

Hard-sphere Results from Experimental Transport Behaviour of Molten Salts and Structural Properties

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A single component hard sphere description molten halides and nitrates, applied to self-diffusion and viscosity data, has led to a hard sphere size which for a given cation depends linearly upon the anionic radius. This correlation has been used to predict viscosity coefficients of fused alkali fluorides and to estimate the effective size of the NO_3^- -anion in molten nitrates. The Stokes-Einstein relationship between η and \bar{D} is satisfied, where $\bar{D} = (D^+ + D^-)/2$, and this relationship in combination with the observed linear dependence of $T^{1/2}/\eta$ and $\bar{D}/T^{1/2}$ on the molar volume can in principle be used as a criterion for data selection.

Introduction

In this paper a hard sphere description of convection and diffusion¹, applied with some success to noble gas and metallic liquids^{2,3}, has been used for molten salts.

Computer simulation studies by the Monte Carlo (MC) and molecular dynamics (MD) methods besides diffraction experiments have successfully been applied to determine structural properties of fused alkali halides⁴. Moreover those studies have resulted in a detailed picture of self-diffusion in some of these alkali halides^{5–7}. On the other hand experimental diffusion data have a fairly large scatter and hence the self-diffusion coefficient generally is not known very accurately. Computer studies related to the shear viscosity of molten salts have hardly been reported so far⁸, while conversely the viscosity has been extensively investigated experimentally. It seems worthwhile, therefore, to make use of the known viscous behaviour of molten salts in order to determine effective hard sphere sizes and relate the latter to both structure and diffusion.

Previous self-diffusion measurements suggest that diffusive transport in monovalent molten salts is largely determined by short-range and not by Coulomb forces⁹. Because of the sorting of charge types by the Coulomb field, the diffusion in molten salts can like the convection be simulated by a single component hard sphere fluid obeying a corrected Enskog theory.

Hard-sphere Transport Coefficients

The coefficients of self-diffusion and shear viscosity have been interpreted in terms of the Van der

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Waals concept of a dense fluid. The applicability of this model, which is equivalent to the hard-sphere model, has been tested by Dymond¹ who used Enskog's expressions for transport coefficients of dense hard spheres corrected for the effect of correlated motions. Though the hard-sphere model corresponds most closely to reality in supercritical conditions, it may provide a reasonable basis for the interpretation of transport coefficients of dense liquids.

Dymond used analytical relationships in which the hard-sphere transport coefficients are expressed in terms of the molar volume V and the temperature T of the fluid. In the case of the self-diffusion coefficient, the expression is

$$10^5 D = (2.306/V_0^{2/3}) (T/M)^{1/2} (V - 1.384 V_0) \quad (1)$$

where D , T , M and V are in units of $\text{cm}^2 \text{s}^{-1}$, K, g and cm^3 , respectively. M is the molar mass and $V_0 = N \sigma^3/2^3$ the volume of a mole of close packed hard spheres with diameter σ . Likewise the shear viscosity coefficient is given by the expression

$$10^{-4}/\eta = (1.452/V_0^{1/3}) (MT)^{1/2} (V - 1.384 V_0) \quad (2)$$

where η is in units of $\text{g cm}^{-1} \text{s}^{-1}$.

Experimental Transport Coefficients

The experimental data on the density and the viscosity of molten salts have been compiled by Janz and coworkers¹⁰, and unless stated otherwise, the data used in the present paper are taken from this compilation. Viscosities of the fused fluorides of lithium, sodium and potassium can be found in reference data collected by Janz and coworkers¹¹, while Murgulescu¹² has reported the viscosity of



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liquid CsBr. Accurate data on the viscosity of the molten alkali chlorides have recently been published by Øye and coworkers¹³, and the density and the viscosity of the molten alkali and silver nitrates are given by Zuca¹⁴. Grothe and coworkers have recently measured the density¹⁵ and the viscosity¹⁶⁻¹⁸ of the molten thallium halides.

Self-diffusion data on molten alkali halides and TlCl compiled by Sjöblom¹⁹ have been applied, while the self-diffusion coefficients of molten LiCl have recently been reported by Klemm and coworkers²⁰. The diffusion data on molten alkali nitrates and AgNO₃ obtained by Dworkin and coworkers²¹ have been used, while the cation diffusion in molten RbNO₃ measured by Zuca and Constantinescu²² and that in molten TlNO₃ obtained by Forcheri and Wagner²³ have been used.

