}{\pi D(q,s)},$$
(6.14)

with

$$\theta_{\alpha\beta}(q,s) = c \delta_{\alpha\beta}(q) \tau^4(q) \omega_0^4(q) [\phi_1^2(s) + \phi_2^2(s)]$$

- 2s \phi_2(s) c \tau^2(q) \omega_0^2(q) \Delta(q) S_{\alpha\beta}(q) (6.15)
+ s^2 \Delta^2(q) G_{\alpha\beta}^2,

$$D(q, s) = \{c\tau^4(q)\omega_0^4(q)[\phi_1^2(s) - \phi_2^2(s)] + s\phi_2(s)X(q)\tau^2(q)\omega_0^2(q) - s^2\Delta(q)\}^2$$

$$+\phi_2^2(s) au^4(q)\omega_0^4(q)$$

$$\times [2c\phi_2(s)\tau^2(q)\omega_0^2(q) - sX(q)]^2, \qquad (6.16)$$

and

$$G_{\alpha\alpha}^2 = 1/m_{\alpha}, \quad G_{12}^2 = G_{21}^2 = 0, \quad c = G_{11}^2 G_{22}^2, \quad (6.17)$$

$$X(q) = (1/m_2)S_{11}(q) + (1/m_1)S_{22}(q), \qquad (6.18)$$

$$\Delta(q) = S_{11}(q)S_{22}(q) - S_{12}^2(q), \qquad (6.19)$$

$$\delta_{11}(q) = (1/m_2)S_{11}^2(q) + (1/m_1)S_{12}^2(q), \qquad (6.20)$$

$$\delta_{12}(q) = \delta_{21}(q) = (1/m_2)S_{11}(q)S_{12}(q) + (1/m_1)S_{21}(q)S_{22}(q), \qquad (6.21)$$

$$\delta_{22}(q) = (1/m_2)S_{21}^2(q) + (1/m_1)S_{22}^2(q).$$
 (6.22)

The charge-charge, charge-mass, and massmass dynamical structure factors $S_{ab}(q, \omega)$ are obtained finally from the transformation (2.14). The resulting spectra satisfy the zeroth- and second-frequency-moment sum rules (2.23)-(2.25), irrespective of the choice of the relaxation time $\tau(q)$. In practice we have calculated $\tau(q)$ as a function of q by forcing agreement with the fourth moment sum rule for $S_{ez}(q, \omega)$, that is to say we have determined $\tau(q)$ numerically by solving the implicit equation

$$\int_{-\infty}^{\infty} \omega^4 S_{zz}(q,\omega) / S_{zz}(q) d\omega = \omega_{zz}^4(q) / S_{zz}(q), \quad (6.23)$$

where $S_{zz}(q, \omega)$ is given by Eq. (6.14) and $\langle \omega_{zz}^4 \rangle_{av}(q)$ by Eq. (2.28).

There are a number of general points to be made here. First, it would clearly be more satisfactory to introduce three independent relaxation times which could be determined by imposing the three fourth-moment sum rules (2.26)-(2.28). This leads to very heavy algebra and tedious numerical calculations. Moreover, the improvement obtained could be not more than marginal, since the values derived for the single relaxation time by imposing the exact $\langle \omega_{mm}^4 \rangle_{av}(q)$ or $\langle \omega_{mz}^4 \rangle_{av}(q)$, rather than $\langle \omega_{zz}^4 \rangle_{av}(q)$, differ by less than 20% for any coupling Γ or any concentration x_1 . Second, it would be equally appropriate to choose for the vector of dynamical variables the set represented by

$$\left|\vec{\mathbf{A}}(t)\right\rangle = \frac{1}{\sqrt{N}} \begin{bmatrix} \rho_{m}(\vec{\mathbf{q}}, t) \\ \\ \\ \rho_{z}(\vec{\mathbf{q}}, t) \end{bmatrix} .$$
(6.24)



FIG. 10. Function $\sigma_{zz}(q,\omega)$ for $\Gamma = 40.0$. Reading from left to right and top to bottom: q = 0.875, 1.384, 1.857, and 2.316. Dots: molecular-dynamics results; curves: results of the memory-function analysis described in the text.

