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MOLECULAR DYNAMICS STUDIES OF SUPERIONIC CONDUCTORS

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MOLECULAR DYNAMICS STUDIES OF SUPERIONIC CONDUCTORS*

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ABSTRACT

Over the last fifteen years computer modeling of liquids and solids has become a useful method of understanding the structural and dynamical correlations in these systems. Some characteristics of the method are presented with an example from work on homogeneous nucleation in monoatomic liquids; the interaction potential determines the structure: a Lennard-Jones system nucleates a close packed structure while an alkali metal potential nucleates a bcc packing.

In the study of ionic systems like CaF_2 the Coulomb interaction together with the short range repulsion is enough to produce a satisfactory model for the motion of F^- ions in CaF_2 at ~ 1600 K. Analysis of this motion shows that F^- ions reside at their fluorite sites for about 6×10^{-12} s and that the diffusion is mainly due to F^- jumps in the 100 direction. The motion can be analysed in terms of the generation and annihilation of anti-Frenkel pairs.

The temperature dependence of the F^- diffusion constant at two different densities has also been calculated. The computer model does not correspond with experiment in this regard.

I. INTRODUCTION

Over the last fifteen years considerable increase in our understanding of liquids and solids has resulted from the study of the structure and dynamics of systems consisting of a few hundred, and more recently a few thousand, particles interacting with one another in a prescribed fashion. Newton's equations of motion are solved on a digital computer and the particle trajectories resulting from the solution of the equations are used to obtain insight into various properties of interest. The purpose of the following presentation is to show that in the field of fast ion conduction this method is of considerable promise.

In Section II a brief description of the method will be given; the special technical problems one encounters when dealing with Coulombic systems will be relegated to Section IV. In Section III a few results obtained while studying homogeneous nucleation in simple monoatomic systems will be presented. The selection of this phenomenon for inclusion in this presentation was not fortuitous; in dealing with properties of superionic conductors it is obviously desirable to be able to study models in which the mobile species goes into an ordered state as the temperature is reduced. Of course, apart from homogeneous nucleation, there are a large number of other properties which could have been chosen to illustrate the use of the method. In sections IV and V a few results obtained while studying CaF_2 near its melting point will be presented. The difficulties encountered in comparing the calculated properties with the experimental values are dealt with in section V.

II. MOLECULAR DYNAMICS IN OUTLINE

In the field covered by this conference the use of the molecular dynamics method is not widespread. In view of this it does not seem inappropriate to indicate in broad outline how the method operates.

Given a system of N particles and a potential function ϕ which depends in a prescribed manner on $\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N$ the positions of the particles, we have the classical equations of motion $M_i \ddot{\underline{r}}_i = -\partial\phi/\partial\underline{r}_i$, M_i being the masses. Since these are $3N$ ordinary differential equations of second order, a knowledge of all \underline{r}_i and $\dot{\underline{r}}_i$ at any time t is, in principal, enough to know their values at any subsequent (or previous) time. There are a multiplicity of ways in which such differential equations can be solved by converting them to a set of difference equations with a finite time interval Δt . In other words the solution is obtained as values of $\underline{r}_i(t + n\Delta t)$, $\dot{\underline{r}}_i(t + n\Delta t)$ for all i and n , given the values for $n = 0$.

It will be out of place here to go into the technical details of particular algorithms that are currently being used in this context; such details are given elsewhere [1]. It will be useful on the other hand to lay down some of the terminology that naturally arises. The set of $6N$ values of \underline{r}_i and $\dot{\underline{r}}_i$ constitute a phase point P of the system which can be followed in time i.e., its trajectory $P(t)$ $P(t + n\Delta t)$ obtained with $P(t)$ as input. All these phase points will have constant total energy E . The kinetic energy, $\sum M_i \dot{\underline{r}}_i^2/2$, varies with time and so does ϕ , the potential energy, leaving the sum constant, (the constancy of the

total energy can be used as a test for the presence of errors in computation). The set of phase points constitutes a microcanonical ensemble, apart from the inaccuracy introduced by the finiteness of Δt .

The kinetic energy, written as $3/2 NkT(t + n\Delta t)$ apart from a change of units, can be called the "temperature" of the system. Only when certain criteria for equilibrium have been satisfied, the average of $T(t + n\Delta t)$ over a long enough interval of time (i.e., many values of n) can be referred to as the temperature $\langle T \rangle$ of the system. The temperature $T(t)$ provides a convenient way of changing E . By simply multiplying the velocities by a constant factor α at any moment of time the phase point can be shifted from one energy shell to another of higher ($\alpha > 1$) or lower ($\alpha < 1$) energy.