As high-temperature viscosimetry is difficult from an experimental point of view²⁴, it is not uncommon that single salt viscosities published by various authors are different by an amount far greater than

the estimated experimental uncertainties reported. The difference between observed values of the self-diffusion coefficient in a given salt is sometimes also considerable. For this reason we do not wish to quote errors but rather refer the reader to the original papers.

Results and Discussion

According to the expressions (1) and (2) the quantities $D/T^{3/2}$ and $T^{1/2}/\eta$ obey the relationship $D/T^{3/2} = A(V - I)$ and $T^{1/2}/\eta = B(V - I)$ respectively, where A and B are constants and I is the value of the molar volume at the intercept. For the molten salts we have taken $\bar{D} = \frac{1}{2}(D^+ + D^-)$, where D^+ and D^- refer to the coefficients for cation and anion diffusion respectively. The transport coefficients of the molten alkali chlorides and nitrates are plotted as $\bar{D}/T^{3/2}$ and $T^{1/2}/\eta$ versus the molar volume V as shown in Figure 1. The corresponding temperature range

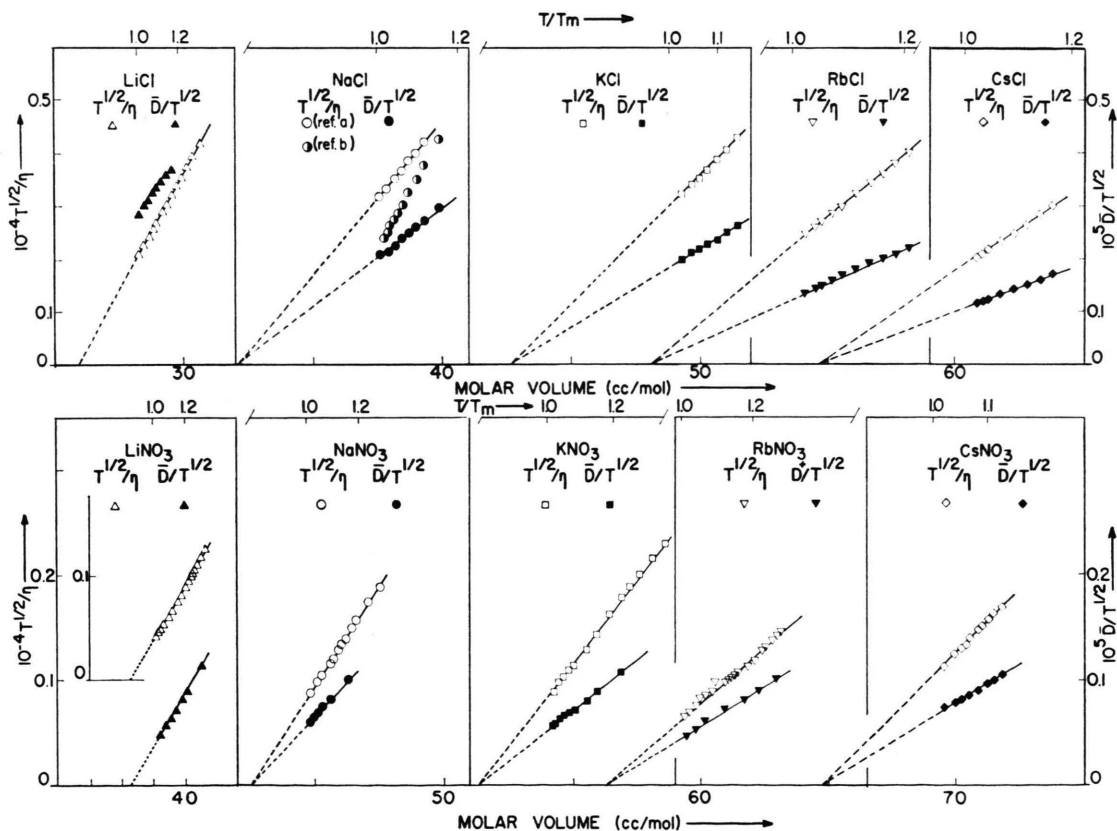


Fig. 1. The transport quantities $\bar{D}/T^{3/2}$ and $T^{1/2}/\eta$ for molten alkali chlorides and nitrates versus the molar volume. The upper scale refers to the temperature in terms of the normal melting point. For the sake of clarity the viscosity scale of the $T^{1/2}/\eta$ versus V plot for LiNO₃ has been shifted as indicated. The viscosity values of NaCl refer to the data by Øye and coworkers¹² (○), and to the data by Janz and coworkers⁹ (◐). In RbNO₃ the self-diffusion refers to the cation diffusion only (D in cm² s⁻¹ and η in g cm⁻¹ s⁻¹).

is expressed in terms of the normal melting temperature T_m on the upper scale.

