# Statistical mechanics of dense ionized matter. IV. Density and charge fluctuations in a simple molten salt

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The results of a molecular-dynamics study of a simple model of a molten salt are reported. The interionic pair potential which is used consists of the Coulombic term and an inverse-power repulsion which is assumed to be the same for all ions. The structure of the liquid is found to be dominated by charge-ordering effects and the calculated equilibrium properties are in good agreement with the predictions of the hypernetted-chain approximation. The relation between the self-diffusion coefficient and the electrical conductivity is discussed, and the observed deviations from the Nernst-Einstein relation in real molten salts are shown to have a natural explanation in terms of short-lived cross correlations. Data on the spectra of charge and particle density fluctuations are presented. At small wave numbers there is a propagating optic-type mode which shows a strong negative dispersion, but no Brillouin peak is seen even at the lowest wave number which is accessible. The data are analyzed in terms of a single-relaxation-time model incorporating the low-order spectral moments, for which we give explicit formulas. The fit achieved is fair, but the low-frequency behavior of the charge fluctuations at small wave numbers is incorrectly reproduced, and there is evidence for the necessity of introducing a second relaxation time. Comparison is made with results previously obtained for the classical one-component plasma.

## I. INTRODUCTION

One of the most interesting results to emerge from recent research on simple liquids is the existence of well-defined collective excitations in a range of wave numbers k up to  $2\pi$  times the inverse of the nearest-neighbor distance  $r_0$ . This information has come both from molecular-dynamics (MD) calculations and from neutron-scattering experiments. For example, the moleculardynamics work of Levesque  $et al.^1$  has shown that in the spectrum of density fluctuations in an argonlike liquid a three-peak structure characteristic of the hydrodynamic regime is still observable at wavelengths as short as  $6r_0$ . The position of the Brillouin peak in these calculations is at a frequency such that  $\omega/k$  is very nearly equal to the macroscopic sound velocity. The persistence of propagating density fluctuations at short wavelengths is apparently closely related to the form of the interparticle potential. Whereas the work of Levesque  $et al.^1$  was based on the familiar Lennard-Jones potential, a more recent computer "experiment" made on liquid rubidium by Rahman.<sup>2</sup> in which a long-range oscillatory potential due to Price<sup>3</sup> was used, has shown that in such a system density waves continue to propagate at wavelengths of order  $2r_0$ . The results obtained by Rahman<sup>2</sup> are in excellent agreement with the neutron-scattering measurements of Copley and Rowe.<sup>4</sup>

In an earlier paper of this series, to be referred

to as I, we have, in collaboration with Pollock,<sup>5</sup> used the method of molecular dynamics to study the collective dynamical properties of the classical one-component plasma (OCP) in a uniform neutralizing background. Because of the assumed rigidity of the background, the dynamical structure factor  $S(k, \omega)$  of the OCP describes simultaneously the spectrum both of density and charge fluctuations. At small wave numbers the dominant feature in  $S(k, \omega)$  is a very sharp peak near the plasma frequency. The dispersion is typical of an optic-type mode, the peak being found at nonzero frequency even in the limit  $k \rightarrow 0$ .

The purpose of the present paper is to report the results of a molecular-dynamics simulation of a system of two components, differing only in the sign of their charges, which may be regarded as a simple model of a monovalent molten salt. The feature of molten salts which is of particular interest in the present context is the fact that the charge and density fluctuations are independent, at least in the long-wavelength limit. The possibility therefore exists of observing both the soundwave propagation at low k which is characteristic of simple liquids and the plasma oscillations which we have previously studied in the case of the OCP. These two phenomena are the liquid-state analogs of the acoustic and optic modes of ionic crystals. In practice, we have been only partly successful, as we have been unable to detect any Brillouin peak in  $S(k, \omega)$ , even at the smallest k value which

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is accessible in the size of system we have studied.

Our interest lies primarily in elucidating the general character of short-wavelength excitations in molten salts rather than in making detailed quantitative calculations for a specific system. We wish in particular to avoid the complications which arise when the ions are of unequal size and mass. The model which we have used is one in which the masses of the cation and anion are equal, the ions are singly charged, and the interaction potential for two ions of either species is given by

$$\varphi(r_{12}) = \frac{e^2}{\lambda} \left[ \frac{1}{n} \left( \frac{\lambda}{r_{12}} \right)^n + Q_1 Q_2 \left( \frac{\lambda}{r_{12}} \right) \right]; \tag{1}$$

 $Q_1$  and  $Q_2$  are the ionic charges in units of e, the electronic charge;  $\lambda$  is a characteristic length parameter which in fact is the separation at which the cation-anion potential is a minimum; and n is an exponent which we set equal to 9. Monte Carlo calculations  $^{\rm 6}$  have shown that a model similar to (1) provides a fair description of the thermodynamic properties of the alkali-metal salts. The only difference between the potential used in Ref. 6 and that employed here is the fact that in the Monte Carlo work the short-range repulsive interactions between ions of like sign were ignored. From a practical point of view the distinction is unimportant because such interactions make a negligible contribution to the total potential energy of a typical configuration of ions. The thermodynamic properties of either model may be scaled on a corresponding-states basis, but the scaling of temperature is not independent of that of volume, as is the case in OCP.

The technical details of the molecular-dynamics calculations are similar to those in our work on the OCP, a few obvious changes being required in order to deal with a two-component system and short-range interionic repulsions. The algorithm adopted by Verlet<sup>10</sup> was used to integrate numerically the classical equations of motion of a system of 216 ions, 108 of each species, enclosed within a cube which is surrounded on all sides by periodically repeating images. The Coulombic force on each ion was computed by the Ewald method and the short-range interactions were truncated at a separation of one-half the length of the cube. As unit of length we choose the characteristic length  $\lambda$ , and as the unit of time we choose the inverse plasma frequency  $\omega_{\phi}^{-1}$ , defined by

$$\omega_p^2 = 4\pi \rho e^2 / m , \qquad (2)$$

where  $\rho = N/V$  is the total number density of ions.