This choice is equivalent to (6.3) only if the calculation is carried through exactly, and not, for example, when the single-relaxation-time approximation is used. In practice the results obtained are very similar to those based on the choice (6.3). Finally, the static structure factors which determine the quantities defined in Eqs. (6.18)-(6.22)can be taken directly from the molecular-dynamics (or Monte Carlo³) calculations or obtained by solving the coupled hypernetted-chain euqations for the mixture. Since the differences in the calculated spectra are only small the hypernettedchain results can be used with confidence in computing spectra at values of Γ and x_1 for which no simulations have been made.

The spectra $\sigma_{ss}(q, \omega)$ predicted by the theory are shown in Figs. 10 and 11 for comparison with the molecular-dynamics results at $\Gamma = 0.4$ and 40.0; for technical reasons the q values do not match exactly, but never differ by more than a few percent. In the strongly coupled case (Fig. 10) the agreement between theory and "experiment" is generally good: the central peak is well reproduced, both in amplitude and in width, and the dispersion of the optical peak is correctly reproduced. The main failing is the fact that the theoretical optical peak is too sharp at small q; this is a familiar weakness of memory-function descriptions which ignore the coupling of the particle densities with other dynamical variables, in this case the energy and momentum desnities. A series of calculations carried out for $\Gamma > 20$ confirms the insensitivity of the optical peak in $S_{\sigma,s}(q,\omega)$ with respect to coupling which is such a striking feature of the molecular-dynamics calculations. The variation with Γ of the amplitude of the central peak in $\sigma_{zz}(q, \omega)$ is also in good agreement with the "experimental" results. The relaxation time $\tau(q)$ is insensitive to Γ , for fixed values of q, in the strong coupling regime, and decreases with decreasing $\boldsymbol{\Gamma}$ at intermediate couplings, as would be expected.

At $\Gamma = 0.4$ the agreement is less satisfactory, since the theoretical and "experimental" spectra have rather different band shapes. The barely resolved central peak is somewhat enhanced by the theory, while the "experimental" spectra have more pronounced high-frequency tails. The optical peak is poorly defined in both cases, but the peak in the molecular-dynamics results is everywhere displaced to higher frequencies. The theoretically determined optical peak sharpens and becomes rather well-defined for $q \leq 0.5$; in that region the characteristic optical frequency is found to increase with q, in agreement with the approximate dispersion relation (5.2), while in the strong coupling regime the dispersion is plainly negative. The theory predicts that for H⁺ - He²⁺ mixtures of concentration $x_1 = \frac{1}{2}$ the cross-



FIG. 11. Function $\sigma_{gg}(q,\omega)$ for $\Gamma=0.4$. Reading from left to right and top to bottom: q=0.619, 0.875, 1.384, and 2.316. Dots: molecular-dynamics results; curves: results of the memory-function analysis described in the text.

(6.25)

over from positive to negative dispersion takes place around $\Gamma = 4$; a similar behavior is found for the OCP.⁵

In the $q \rightarrow 0$ limit the theoretical experession for the charge-fluctuation spectrum takes on a particularly simple form. On combining Eqs. (2.14), (2.19), (5.1), and (6.16), we find that

$$\sigma_{zz}(q=0, \omega) = \frac{1}{\pi} \frac{\xi^3 \tau^3(0) \phi_1(s)}{[\xi^2 \tau^2(0) \phi_1(s)]^2 + [\xi^2 \tau^2(0) \phi_2(s) - s]^2},$$

where ξ^2 is defined by Eq. (2.29), $s = \omega \tau(0)$, and the relaxation time $\tau(0)$ is determined by Eq.