It turns out that in this temperature range $D/T^{1/2}$ and $T^{1/2}/\eta$ depend linearly upon V and within this limited range, the viscosity is related to the molar volume in a similar way as described by the well-known equation of Batschinski¹⁴. The $\bar{D}/T^{1/2}$ and $T^{1/2}/\eta$ versus V straight lines intersect at the same molar volume, indicating that $\bar{D}\eta/T$ is a constant which is equivalent to the Stokes-Einstein relationship between the self-diffusion and shear viscosity coefficients. The Stokes-Einstein relationship between \bar{D} and η shows surprisingly consistent results for the molten alkali nitrates and chlorides in spite of the fact that near the normal melting temperature the self-diffusion coefficients of the nitrates are substantially smaller and the shear viscosity coefficients much larger than those of the chlorides. The two different sets of data for NaCl refer to the viscosity coefficients originally recommended by the U.S. National Bureau of Standards¹⁰, and the more recent ones reported by Øye and coworkers¹³. The latter are considered to be more accurate and it is evident that they obey the systematic trend in Fig. 1 much better. For that reason the viscosity data of all the alkali chlorides are taken from this reference. From Fig. 1 it is evident that the available experimental data on D and η for molten LiCl do not satisfy the Stokes-Einstein relationship, while on the other hand the relationship does apply to molten LiNO₃, though in this case the value of the constant $\bar{D}\eta/T$ is relatively high. It is, therefore, most likely that either Øye's shear viscosity coefficient¹³ for molten LiCl is too small or the reported self-diffusion coefficients²⁰ are too high by 30 to 40%.

It can be shown that $\bar{D}/T^{1/2}$ and $T^{1/2}/\eta$ for the fused halides and nitrates of silver and thallium also obey linear relationships with the molar volume. However, in plotting $\bar{D}/T^{1/2}$ and $T^{1/2}/\eta$ versus V , the intercept for the two transport quantities differs by 1% in the case of fused TiCl and 0.5% in the case of molten AgNO₃, whereas for each salt $\bar{D}\eta/T$ gradually decreases with increasing temperature¹⁶. The reason for these discrepancies is not known.

We have used the known density and viscosity of molten salts to determine the hard sphere size σ applying expression (2). The value of σ of the fused alkali halides is plotted versus the anionic radius in Figure 2. It turns out that the σ values follow closely a linear relationship with the anionic

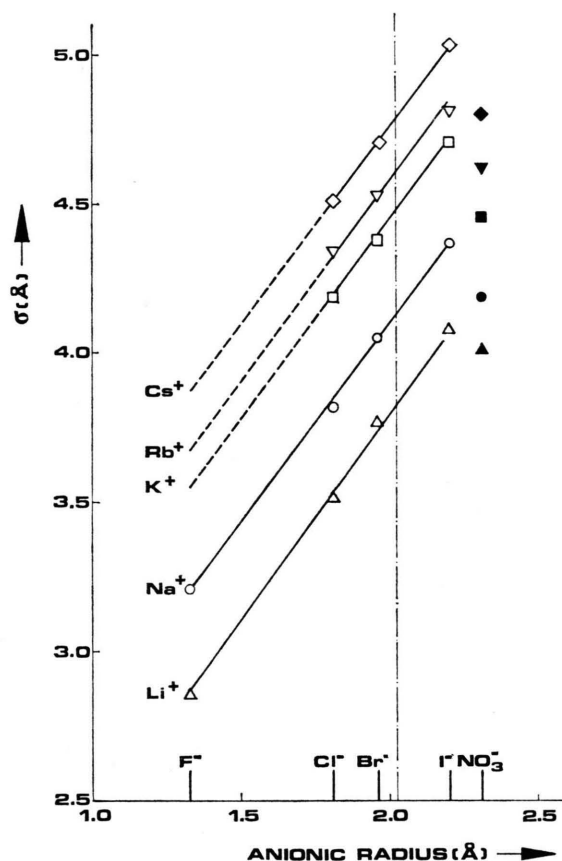


Fig. 2. The hard core size σ of the molten alkali halides (open symbols) and nitrates (closed symbols) versus the anionic radius. The possible radius of the NO₃⁻ anion is indicated by the dotted-dash line.