The molecular-dynamics "experiment" was made at a volume  $V/N\lambda^3 = 2.72$  and the trajectories of the ions were followed for  $2.5 \times 10^4$  time steps of length  $\Delta t = 0.2$ , extended to  $5 \times 10^4$  steps for the calculation of electrical conductivity. The mean temperature of the run was  $\lambda k T/e^2 = 0.0177$ . To give some feeling for the magnitude of the quantities involved, we shall make a conversion to real units for the case of liquid NaCl. Taking the Monte Carlo calculations<sup>6</sup> as a guide, we choose  $\lambda = 2.34$ Å and find V = 41.9 cm<sup>3</sup> mol<sup>-1</sup>, T = 1267 K, and  $\Delta t$  $= 0.48 \times 10^{-14}$  sec. For comparison, the triple point<sup>7</sup> of NaCl is at V = 37.52 cm<sup>3</sup> mol<sup>-1</sup>, T = 1073 K.

In order to simplify comparison with our results on the OCP, it is convenient to introduce two further quantities. These are in the ion-sphere radius a given by

$$a = (3/4\pi\rho)^{1/3},\tag{3}$$

and the (dimensionless) plasma parameter  $\Gamma$  defined as

$$\Gamma = e^2 / ak_B T \,. \tag{4}$$

Under the conditions of our "experiment" we find that  $a = 0.866\lambda$  and  $\Gamma = 64.6$ .

The outline of the paper is as follows. Equilibrium properties are discussed in Sec. II and comparison made with results of the hypernettedchain (HNC) theory. Section III is concerned with the phenomena of self-diffusion and electrical conductivity and the correlation of the two transport coefficients through the Nernst-Einstein relation; a brief account of this part of the work has previously appeared elsewhere.<sup>8</sup> Sections IV and V are devoted to the analysis, respectively, of density and charge fluctuations. Expressions for the low-order moments of the corresponding current correlation functions are derived and used to build a simple phenomenological model which provides a fair description of the observed spectra. Finally, in Sec. VI, we make some suggestions for future work.

## **II. EQUILIBRIUM PROPERTIES AND STRUCTURE**

The equilibrium structure of a molten salt may be described in terms of the three partial radial distribution functions:  $g_{++}(r)$ ,  $g_{--}(r)$ , and  $g_{+-}(r)$ . For our simple model there is some simplification because  $g_{++}(r)$  and  $g_{--}(r)$  are identical on grounds of symmetry. This makes it convenient to discuss the problem in terms of only two distribution functions:

$$g_1(r) = \frac{1}{2} [g_{++}(r) + g_{--}(r)], \qquad (5)$$

$$g_2(r) = g_{+-}(r)$$
. (6)

Corresponding to  $g_1(r)$  and  $g_2(r)$  we have two total correlation functions,  $h_1(r)$  and  $h_2(r)$ , two direct correlation functions,  $c_1(r)$  and  $c_2(r)$ , and two structure factors:

$$S_{1}(k) = 1 + \frac{1}{2} \rho * \tilde{h}_{1}(k), \qquad (7)$$

$$S_{2}(k) = \frac{1}{2} \rho * \tilde{h}_{2}(k), \qquad (8)$$

where  $\rho^* = \rho \lambda^3$  and the tilde is used to denote a Fourier transform. Charge neutrality<sup>9</sup> requires that

$$\lim_{k \to 0} S_1(k) = \lim_{k \to 0} S_2(k),$$
(9)

and the perfect-screening condition<sup>9</sup> requires that

$$S_1(k) - S_2(k) \sim k^2 / \kappa^2,$$
 (10)

where  $\kappa$  is the inverse Debye length

$$\kappa = (4\pi\rho e^2/k_B T)^{1/2} \,. \tag{11}$$

Fluctuations in density are described in k space by the structure factor S(k), given by

$$S(k) = S_1(k) + S_2(k),$$
 (12)

and those in charge by the structure factor S'(k):

$$S'(k) = S_1(k) - S_2(k)$$
. (13)

The long-wavelength limits of (12) and (13) are determined by

$$\lim_{k \to 0} S(k) = \frac{1}{k_B T} \left[ \left( \frac{\partial P}{\partial \rho} \right)_T \right]^{-1}, \qquad (14)$$

$$\lim_{k \to 0} S'(k) = 0.$$
 (15)

If we attempt to use the computed distribution functions to calculate the various structure factors, we encounter the usual problem, namely that the molecular-dynamics "experiment" yields values for the distribution functions only for interionic separations less than some cutoff distance  $r_c$ . In our case  $r_c$  is equal to one-half the length of the cube, i.e.,  $r_c = 4.185\lambda$ . We have therefore extrapolated our results on  $g_1(r)$  and  $g_2(r)$  beyond  $r = r_c$  by the method devised by Verlet,<sup>10</sup> except that we approximate the direct correlation functions at large r by means of the hypernetted-chain (HNC) approximation rather than the Percus-Yevick (PY) approximation. The justification for this change is the fact that HNC is known to be superior to the PY approximation in the case of long-range potentials, as evidenced by the work of Springer et al.<sup>11</sup> on the OCP.

To implement the method of Verlet,<sup>10</sup> we require a good initial guess for  $c_1(r)$  and  $c_2(r)$ . In practice, we have found that this requires the solution to the full coupled HNC equations for our system. To obtain this we have adapted the very efficient method of Springer *et al.*<sup>11</sup> to the case of two components, but even then the calculations have proved very time consuming. We have been compelled to solve the HNC equations for a range of temperatures, starting at very high temperature and reducing in stages to the temperature of interest. At each new step in this procedure we used as input the direct correlation functions obtained at the previous stage. Approximately 500 iterations were needed at each step before satisfactory convergence was achieved and the extrapolation itself finally required 4000 iterations. The calculations, though lengthy, do have the advantage of yielding the HNC solution as a by-product. Though the HNC equation has often been used for electrolytes,<sup>12</sup> we are not aware of any previous calculations at charge densities typical of molten salts apart from some unpublished work by Larsen<sup>13</sup> on systems of hard-sphere ions.