(6.23). Since the ratio

$$\omega_m^2(q) = \langle \omega_{zz}^4 \rangle_{av}(q) / \langle \omega_{zz}^2 \rangle_{av}(q) \simeq \langle \omega_{zz}^4 \rangle_{av}(q) / \xi^2 S_{zz}(q)$$
(6.26)

is independent of Γ in the limit $q \rightarrow 0$,¹⁰ it follows that $\tau(0)$ and hence $\sigma_{zz}(q=0,\omega)$ are also independent of Γ , in agreement with the molecular-dynamics results in the strong coupling regime. The numerical results for $\tau(0)$ at small q suggest that $\tau(0)$ is sufficiently large to justify neglecting $\phi_1(s)$ in comparison with $\phi_2(s)$; if the asymptotic expansion of Dawson's integral is used to approximate $\phi_2(s)$, the integral (6.23) can be evaluated analytically. The relaxation time $\tau(0)$ is then given in terms of the small parameter

$$\gamma = \omega_m^2(0)/\xi^2 - 1 \tag{6.27}$$

by the expansion which begins

$$1/\xi^2 \tau^2(0) = \frac{1}{2}\gamma + \frac{19}{4}\gamma^3 + \dots$$
 (6.28)

and the characteristic frequency of the optical mode is given by

$$\omega(q=0) = \xi\left(1 + \frac{1}{2}\gamma + \frac{7}{8}\gamma^2 + \frac{133}{16}\gamma^3 + \cdots\right), \quad (6.29)$$

where, as always, the unit of frequency is ω_p . Since $\xi = \Omega_p / \omega_p$, it follows that the optical frequency at long wavelength is shifted above the mean-field frequency Ω_p . Furthermore, the shift depends only on concentration and not on the strength of the coupling. For a H^{*} + He^{2*} mixture with $x_1 = \frac{1}{2}$, Eq. (6.28) yields $\tau(0) = 6.5$. Thus, from (6.29), $\omega(q=0) \simeq 1.079$. This result, and the fact that the shift is independent of Γ , are in good accord with the molecular-dynamics results at large Γ , but are in disagreement with a calculation by Baus⁹ which is exact in the weak coupling limit. Our approach therefore represents a strong coupling theory; the main conclusion we draw is that the characteristic optical frequency is always greater than Ω_p and hence, from the inequality $\Omega_p \ge \omega_p$, can never reach the "hydrodynamic" value ω_p . This surprising result is in contradiction with the speculation in Refs. 9 and 10, but is in good agreement with the "experimental" data.

The mass-mass and mass-charge dynamical structure factors predicted by the theory exhibit the qualitative features of the hydrodynamic calculation summarized in Table III, and the three partial dynamical structure factors $S_{\alpha\beta}(q,\omega)$ are nearly identical, again in good agreement with the molecular-dynamics results.

VII. CONCLUSIONS

The molecular-dynamics results show that the dynamical properties of the binary ionic mixture are in some respects very different from those of the corresponding one-component system, i.e., the OCP. In particular, interdiffusion causes a broadening and shift of the optic mode, effects which persist even in the limit $k \rightarrow 0$. Qualitatively the main features of the observed spectra are in good agreement both with the predictions of a simple hydrodynamic calculation and with some exact results due to Baus.8,9 The most striking "experimental" result is that the hydrodynamic limit is apparently never reached: the characteristic frequency of the optical mode is always larger than the "hydrodynamic" plasma frequency ω_{b} , and is essentially independent of Γ at high charge densities. A memory-function treatment which incorporates the coupling of mass and charge fluctuations accounts well for the "experimental" results at large Γ but is less successful in the intermediate regime ($\Gamma \sim 1$), where temperature fluctuations clearly play an important role. The same formalism should also be useful in the analysis of the behavior of related systems, particularly of the two-component plasma (or TCP^{7}).

Overall the work described here and in earlier papers^{5,7,10} illustrates the remarkable variety of behavior that can be found in the dynamical properties of ionic fluids.

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