radius for each alkali metal cation. The linear relationship found between σ and the anionic radius enables us to estimate the σ values for the fluorides of potassium, rubidium and cesium as shown in Figure 2. Hence in combination with the known density, we have calculated the values $\eta = (1.4 \pm 0.2)$, (1.7 ± 0.2) and (1.8 ± 0.2) cP for the viscosities of molten KF, RbF and CsF at their respective melting temperatures. It is noteworthy that the viscosities of all the molten alkali halides near T_m with the exception of LiI lie within a range between 1 and 2 cP and that for a given cation η increases with the size of the anion with the exception of the fluorides. An increase of the viscosity of LiCl by 20% or more would mean that this alkali halide would not fit any more the overall pattern illustrated in Figure 3.

Since σ hardly depends upon the temperature, it is in principle possible to obtain the viscosity coef-

ficient at any temperature above T_m provided the density is known. We have calculated that the viscosity of fused KF at $T = 1246$ K is about 1.0 cP which is nearly 40% smaller than the experimental value that has been reported¹¹. In this connection it should be noted that an increase of one percent in σ corresponds to a 20% increase for η .

The hard core size for the molten alkali nitrates has been included in Fig. 2 with the anionic radius chosen equal to the radius of the free rotation sphere reported by Janz and James²⁵. The hard core size of the alkali nitrates exceeds that of the corresponding alkali chlorides by an amount of about 0.30 Å, while the σ values of the lithium salts differ considerably more. The σ values of the alkali nitrates with the exception of LiNO_3 would fit the linear relationship between σ and the anionic radius provided that the radius of the NO_3^- -ion in the molten nitrates is 2.02 Å instead of that of a free rotating sphere. On the base of the structural properties of molten nitrates near T_m free rotation of the NO_3^- -ion is indeed highly unlikely²⁶. From the results of recent neutron diffraction experiments on molten nitrates, Suzuki²⁷ determined the N-O bond length, and hence he could make an estimate of the radius of NO_3^- . The result is a radius of about 2 Å which is remarkably close to the value suggested by our correlation.

Table 1. Hard core size σ , packing fraction μ , Stokes-Einstein product and mean spacing for molten alkali chlorides and nitrates near T_m .

Sub- stance	σ (Å)	μ	$\sigma \bar{D} \eta / k T$	r_{\max} (Å)	Ref.	σ / r_{\max}
LiCl	3.52	0.49		3.85	4	0.91
NaCl	3.82	0.47	0.180 ± 0.005	4.2	4	0.91
KCl	4.19	0.47	0.185	4.7	35	0.89
RbCl	4.34	0.48	0.175			
CsCl	4.52	0.48	0.185	5.0	35	0.90
LiNO_3	4.01	0.525	0.29			
NaNO_3	4.19	0.515	0.21			
KNO_3	4.46	0.515	0.20			
RbNO_3	4.60	0.52	$0.24 (D^+)$			
CsNO_3	4.82	0.51	0.215			

The σ values of the alkali chlorides and nitrates are listed in Table 1. The hard-sphere packing fraction $\mu = \pi \sigma^3 N / 6 V_m$ where V_m is the molar volume of the molten salt at the melting temperature, has been determined. For the fused alkali chlorides at

T_m $\mu = 0.48$ on the average while for the alkali nitrates the packing fraction is about 7% higher. The values of μ are also given in Table 1. The packing fraction for molten LiNO_3 near T_m is very high and this is related to the high viscosity near the normal melting temperature.

For most of the fused alkali halides the packing fraction at the melting temperature is the same and its value is equivalent to that found for the liquid metals². However, contrary to usual assumptions²⁸, the packing fraction among different molten salts at T_m varies substantially e. g. it ranges from $\mu = 0.48$ for the fused alkali halides to $\mu = 0.52$ for the molten alkali nitrates. It means that in the melt the available volume which is a factor in Dymond's expression for the viscosity, is relatively small for the alkali nitrates compared with the alkali halides. It should be mentioned that in comparing alkali nitrates and halides Angell²⁹ has noted that at equivalent temperatures the molten halides are considerably more loosely packed than the nitrates, which is consistent with the results found here.