The distribution functions  $g_1(r)$  and  $g_2(r)$  are plotted in Fig. 1,  $c_1(r)$  and  $c_2(r)$  in Fig. 2, and the structure factors S(q) and S'(q), where  $q = \lambda k$ , are shown in Fig. 3. What is very clear from Figs. 1 and 3 is the extent to which the structure of an ionic melt is determined by charge-ordering effects, a feature which has previously been discussed on the basis of Monte Carlo calculations by Woodcock and Singer.<sup>14</sup> The function  $g_2(r)$  has a very sharp peak near  $r = \lambda$  and the later oscillations differ in phase from those in  $g_1(r)$  by almost exactly half a period. The result is that the overall radial distribution function has virtually no structure beyond its first peak. The function  $g_1(r)$ , in contrast to  $g_2(r)$ , has a rather weak and broad first peak near  $r = 1.75\lambda$ . However, the tail of  $g_1(r)$ at small r extends inwards as far as the peak in  $g_2(r)$ , indicating that there is some small pene-



FIG. 1. Radial distribution functions.

tration of ions of like charge into the first coordination shell around a given ion. In q space the importance of charge ordering is equally obvious. The charge-charge structure factor S'(q)has a very pronounced first peak and displays much more structure than the number-number structure factor S(q). It should be noted that the main peak in S'(q) occurs at a significantly smaller value of k than that in S(q). The difference arises from the fact that the position of the peak in S'(q)is determined by the period of oscillation of mean charge density around a reference ion, whereas that in S(q) is determined by the value of the nearest-neighbor distance. As a check on the numerical accuracy we have confirmed that the conditions (8) and (9) are both very well obeyed.

The direct correlation function  $c_1(r)$  is a monotonic function of r and qualitatively is very similar to that obtained for the OCP. The function  $c_2(r)$ , on the other hand, shows a break in slope near  $r = \lambda$ ; this is a remnant of the hard-core type of discontinuity observed by Larsen.<sup>13</sup> Both  $c_1(r)$ and  $c_2(r)$  tend very rapidly to their Debye-Huckel limits. At  $r = 1.6\lambda$  the discrepancies in either case are already less than 1%.

For the sake of easy reference we list the results on the distribution functions in Table I and those on the structure factors in Table II. In Table I we also report the results of the HNC calculations. We have not plotted the HNC results in



FIG. 2. Direct correlation functions.

the figures simply because the differences are generally too small to make fair comparison possible, particularly in the steeply rising part of  $g_2(r)$ . In this case we find that

$$PV/NkT = 1 + 11.80 - 12.48 = 0.32$$
 (MD)  
= 1 + 12.51 - 12.53 = 0.96 (HNC).

Overall the agreement with the molecular-dynamics calculations is surprisingly good, and better than might be expected on the basis of results obtained for the OCP.<sup>11</sup> The only major discrepancy is in the values of S(k) at small k. In particular, we find in the long-wavelength limit that

$$S(0) = 0.16 (MD)$$
  
= 0.50 (HNC),

so that the HNC approximation yields a compressibility which is approximately three times too large.

For other thermodynamic properties the HNC results are much more satisfactory. For the excess internal energy we may divide the net result into contributions from short-range (SR) and Coulombic (C) interactions:

$$\frac{U}{Nk_BT} = \frac{U^{SR}}{Nk_BT} + \frac{U^C}{Nk_BT} .$$
(16)

On dividing the calculated values in the same way, we find that

$$U/Nk_BT = 3.93 - 37.45 = -33.52$$
 (MD)  
= 4.17-37.59 = -33.42 (HNC).

A similar division may be made for the equation of state

$$\frac{PV}{Nk_BT} = 1 + \frac{P^{SR}V}{Nk_BT} + \frac{P^{C}V}{Nk_BT} .$$
 (17)



FIG. 3. Structure factors as functions of the dimensionless wave number  $q = \lambda k$ .

~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	g. (Y)	oHNC (r)	$\mathcal{P}_{n}(\mathbf{r})$	gHNC(r)	C; (2)	C <sup>HNC</sup> (X)	$C_{\alpha}(\mathbf{r})$	C <sup>HNC</sup> (x)
	51(7)	61 (7	82(17	82 (77				
0.0	0.0	0.0	0.0	0.0	-75.76	-74.42	66.38	65.55
0.084	0.0	0.0	0.0	0.0	-75.08	-73.68	66.20	65.37
0.167	0.0	0.0	0.0	0.0	-73.40	-71.94	65.63	64.80
0.251	0.0	0.0	0.0	0.0	-71.34	-69.91	64.66	63.86
0.335	0.0	0.0	0.0	0.0	-69.20	-67.85	63.33	62.59
0.419	0.0	0.0	0.0	0.0	-67.03	-65.81	61.70	61.06
0.502	0.0	0.0	0.0	0.0	-64.84	-63.75	59.86	59.35
0.586	0.0	0.0	0.0	0.0	-62.62	-61.66	57.89	57.53
0.670	0.0	0.0	0.0	0.0	-60.37	-59.53	55.86	55.66
0.754	0.0	0.0	0.0	0.0	-58.10	-57.37	53.83	53.75
0.837	0.0	0.0	0.0	0.0	-55.81	-55.19	51.81	51.82
0.921	0.0	0.0	0.048	0.042	-53.52	-53.00	49.86	49.93
0.963	0.0	0.0	0.516	0.575	-52.37	-51.89	49.33	49.49
1.005	0.0	0.0	1.882	2.183	-51.23	-50.80	49.70	50.12
1.047	0.0	0.0	3.489	3,900	-50.09	-49.70	50.31	50.86
1 088	0.0	0.001	4.275	4.526	-48.96	-48.60	50.10	50.51
1 130	0.002	0.006	4 115	4 137	-47.84	-47.51	48.95	49.14
1.172	0.009	0.023	3.453	3.345	-46.73	-46.42	47.29	47.37
1 914	0.028	0.619	2 718	2 566	-45.62	-45 32	45.56	45.61
1.056	0.020	0.019	2.110	1 046	-44.50	-44 19	43.95	44 02
1.200	0.000	0.133	2.034	1 405	-44.00	-43.04	12.00	42.60
1.290	0.140	0.244	1.012	1 179	49.91	-41.97	42.45	41 39
1.340	0.251	0.392	1.209	1.178	-42.21	-41.07	41.10	41.52
1.382	0.401	0.568	1.016	0.956	-41.03	-40.70	09.91 90.0F	40.10
1.423	0.586	0.758	0.844	0.805	-39.64	-39.02	30.00	39.00
1.465	0.790	0.947	0.720	0.699	-38.00	-38.37	37.00	30.03
1.507	1.001	1.120	0.632	0.626	-37.49	-37.26	30.01	37.00
1.549	1,198	1.267	0.572	0.076	-30.35	-36.20	22.00	30.12
1.591	1.368	1.384	0.530	0.545	-35.28	-35.20	34.95	35.22
1.633	1.502	1.468	0.503	0.526	-34.26	-34.25	34.08	34.35
1.674	1.590	1.523	0.487	0.517	-33.32	-33.36	33.25	33.52
1.716	1.642	1.551	0.481	0.516	-32.45	-32.52	32.45	32.72
1.758	1.658	1.558	0.484	0.522	-31.64	-31.74	31.68	31.95
1.800	1.650	1.550	0.492	0.535	-30.89	-30,99	30.94	31.20
1.842	1.621	1.532	0.508	0.553	-30.19	-30.29	30.24	30.49
1.926	1.526	1.478	0.556	0.603	-28.92	-28.97	28.92	29.13
9.010	1 /19	1 414	0 695	0 660	97 70		97 71	27 00
2.010	1 990	1,414	0.025	0.009	-21.10	-21.10	21.11	21.30
2.093	1.409	1.309	0.112	0.731	40.73	-20.09	20.00	20.10
2.177	1.145	1,145	0.823	0.847	-25.75	-25.69	23,60	20.70
2.261	0.997	0.976	0.947	0.956	-24.79	-24.75	24.68	24.74
2.344	0.873	0.851	1.078	1.071	-23.90	-23.85	23.84	23,86
2.428	0.783	0.778	1.199	1.179	-23.08	-23.01	23.06	23.05
2.512	0.731	0.746	1.285	1.261	-22.32	-22.23	22.32	22.30
2.596	0.712	0.743	1.321	1.299	-21.61	-21.51	21.61	21.59
2.721	0.735	0.779	1.285	1.266	-20.64	-20.52	20.60	20.58
2.847	0.809	0.848	1.182	1.165	-19.75	-19.64	19.69	19.66
2.972	0.913	0.937	1.059	1.049	-18.92	-18.82	18.86	18.82
3.098	1.027	1.028	0.954	0.953	-18.14	-18.06	18.09	18.06
3.224	1.118	1.102	0.880	0.888	-17.42	-17.35	17.40	17.36
3.349	1.167	1.144	0.845	0.861	-16.75	-16.69	16.74	16.71
3.475	1.165	1.145	0.844	0.869	-16.14	-16.09	16.12	16.11
3.600	1.124	1.108	0.875	0.902	-15.56	-15.53	15.55	15.54
3.726	1.059	1.050	0.931	0.950	-15.03	-15.01	15.02	15.01
3.852	1.001	0.990	0.997	1.003	-14.52	-14.52	14.52	14.52