The definition of the density of the system requires consideration of the boundaries. For this there are many possibilities. One is obviously the absence of boundaries in which case the density profile of the free droplet in space may itself be the object of investigation. In most cases however standard periodic boundary conditions with a cube of volume $\Omega = L^3$ are used which confine the system of N particles and keep the total number N in volume Ω strictly constant. This method of confinement produces an infinite system with no surfaces or boundaries whatsoever. Needless to mention that periodic boundary conditions will have their own special role to play in the ensuing dynamics and this needs to be kept constantly in view. The mass density will obviously be $\Sigma M_i / \Omega$ and will be strictly conserved in the total volume $\Omega = L^3$ but will vary in various regions of the cubic volume. When all $M_i = M$, the more usual quantity to specify the density is the number density N/Ω .

The dependence of $\langle T \rangle$ on E constitutes the equation of state. This dependence will of course change with density. The pressure can be calculated using the virial of forces.

Given all r_i at any time the structural properties can be calculated at that time. If the system is in equilibrium the structural information for different times can be lumped together for better statistical averaging. In many studies the pair correlation $g_{\alpha\beta}(r)$ plays a central role. This is obtained by counting the number of times v when two particles, one of species α one of β , are found at distances between $r, r + \Delta r$; Δr then is the finite resolution of the statistics collected for the purpose. If there are N_α of species α and N_β of β in volume Ω then in a given configuration (i.e. all r_i) $v_{\alpha\beta}(r) = N_\alpha N_\beta \Omega^{-1} 4\pi r^2 \Delta r g_{\alpha\beta}(r)$. Averaging over many configurations will improve the statistics. A more detailed picture of the structure is given by $\rho_\alpha(k) = N_\alpha^{-1} \sum \exp(ik \cdot r_\alpha)$. The Fourier transform of $v_{\alpha\beta}(r)$, and hence of

$g_{\alpha\beta}(r)$, is $\rho_\alpha(k) \rho_\beta^*(k)$. Neutron and X-ray diffraction experiments are a means of measuring such Fourier transforms.

In the case of solids the mean position in time of every particle provides a lattice point and the lattice structure provides a means of determining the one particle density map of the system. In superionic conductors at least one species does form a thermally agitated lattice and hence provides a frame of reference for analysing density maps. In liquids no such analysis is possible.

$\rho_\alpha(k)$ is obviously a function of time: it is the value of the k 'th Fourier component at time t of the density of particles of species α . Thus in a more formal language than the one used above $g_{\alpha\beta}$ is the momentary density-density correlation function in space for particles of species α and β ; the time displaced correlation function then gives information about the propagation of density-density correlations in space and time and hence the velocity of propagation (provided the changes with time are not overdamped).

The motion of the point $R(t)$ in configuration space ($R(t)$ has coordinates $x_1, y_1, z_1, x_2, y_2, z_2, \dots, z_N$) can be obtained by calculating $(\tilde{R}(t) - R(0))^2 / N$. The division by N converts this into a mean square displacement of a particle and gives a direct way of measuring diffusion of particles. Of course, for a multicomponent system the diffusive motion of particles of species α will be measured by $(R_\alpha(t) - R_\alpha(0))^2 / N_\alpha$. For large t the behavior of this quantity is of prime importance in determining whether particles of species α form a stable non-diffusing structure or a system of diffusing particles with a non-zero constant of self-diffusion. In the former case the width of the thermal Debye-Waller cloud can be measured in this way. As in the case of density fluctuations a more detailed picture of diffusion of species α is obtained by calculating the time dependence of $F_\alpha(k, t) \equiv \exp(ik \cdot d_\alpha(t))$, where $d_\alpha(t) = r_\alpha(t) - r_\alpha(0)$. This gives the diffusive properties in particular directions.

It is useful to end this brief outline by the statement that this method of study is ill suited for systems which, to a good approximation, can be reduced to a collection of N non-interacting one-body problems. A slightly non-ideal gas or a system of particles with harmonic forces with a small degree of anharmonicity are two examples.

III. HOMOGENEOUS NUCLEATION IN LIQUIDS (AN EXAMPLE OF THE USE OF MOLECULAR DYNAMICS).

In the study of superionic conductors a property of some interest is the manner in which, with lowering of temperature, the

"melted" sublattice goes into a frozen, crystalline state. It is therefore relevant to present for this conference some results related with the onset of order in a disordered system.