The hard sphere diameter for KCl and the hard sphere packing fraction computed from PVT properties by Lind³⁰ are appreciably smaller than the corresponding values shown in Table 1. The author concludes from the low density of molten KCl near the melting temperature that a Gaussian autocorrelation function might be appropriate to describe diffusion. However, Lewis and Singer⁶ recently have shown that pronounced negative portions exist in the velocity auto-correlation functions for both ions in molten NaCl that has the same packing as molten KCl. Therefore, the hard core size and packing fraction given by Lind do not seem to be correct, while the values of these parameters obtained in the present paper are more consistent with the results of MD calculations.

The classical Stokes-Einstein equation predicts a simple relationship between D and η of the liquid. Though in molten salts Stokes-Einstein plots usually³¹ are made for cation diffusion only, we have taken a diffusion coefficient \bar{D} that is the mean of the cation and anion diffusion constants. According to Table 1 the dimensionless quantity $\sigma \bar{D} \eta / k T$ for the alkali chlorides and nitrates with the exception of the lithium salts is essentially constant, but its value is systematically too high by about 20% compared with the constant of proportionality appropriate to slipping boundary conditions ($1/2 \pi$

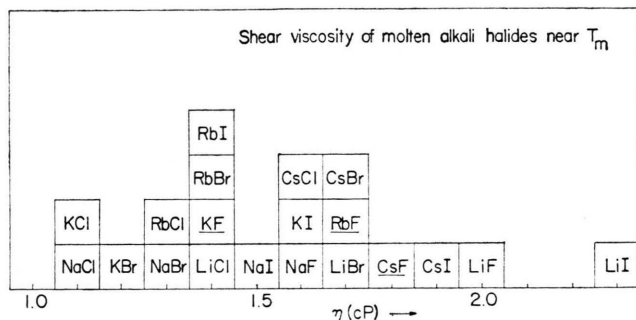
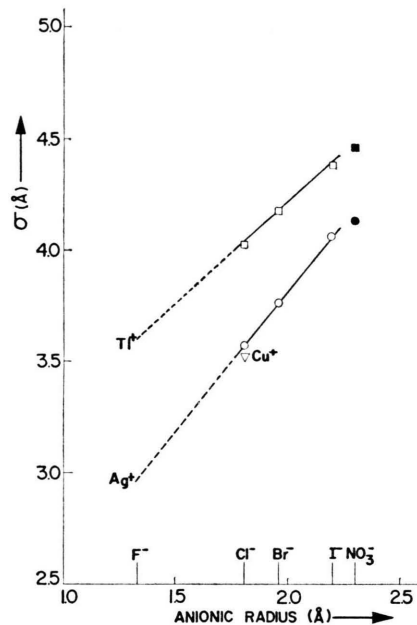


Fig. 3. Histogram of the alkali halides arranged according to their viscosity near T_m the value of which is expressed to one place of a decimal. The viscosities of the underlined fluorides have been calculated (see text).

Fig. 4. The hard core size σ of the molten halides of silver and thallium (open symbols) and of the molten nitrates of silver and thallium (closed symbols) versus the molar volume. The hard core size of CuCl is also given.



$= 0.159$). A similar result has been obtained previously in discussing mass transport properties of liquid metals² in terms of a hard-sphere model. This discrepancy can be interpreted such that starting with the experimental viscosity data for the molten salts, the hard-spheres approach leads to a value for \bar{D} which is too small compared with available experimental data. This turns out to be consistent with the results of molecular dynamics calculations based on rigid-ion pair potentials reported by McDonald and coworkers⁸, though in the present paper nothing is said about the cation and anion diffusion coefficients separately.

From both computer simulation studies⁴, and neutron diffraction measurements^{32, 33}, the radial distribution functions can be found, and for a number of molten alkali halides detailed information about the equilibrium properties is available. We have compared the hard core size with the peak position r_{\max} in $4\pi r^2 g_m(r) \rho$, where $g_m(r)$ represents the mean radial distribution function⁴ and ρ the density. It is found that for the various halides $\sigma/r_{\max} = 0.90 \pm 0.01$ (Table 1) indicating which relation exists between σ and the distance r_{\max} that might be considered a mean spacing in the quasi-ordered molten salt.