TABLE I. Radial distribution functions.

# III. SELF-DIFFUSION AND ELECTRICAL CONDUCTANCE

The self-diffusion of ions of species  $\alpha$  (where  $\alpha$  may be + for cations, or - for anions) is usefully discussed in terms of the velocity autocorrelation function  $Z_{\alpha}(t)$ , defined as

$$Z_{\alpha}(t) = \langle \vec{\mathbf{v}}_{i\alpha}(t) \cdot \vec{\mathbf{v}}_{i\alpha}(0) \rangle, \qquad (18)$$

where the angular brackets denote an average over (a) all ions, labeled *i*, of species  $\alpha$ , and (b) all choices of the time origin. For our simple model the autocorrelation functions  $Z_+(t)$  and  $Z_-(t)$ are identical and the subscripts may therefore be dropped. Then the coefficients of self-diffusion, D, is related to Z(t) through the well-known expression

$$D = \frac{1}{3} \int_0^\infty Z(t) \, dt \, . \tag{19}$$

From our calculations we find that D = 0.0049. For NaCl, taking the value of  $\lambda$  which we have already used, we find that our result corresponds to D=  $9.5 \times 10^{-5}$  cm<sup>2</sup> sec<sup>-1</sup>. Experimentally,<sup>7</sup> for NaCl at V = 38.2 cm<sup>3</sup> mol<sup>-1</sup> and T = 1121 K we find  $D_{+}$ =  $9.99 \times 10^{-5}$  cm<sup>2</sup> sec<sup>-1</sup>,  $D_{-} = 7.21 \times 10^{-5}$  cm<sup>2</sup> sec<sup>-1</sup>.

The electrical conductivity  $\sigma$  is related to the normalized autocorrelation function of the total current J(t), defined as

$$J(t) = \left\langle \left( \sum_{i} \vec{\nabla}_{i+}(t) - \sum_{j} \vec{\nabla}_{j-}(t) \right) \times \left( \sum_{i} \vec{\nabla}_{i+}(0) - \sum_{j} \vec{\nabla}_{j-}(0) \right) \right\rangle .$$
(20)

The principle of conservation of momentum may be used to rewrite this expression in several equivalent forms. The conductivity is given by

$$\sigma = \frac{e^2}{3 \, V k \, T} \, \int_0^\infty J(t) \, dt \, . \tag{21}$$

The electrical current is a collective property of the system and the averaging process labeled (a) above, which is used to improve the statistics on Z(t), cannot be applied to the calculation of J(t). Thus our estimate for  $\sigma$  is probably not accurate to better than 5%. In fact we find a value which for NaCl corresponds to 3.2 mho cm<sup>-1</sup>. The experimental result<sup>7</sup> for NaCl at the state defined above is 3.7 mho cm<sup>-1</sup>. We include this comparison with experiment both for D and  $\sigma$  primarily as evidence that our potential model is adequate to describe the main features of transport in molten salts.

A useful empirical link between the coefficients of self-diffusion and electrical conductivity is provided by the Nernst-Einstein relation. If we introduce a deviation parameter  $\Delta$ , we may write this relation in a generalized form as

$$\sigma = \frac{1}{2} \left( N e^2 / V k T \right) \left( D_+ + D_- \right) \left( 1 - \Delta \right).$$
 (22)

From the data tabulated by Young and O'Connell<sup>7</sup> it is possible to compute values of  $\Delta$  for eight alkali-metal salts at zero pressure and temperatures close to the respective triple points. We find that  $\Delta$  is invariably positive, varying from 0.08 in the case of NaI to 0.43 for LiNO<sub>3</sub>, with a mean of 0.26. Our own results on *D* and  $\sigma$  lead to a value of  $\Delta = 0.19$ . This compares particularly well with the experimental results for the chlorides: 0.15 (RbCl), 0.18 (NaCl), and 0.23 (CsCl).