Using expression (2) the hard core size of the univalent halides and nitrates of silver and thallium

and that of CuCl has been determined from the known viscosity and density at T_m . It turns out that the σ values of the silver and thallium halides closely follow a linear relationship with the anionic radius for each cation as shown in Figure 4. The σ values of the nitrates of silver and thallium are also given in Figure 4. It seems that they fit the linear relationship of the corresponding halides rather well provided the NO_3^- -radius is nearly that of a free rotation sphere. However from neutron diffraction experiments by Suzuki²⁷ it follows that the radius of NO_3^- in molten AgNO_3 is close to 2.0 Å. This indicates that the radius of Ag^+ in molten AgNO_3 does not match that in fused silver halides. On the other hand the σ values of AgNO_3 and NaNO_3 turn out to be rather similar. It is, therefore, more likely that the silver ions in molten AgNO_3 have a size rather more equal to that of the Na^+ ion, in agreement with a suggestion made by Zuca and coworkers²² for different reasons previously. The radius of Tl^+ in molten TlNO_3 does not necessarily match that in fused thallium halides, though no experimental information is available concerning the radius of NO_3^- in molten TlNO_3 . From the striking resemblance of the σ values of TlNO_3 and KNO_3 it is reasonable to assume that the size of the thallium ions in molten TlNO_3 is rather more equal to that of the K^+ ion.

The σ value, packing fraction and the quantity $\sigma \bar{D} \eta / k T$ for the chlorides and nitrates of silver and thallium and of CuCl near T_m are listed in Table 2. The measured viscosity of fused CuCl¹⁰

Table 2. Hard core size σ , packing fraction μ , Stokes-Einstein product and mean spacing for molten chlorides and nitrates of copper, silver and thallium near T_m .

Substance	σ (Å)	μ	$\sigma \bar{D} \eta / k T$	r_{\max} (Å)	Ref.	σ / r_{\max}
CuCl	3.52	0.51		3.85	34	0.91
AgCl	3.58	0.49		3.9	35	0.91
TlCl	4.02	0.48	0.22 *			
AgNO ₃	4.13	0.52	0.25 *			
TlNO ₃	4.46	0.51	0.18 (D ⁺)			

* vary with temperature.

at 800 K is 2.54 cP and its value is estimated to be nearly twice as large at the normal melting point of 695 K. This means that molten CuCl is considerably more viscous than any of the other univalent halides, and hence the packing fraction at T_m is substantially higher than that of the other chlorides. From neutron diffraction measurements on molten CuCl by Page and Mika³⁴ and on fused AgCl by Derrien and Dupuy³⁵ a value of r_{\max} has been found with the result that $\sigma / r_{\max} = 0.91$. Apparently this ratio is rather insensitive to the detailed structure of the molten salt, which in the case of the copper and silver chlorides is considered to be more of a molecular type than the alkali chlorides.

Conclusions

The most striking result of using a single component hard sphere description of the transport coefficients of fused salts is the linear relationship found for each cation between the hard core size and

the anionic radius. This new correlation for mass transport behaviour in molten salts has been used to predict viscosity coefficients for fused alkali fluorides and to estimate the effective size of the NO₃⁻ anion in molten nitrates.

In the molten salts studied the Stokes-Einstein relationship between \bar{D} and η is satisfied, and this correlation in combination with the simple dependence of the transport properties on the molar volume can in principle be used as a criterion to select data. This has been applied to the viscosity coefficients of the molten alkali chlorides as illustrated by the NaCl data. The mass transport coefficients reported for LiCl do not obey the phenomenological correlation observed between \bar{D} and η for the other alkali chlorides and the nitrates, and therefore they may be open to some doubt.

A large difference has been found among the various molten salts with respect to the packing fraction near T_m , which has a close bearing upon the structural properties of dense liquids. In this connection it is of interest that the structural properties of the alkali chlorides and those of CuCl are quite different. Powles³⁶ has reinterpreted the diffraction data of molten CuCl in terms of a molecular liquid in which correlations of molecular orientations may even have to be assumed. Such a picture would most likely result in a high packing and hence qualitatively fit the classification of high density liquids on the base of their packing fraction which has been proposed recently³⁷.

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¹ J. H. Dymond, J. Chem. Phys. **60**, 969 [1974].

² J. J. van Loef, Physica **75**, 115 [1974].

³ P. Protopapas, H. C. Andersen, and N. A. D. Parlee, Chem. Physics **8**, 17 [1975].