The validity of the Nernst-Einstein relation, with  $\Delta = 0$ , can be deduced from Eqs. (18)-(21) if it is assumed that cross correlation terms of the type  $\langle \bar{\mathbf{v}}_{i-}(t) \cdot \bar{\mathbf{v}}_{j+}(0) \rangle$  make zero contribution to J(t). In such circumstances it follows that J(t) = NZ(t)and the two normalized autocorrelation functions should be identical. The obvious explanation of deviations from the Nernst-Einstein relation lies in the formation of ionic complexes which contribute to the diffusive flux but not to the electrical current. Our results on Z(t) and J(t), normalized to unity at t = 0, are shown in Fig. 4. From the figure we see that there are some significant differences between the two functions. In particular,

TABLE II. Structure factors.

$q = \lambda k$	S (q)	S'(q)	$q = \lambda k$	S (q)	S' (q)
0.0	0.160	0.0	5.4	0.998	0.745
0.2	0.162	0.00015	5.8	1.073	0.651
0.4	0.166	0.00063	6.2	1.145	0.634
0.6	0.174	0.00148	6.6	1.192	0.667
0.8	0.187	0.00276	7.0	1.208	0.737
1.0	0.206	0.0046	7.4	1.205	0.829
1.2	0.228	0.0072	7.8	1.160	0.937
1.4	0.253	0.0108	8.2	1.049	1.045
1.6	0.277	0.0158	8.6	1.938	1.128
1.8	0.299	0.0228	9.0	0.866	1.168
2.0	0.321	0.0326	9.4	0.837	1.165
2.2	0.344	0.0464	9.8	0.844	1.133
2.4	0.371	0.0665	10.2	0.876	1.086
2.6	0.404	0.097	10.6	0.925	1.035
2.8	0.444	0.146	11.0	0.981	0.990
3.0	0.489	0.228	11.8	1.078	0.933
3.2	0.537	0.377	12.6	1.097	0.921
3.4	0.585	0.672	13.4	1.045	0.958
3.6	0.629	1.279	14.2	0.979	1.013
3.8	0.671	2.392	15.0	0.948	1.049
4.0	0.710	3.355	15.8	0.954	1.046
4.2	0.750	2.969	16.6	0.986	1.016
4.4	0.791	2.136	17.4	1.018	0.982
4.6	0.834	1.550	18.2	1.033	0.968
4.8	0.878	1.195	19.0	1.024	0.976
5.0	0.920	0.976	19.8	1.003	0.996
			1		

the negative region is much more pronounced in J(t) than in Z(t). It is also clear that deviations from the Nernst-Einstein relation are not necessarily the result of a permanent association of ions of opposite charge. Figure 4 shows that the difference between the two normalized autocorrelation functions reaches a maximum near the first zero in each, and then rapidly disappears as t increases. In this case, at least, the Nernst-Einstein deviation has a natural explanation in terms of short-lived cross-correlation functions.

Finally, we mention that the velocity autocorrelation function resembles very closely that observed in an argonlike liquid at high density.<sup>15</sup> The work reported in I has shown that in the OCP the single-particle motion is very strongly coupled to the collective modes. This coupling is seen in the fact that the velocity autocorrelation function is characterized by well-defined oscillations, at a frequency close to  $\omega_{\mu}$ , which are already evident at  $\Gamma \approx 10$  and become increasingly more pronounced as the crystallization point ( $\Gamma$  $\approx$ 155) is approached. In the present case, however, the power spectrum  $\tilde{Z}(\omega)$  displays only a low-frequency diffusive peak and a weak shoulder at higher frequency which arises from the long tail in Z(t). There is no evidence of any remnant of a plasma-type oscillation.

Self-diffusion in molten salts has also been studied by molecular dynamics by Lantelme etal.<sup>16</sup> and by Lewis and Singer<sup>17</sup>; the potential model used by these workers is considerably more complicated than that employed here.

## **IV. DENSITY FLUCTUATIONS**

In order to discuss the collective longitudinal modes of the system under study, we first introduce the operators  $\rho_k^{\pm}(t)$  and  $\rho_k^{\pm}(t)$  which represent the Fourier components of the density of cations and anions

$$\rho_{\vec{k}}^{+}(t) = \sum_{i} e^{i \vec{k} \cdot \vec{r}_{i+1}(t)} , \qquad (23)$$

$$\rho_{\vec{k}}(t) = \sum_{j} e^{i\vec{k}\cdot\vec{r}_{j-}(t)} .$$
(24)

From these quantities we may construct a total number density operator  $\rho_{\vec{k}}(t)$  given by

$$\rho_{k}^{-}(t) = \rho_{t}^{+}(t) + \rho_{t}^{-}(t) .$$
(25)

The time dependence of fluctuations in  $\rho_{\overline{t}}(t)$  is described by the density-density correlation function F(k, t)

$$F(k, t) = (1/N) \langle \rho_{k}(t) \rho_{-k}(0) \rangle$$
(26)

The Fourier transform of F(k, t) is the dynamical structure factor:

$$S(k, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} F(k, t) dt$$
(27)

 $S(k, \omega)$  represents the spectrum of number density fluctuations in the system.

It is also convenient to introduce the total particle current operators  $\overline{j}_{\mathbf{k}}(t)$ , defined as

$$\mathbf{\bar{j}}_{\vec{k}}(t) = \mathbf{\bar{j}}_{\vec{k}}(t) + \mathbf{\bar{j}}_{\vec{k}}(t),$$
 (28)

where

$$\vec{j}_{\vec{k}}^{+}(t) = \sum_{i} \vec{v}_{i+} e^{i\vec{k}\cdot\vec{r}_{i+}(t)}, \qquad (29)$$

$$\vec{\mathbf{f}}_{\vec{k}}(t) = \sum_{j} \vec{\mathbf{v}}_{j-} e^{i\vec{k}\cdot\vec{\mathbf{r}}_{j-}(t)} .$$
(30)

The current  $j_{\vec{k}}(t)$  may be separated into its components parallel and perpendicular to the wave vector  $\vec{k}$ . The time dependence of the parallel component is determined by the longitudinal current correlation function

$$C_1(k,t) = (1/N) \langle \vec{k} \cdot \vec{j}_k(t) \vec{k} \cdot \vec{j}_{-\vec{k}}(0) \rangle .$$
(31)

We now form the Fourier-Laplace transforms of



FIG. 4. Normalized autocorrelation functions of velocity and electrical current. The dots show the difference between the two curves.

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(26) and (31)

$$\tilde{F}(k,\,\omega) = \int_0^\infty e^{i\,\omega\,t}\,F(k,\,t)\,dt\,,\qquad(32)$$

$$\tilde{C}_{1}(k,\,\omega) = \int_{0}^{\infty} e^{i\,\omega\,t} C_{1}(k,\,t)\,dt \,\,, \tag{33}$$

from which we obtain two simple expressions for  $S(k, \omega)$ :

$$S(k, \omega) = (1/\pi) \operatorname{\mathfrak{R}} F(k, \omega) \tag{34}$$

and

$$S(k, \omega) = (1/\pi\omega^2) \, \Re \tilde{C}_1(k, \omega) \,. \tag{35}$$

Equation (34) shows that the function  $\omega^2 S(k, \omega)$  is proportional to the spectrum of fluctuations in the longitudinal current of particles.

We now introduce the dimensionless wave vector  $q = \lambda k$  and make a short-time expansion of F(q, t) in the form

$$F(q, t) = F(q, 0) + \frac{t^2}{2!} \left. \frac{d^2 F(q, t)}{dt^2} \right|_{t=0} + \frac{t^4}{4!} \left. \frac{d^4 F(q, t)}{dt^4} \right|_{t=0} + \cdots .$$
(36)

The evaluation of the first two coefficients in (36) is straightforward and yields the same results as in the case of one-component uncharged fluids, namely

$$F(q, 0) = (1/N) \langle \rho_{\bar{q}} \rho_{-\bar{q}} \rangle = S(q) , \qquad (37)$$

$$\frac{d^2 F(q, t)}{dt^2} \Big|_{t=0} = -\frac{1}{N} \langle \dot{\rho}_{\bar{q}} \dot{\rho}_{-\bar{q}} \rangle = -q^2 k_B T/m = -\omega_0^2. \qquad (38)$$

The evaluation of the coefficient of the term in  $t^4$  is considerably more lengthy. After some tedious but straightforward algebra, following the classic method of de Gennes,<sup>18</sup> we find the following result, applicable only to the potential (1) with n=9 and with r expressed in units of  $\lambda$ :

$$\frac{d^{4}F(q,t)}{dt^{4}}\Big|_{t=0} = \frac{1}{N} \langle \ddot{p}_{q}\ddot{p}_{-q} \rangle = 3\omega_{0}^{4} + \omega_{0}^{2}\omega_{p}^{2} \left( \int_{0}^{\infty} \frac{dr}{r^{9}} \left[ g_{1}(r) + g_{2}(r) \right] \left[ F_{2}(qr) + \frac{4}{3} \right] - \int_{0}^{\infty} \frac{dr}{r} \left[ g_{1}(r) - g_{2}(r) \right] F_{1}(qr) \right) ,$$
(39)

where

$$F_1(x) = \frac{\sin x}{x} + \frac{3\cos x}{x^2} - \frac{3\sin x}{x^3}, \qquad (40)$$

$$F_2(x) = \frac{11\sin x}{x^3} - \frac{11\cos x}{x^2} - \frac{5\sin x}{x} .$$
 (41)

The properties of the Fourier transform ensure that the derivatives of F(q, t) at t = 0 are related to the spectral moments of  $S(q, \omega)$ . Specifically,

$$\langle \omega^{2n} S \rangle = \int_{-\infty}^{\infty} \omega^{2n} S(q, \omega) d\omega$$
$$= (-1)^n \left. \frac{d^{2n} F(q, t)}{dt^{2n}} \right|_{t=0}.$$
(42)

A more general expression for the fourth moment of  $S(k, \omega)$  in a molten salt has been given earlier by Abramo *et al.*<sup>19</sup> but is cast in a form which is unnecessarily complicated for our purposes.

In Fig. 5 we plot as a function of the dimensionless wave number q the theoretical values of the fourth root of the normalized fourth moment

$$[\omega_{1A}(q)]^4 = \langle \omega^4 S \rangle / S(q), \qquad (43)$$

where the subscript LA, denoting "longitudinal acoustic," is introduced by analogy with solid-state work. Equation (43) provides an approximate dispersion relation for longitudinal number density currents. There is much less structure in  $\omega_{LA}(q)$  than in the corresponding curve for argonlike liquids. In particular, the curve is very flat in the neighborhood of the maximum in S(q), which is a

region where the dispersion of longitudinal currents in argon shows a well-defined double peak.

We have computed the density-density correlation function F(q, t) for seven values of q, namely 0.751, 1.062, 1.678, 2.252, 2.809, 3.753, and 7.506. These wave numbers were chosen to facilitate comparison with the dynamical structure factor of the OCP which we discuss in I. The following conclusions emerge. First, F(q, t) is a monotonically decreasing function of t at all values of q which we have studied. Even at the lowest q, therefore, there is no evidence of any Brillouin peak in  $S(q, \omega)$ . (Smaller values of q are inacces-



FIG. 5. Characteristic frequencies of the spectrum of density fluctuations. The curve is  $\omega_{LA}(q)$  from Eq. (43), the open circles are the peaks in  $\omega^2 S(q, \omega)$ , and the dots are the inverse relaxation time  $1/\tau(q)$ .

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sible to us because of the periodic nature of our system.) Second, the spectrum of the longitudinal current of particles is very broad and flat at all except the smallest q values, a behavior which again is very different to that observed for the Lennard-Jones fluid. It is therefore impossible to draw an unambiguous dispersion curve for  $q \ge 1.5$ .

Selected results on  $S(q, \omega)$  are shown in Fig. 6. For the two lowest values of q it is possible to locate the peak in the current spectrum with reasonable precision; the resulting frequencies are plotted in Fig. 5 and agree quite well with the approximate dispersion relation, Eq. (43). Our results enable us to estimate the velocity of sound as 0.24. For NaCl this corresponds to  $2.0 \times 10^5$ cm sec<sup>-1</sup>, compared with the experimental<sup>20</sup> value (1100 K) of  $1.7 \times 10^5$  cm sec<sup>-1</sup>.