⁴ J. W. E. Lewis, K. Singer, and L. V. Woodcock, J. Chem. Soc. F. T. II, **71**, 308 [1975].

⁵ F. Lantelme, P. Turq, B. Quentrec, and J. W. E. Lewis, Mol. Phys. **28**, 1537 [1974].

⁶ J. W. E. Lewis and K. Singer, J. Chem. Soc. F. T. II, **71**, 41 [1975].

⁷ J. Michielsen, P. Woerlee, F. v. d. Graaf, and J. A. A. Ketelaar, J. Chem. Soc. F. T. II, **71**, 1730 [1975].

⁸ G. Ciccotti, G. Jacucci, and I. R. McDonald, Phys. Rev. **13 A**, 426 [1976].

⁹ C. A. Angell and J. W. Tomlinson, Trans. Faraday Soc. **61**, 2312 [1965].

¹⁰ G. J. Janz, F. W. Dampier, G. R. Lakshminarayanan, P. K. Lorentz, and R. P. T. Tomkins, Molten Salts: Vol. 1, Electrical Conductance, Density and Viscosity Data, NSRDS-NBS 15, Washington 1968.

¹¹ G. J. Janz, G. L. Gardner, V. Krebs, and R. P. T. Tomkins, J. Phys. Chem. Ref. Data **3**, 1 [1974].

¹² G. I. Murgulescu, J. Chim. Phys. **66**, Suppl. 43 [1969].

¹³ W. Brockner, K. Grjotheim, T. Ohta, and H. A. Øye, Ber. Bunsenges. physik. Chem. **79**, 344 [1975].

¹⁴ S. Zuca, Rev. Roum. Chim. **15**, 1277 [1970].

¹⁵ K. H. Grothe and L. Schrader, Naturwiss. **57**, 496 [1970].

¹⁶ K. H. Grothe, Z. Anorg. Allg. Chemie **378**, 225 [1970].

- ¹⁷ K. H. Grothe and L. Schrader, *Naturwiss.* **57**, 452 [1970]
¹⁸ K. H. Grothe and L. Franke, *Naturwiss.* **60**, 473 [1973].
¹⁹ C. A. Sjöblom, *Z. Naturforsch.* **23 a**, 93 [1968].
²⁰ R. Lenke, W. Uebelhack, and A. Klemm, *Z. Naturforsch.* **28 a**, 881 [1973].
²¹ A. S. Dworkin, R. B. Escue, and E. R. van Artsdalen, *J. Phys. Chem.* **64**, 872 [1960].
²² S. Zuca and M. Constantinescu, *Rev. Roum. Chem.* **17**, 385 [1972].
²³ S. Forcheri and V. Wagner, *Z. Naturforsch.* **22 a**, 1171 [1967].
²⁴ T. Ohta, O. Borgen, W. Brockner, D. Fremstad, K. Grjotheim, K. Tørklep, and H. A. Øye, *Ber. Bunsenges. physik. Chem.* **79**, 335 [1975].
²⁵ G. J. Janz and D. W. James, *Electrochim. Acta* **7**, 427 [1962].
²⁶ K. Furukawa, *Disc. Faraday Soc.* **32**, 53 [1961].
²⁷ K. Susuki, private communication.
²⁸ R. De Witt and L. J. Wittenberg, *Phys. Chem. Liq.* **4**, 113 [1974].
²⁹ C. A. Angell, *Ann. Rev. Phys. Chem.* **22**, 429 [1971].
³⁰ J. E. Lind, Jr., *Adv. in Molten Salt Chemistry*, Vol. 2, Plenum Press Ed., New York 1973, p. 20.
³¹ C. T. Moynihan, in *Ionic Interactions* ed. S. Petrucci, Vol. 1, Acad. Press, New York 1971.
³² J. Y. Derrien and J. Dupuy, *J. Physique* **36**, 191 [1975].
³³ F. G. Edwards, J. E. Enderby, R. A. Howe, and D. I. Page, *J. Phys. C* **8**, 3483 [1975].
³⁴ D. I. Page and K. Mika, *J. Phys. C* **4**, 3034 [1971].
³⁵ J. Dupuy, private communication.
³⁶ J. G. Powles, *J. Phys. C* **8**, 895 [1975].
³⁷ J. J. van Loef, *Physica* **79 B**, 86 [1975].