We now look for a more detailed phenomenological description of the density fluctuations, which we base on the memory function formalism of Mori.<sup>21</sup> We begin by writing a continued fraction expansion of  $\tilde{F}(q, \omega)$  in the form

$$\tilde{F}(q,\omega) = \frac{\langle \rho_{\bar{q}}\rho_{-\bar{q}}\rangle}{-i\omega + \frac{\Delta_1}{-i\omega + \Delta_2 \tilde{n}(q,\omega)}},$$
(44)

where

$$\Delta_1 = \frac{\langle \dot{\rho}_{\vec{q}} \dot{\rho}_{-\vec{q}} \rangle}{\langle \rho_{\vec{q}} \rho_{-\vec{q}} \rangle} , \qquad (45)$$

$$\Delta_{2} = \frac{\langle \vec{p}_{\dagger} \vec{p}_{-\dagger} \vec{q} \rangle}{\langle \dot{\rho}_{\dagger} \dot{\rho}_{-\dagger} \vec{q} \rangle} - \frac{\langle \dot{\rho}_{\dagger} \dot{\rho}_{-\dagger} \vec{q} \rangle}{\langle \rho_{\dagger} \dot{\rho}_{-\dagger} \vec{q} \rangle}, \qquad (46)$$

and n(q, t) is an unknown memory function. We now choose a simple exponential form for n(q, t), thereby introducing a single unknown relaxation time  $\tau(q)$ :

$$n(q, t) = e^{-t/\tau(q)} . (47)$$

The assumption of an exponential form for n(q, t) has the advantage of leading to a closed form for  $S(q, \omega)$  in terms of the moments of order 0, 2, and 4 and the unknown  $\tau(q)$ :

$$\frac{S(q,\omega)}{S(q)} = \frac{1}{\pi} \frac{\tau(q) \{ \langle \omega^4 S \rangle / S(q) - [\omega_0^2 / S(q)]^2 \}}{[\omega \tau(q) (\langle \omega^4 S \rangle / \omega_0^2 - \omega^2)^2]^2 + (\omega_0^2 - \omega^2)^2} .$$
(48)

This single-relaxation-time approximation is known to work well for argonlike liquids, at least at large k, and a number of specific prescriptions for  $\tau(k)$  have been proposed.<sup>22-24</sup> Equation (48) implies the assumption of a Maxwellian-type relaxation of the viscosity and the neglect of temperature fluctuations. The latter approximation is rather better justified for molten salts than for argon because the specific-heat ratio  $\gamma = C_p / C_v$  is closer to 1, and the coupling between heat conduction and the stress tensor, which is determined by the quantity  $(\gamma - 1)$ , is presumably smaller.

To evaluate  $S(q, \omega)$  from Eq. (48) we use as input the calculated moments and adjust the parameter  $\tau(q)$  so as to obtain a least-squares fit to the molecular-dynamics data. The results are shown in Fig. 6, from which we see that a very good fit is achieved. The inverse of the relaxation time which is obtained by this procedure is plotted in Fig. 5; the variation with q is roughly the same as that of  $\omega_{LA}(q)$ .

## V. CHARGE FLUCTUATIONS

The formalism for the description of longitudinal charge currents may be developed by adapting that already laid down in Sec. IV for the case of number density fluctuations. We introduce a charge density operator  $\rho_k^{-}(t)$ , defined as

$$\rho_{\overline{k}}^{\star}(t) = e \sum_{i} Q_{i} e^{i \overline{k} \cdot \overline{\tau}_{i}(t)}$$
$$= e \left[ \rho_{\overline{k}}^{\star}(t) - \rho_{\overline{k}}^{-}(t) \right].$$
(49)



FIG. 6.  $S(q, \omega)$  for (reading from left to right and top to bottom) q = 0.751, 2.252, 2.809, and 7.506. The circles are the molecular-dynamics results and the curves show the single-relaxation-time approximation.

The charge-charge correlation function F'(k, t) is defined as

$$F'(k,t) = (1/Ne^2) \langle \rho'_{\vec{k}}(t) \rho_{-\vec{k}}(0) \rangle$$
(50)

with a Fourier transform, given by

$$S'(k,\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} F'(k,t) dt , \qquad (51)$$

which describes the spectrum of charge density fluctuations.

We now make a short-time expansion of F'(q, t)in a form entirely analogous to (36). The first two coefficients are again easy to evaluate

$$F'(q, 0) = (1/Ne^2) \langle \rho'_{q} \rho'_{-\dot{q}} \rangle = S'(q), \qquad (52)$$

$$\frac{d^2 F'(q,t)}{dt^2} \bigg|_{t=0} = \frac{-1}{Ne^2} \langle \dot{\rho}'_{\mathbf{q}} \dot{\rho}'_{-\mathbf{q}} \rangle$$
$$= -\frac{q^2 k_B T}{m} = -\omega_0^2.$$
(53)

Note that the coefficient of  $t^2$  is the same for both F(k, t) and F'(k, t). For the coefficient of  $t^4$  we find, by essentially the same methods used to obtain (39), that

$$\frac{d^{4}F'(q,t)}{dt^{4}}\bigg|_{t=0} = \frac{1}{Ne^{2}} \langle \ddot{p}_{q}^{L}\ddot{p}_{-q}^{L} \rangle$$

$$= 3\omega_{0}^{4} + \omega_{0}^{2}\omega_{p}^{2} \left(\frac{2}{3} + \frac{4}{3}\int_{0}^{\infty} \frac{dr}{r^{9}}[g_{1}(r) + g_{2}(r)] + \int_{0}^{\infty} \frac{dr}{r^{9}}[g_{1}(r) - g_{2}(r)]F_{2}(qr)$$

$$- \int_{0}^{\infty} \frac{dr}{r}[g_{1}(r) + g_{2}(r) - 2]F_{1}(qr)\bigg), \qquad (54)$$

where  $F_1$  and  $F_2$  are the functions already defined in (40) and (41).

The moments of  $S'(q, \omega)$  are given by a relation analogous to (42):

$$\langle \omega^{2n} S' \rangle = \int_{-\infty}^{\infty} \omega^{2n} S(q, \omega) d\omega$$
$$= (-1)^n \left. \frac{d^{2n} F'(q, t)}{dt^{2n}} \right|_{t=0} .$$
(55)

However, the normalized moments, unlike those of  $S(q, \omega)$ , all tend to finite values in the limit q  $\rightarrow$  0, a behavior which is characteristic of optictype modes. In particular we find that

$$\langle \omega^2 S' \rangle / S'(q) \underset{q \to 0}{\sim} \omega_p^2 ,$$

$$[ \omega \quad (q) ]^4 - \frac{\langle \omega^4 S' \rangle}{2} \quad c \mapsto \frac{2}{\pi} \omega^4 \left( 1 + 4 \int_{-\infty}^{\infty} \frac{dr}{dr} q(r) \right)$$

$$(56)$$

$$[\omega_{\rm LO}(q)]^{-} = \frac{S'(q)}{S'(q)} \sim_{q \to 0} \frac{1}{3} \omega_{p} \left(1 + 4 \int_{0}^{1} \frac{1}{r^{9}} g_{2}(r)\right),$$
(57)

where (57) also serves to define the "longitudinal optic" frequency,  $\omega_{LO}(q)$ . The latter is plotted as a function of q in Fig. 7. At small q it varies in a manner reminiscent of the longitudinal optic branches in an ionic crystal, but later passes through a minimum at a point almost coincident with the main peak in the static charge-charge structure factor.

In marked contrast to the featureless curves obtained for F(q, t), those for F'(q, t) display pronounced oscillations at small values of q. This behavior is illustrated in Fig. 8. An important point to note is the fact that the oscillations do not take place about the axis F'(q, t) = 0, but about a small positive level which tends to zero only as the oscillations themselves disappear. This implies that at least two relaxation times are required to describe the underlying physical processes. The correlation function retains its oscillatory character to up to a critical wave number  $q_0$  which we cannot locate precisely but is close to the first peak in S'(q), hence also close to the minimum in  $\omega_{LO}(q)$ . At  $q \approx q_0$ , the form of F'(q, t)changes dramatically; the oscillations disappear and the function decays very slowly with time. At still higher values of q the monotonic character is retained but the rate of decay increases with increasing q.

The variation in the form of F'(q, t) is reflected in the q dependence of  $S'(q, \omega)$ , which we show in Figs. 9-11. For  $q < q_0$  there is a well-defined optic-type peak at finite frequency, and another peak at  $\omega = 0$ , so that  $S'(q, \omega)$  appears as the superposition of two almost symmetrical bell-shaped



FIG. 7. Characteristic frequencies of the spectrum of charge fluctuations. The curve is  $\omega_{LO}(q)$  from Eq. (57) and the circles are the peaks in  $S'(q, \omega)$ .

 $d^4F'(q, t)$ 

curves. The two peaks correspond to the two different relaxation processes which we discussed above. As q increases the "optic" peak moves to lower frequency. This negative dispersion corresponds to what we have already observed<sup>5</sup> in the OCP at high charge densities, but there the rate of dispersion is significantly slower. For example, at both  $\Gamma = 110$  and  $\Gamma = 152$  the frequency of the plasmon mode of the OCP at a wave number ak = 2.3 is approximately 20% lower than its value at k = 0; in the present work the corresponding figure is 50%. The dispersion of the "optic" peak in S'(q,  $\omega$ ) is plotted in Fig. 7; it follows quite closely the curve of  $\omega_{LO}(q)$ .

We can adapt the phenomenological model used to describe the number density fluctuations by making a continued-fraction expansion of  $\vec{F}'(q, \omega)$ , the Fourier-Laplace transform of F'(q, t). The details are the same as before and need not be repeated here. The result is an expression for  $S'(q, \omega)$  which is identical to (48) except that S'(q)replaces S(q),  $\langle \omega^4 S \rangle$  replaces  $\langle \omega^4 S \rangle$ , and a new relaxation time  $\tau'(q)$  replaces  $\tau(q)$ . The results obtained for  $S'(q, \omega)$  from a least-squares adjustment of  $\tau'(q)$  are shown in Figs. 9–11. At high qthe fit to the molecular-dynamics data is again very good. For  $q < q_0$  the position of the "optic"



FIG. 8. F'(q,t) at four values of q. Upper graph: full line, q = 0.751; dotted line, q = 2.809. Lower graph: full line, q = 3.753; dotted line, q = 7.506.

peak is satisfactorily reproduced, particularly at the smallest values of q, but the use of a singlerelaxation-time approximation necessarily means that the low-frequency behavior is incorrect. The situation that one encounters here is rather different than that which arises in the OCP.

In the latter case the spectrum of charge fluctuations at small q consists of a sharp peak at finite frequency and a low-frequency tail. The shape of the spectrum is therefore adequately described by a memory function with a single adjustable parameter.<sup>5</sup>

The values of  $\tau'(q)$  which result from the fit to  $S'(q, \omega)$  are listed in Table III, together with those of  $\tau(q)$ .

#### VI. CONCLUSIONS

We have carried out a molecular-dynamics calculation of the transport properties of an idealized molten salt, and have obtained in addition some rather precise information on the equilibrium properties of the system, particularly on the



FIG. 9. S'  $(q, \omega)$  for q = 0.751 (upper graph) and q = 1.678 (lower graph). The circles are molecular-dynamics results and the curves show the single-relaxation-time approximation.

static structure factors. By utilizing some of the equilibrium results, we have been able to build a simple phenomenological model to describe the spectra of fluctuations in number density and in charge, each mode being characterized by a single k-dependent relaxation time. The model works well at large values of k, but cannot reproduce satisfactorily the low-frequency part of the spectrum of charge fluctuations at small k. Its defects help to emphasize the features which a satisfactory theory must possess. To obtain a better description of the spectrum it is necessary, at least, to introduce a second relaxation time. We have not attempted a more elaborate parametrization because we believe that such a program must be carried through in parallel with a calculation of the transverse currents, which for practical reasons we have not attempted to compute. A meaningful discussion of the collective modes requires, in addition, that proper account be taken of the limiting hydrodynamic form of the correlation functions and of the coupling between the modes of optic and acoustic character. These are all obvious topics for future investigation. It would also be of great interest to extend the calculations to smaller values of k, where it should be possible to observe a propagating mode in the



FIG. 10. Same as Fig. 9 but for q = 2.252 (upper graph) and q = 2.809 (lower graph).



FIG. 11. Same as Fig. 9 but for q = 3.753 (upper graph) and q = 7.506 (lower graph).

number density fluctuations. This requires a significant increase in the numbers of ions in the molecular-dynamics cube and is necessarily an expensive undertaking.

## ACKNOWLEDGMENTS

We thank Björn Larsen and Mario Tosi for a number of useful discussions. The work was initiated while I.R.McD. was a visitor in the Laboratoire de Physique Théorique et des Hautes Energies at Orsay, and he wishes to thank Loup Verlet and others for their hospitality. He is also indebted to the United Kingdom Science Research Council for financial support.

TABLE III. Values of the parameters  $\tau(q)$  and  $\tau'(q)$ .

q	$ au^{\prime}\left(q ight)$	$\tau(q)$
0.751	1.089	3.386
1.062	1.081	2.639
1.678	0.939	1.641
2.252	0.785	1.526
2.809	0.690	1.308
3.753	0.498	1.078
7.506	0.525	0.942

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