Recently there has been some discussion concerning the importance of the pair potential in determining the symmetry of the solid which is nucleated from a liquid. In this context lengthy calculations were made by Hsu and Rahman [2] using a variety of pair potentials. One of their calculations is summarized here.

A few years ago it was found that liquid alkali metals, in particular liquid Rubidium, could be studied by molecular dynamics to obtain results in good agreement with neutron inelastic scattering experiments on the propagation of sound (i.e., density fluctuations) in that liquid [3]. Hence this liquid was chosen for the study of homogeneous nucleation in addition, of course, to the Lennard-Jones liquid. The potential [4] function is dominated by Friedel oscillations and it is given in Ref. 2. The liquid of 500 particles is rapidly quenched from about 320°K to about 40°K, and then the molecular dynamics trajectories are monitored for various properties of interest. In Fig. 1 we see the behavior of the temperature, pressure and the square of the displacement of the system in its configuration space (see Section II above for the definition of this quantity).

From Fig. 1 it is quite apparent that the system undergoes a transformation after a lengthy relaxation; during this long relaxation the temperature and pressure do not show sensitivity to the fact that the system is inexorably "going somewhere". It is during a very short interval of time (~ 7 ps) that all three quantities shown in Fig. 1 undergo a catastrophic change after which there is completely uneventful dynamical behavior.

A multiplicity of ways of analysing the structure of the system before and after the sudden change show that a bcc structure is nucleated out of the liquid and it is the latent heat which shows up in the rise of temperature on nucleation, with a simultaneous drop in pressure.

To investigate further the short period of time during which the sudden changes occur, the shapes of Voronoi polyhedra were used to characterise the precise arrangement of the neighbors of each particle. (Voronoi polyhedra are generalizations of the familiar concept of Wigner-Seitz cells in a lattice). By this analysis it was found that there is a critical nucleus size of about 50 particles and that crystallization is a consequence of the catastrophic growth of one nucleus; the surface of the nucleus was found to advance at about 120 msec⁻¹.

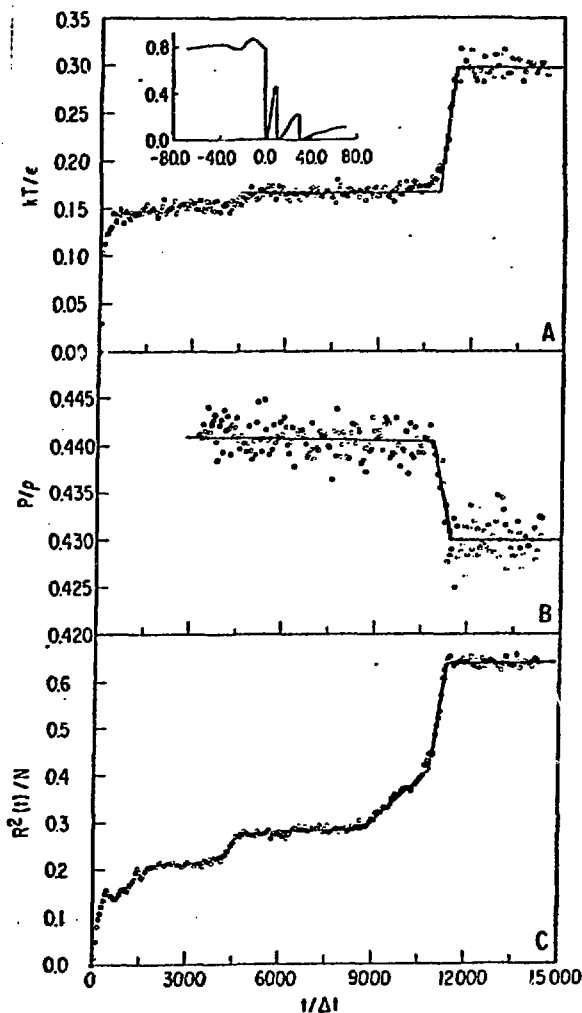


Fig. 1. Change of temperature, pressure, and displacement squared in configuration space for a Rubidium system. Quenching occurred at $t = 0$. Insert in A is the enlargement of variations of temperature just before and after quenching; this detail is invisible in the main figure due to scale discrepancy. $\epsilon = 403^\circ\text{K}$, $\sigma = 4.4 \text{ \AA}$, $N\sigma^3/V = 0.95$. Nucleation occurs at $\sim 11000 \Delta t$ i.e. $\sim 200 \text{ ps}$ after quenching.

Similar calculations² on a Lennard-Jones system give rise to close packed structures showing that the interaction potential is of primary importance in determining the symmetry of the ordered phase which is nucleated out of the disordered liquid-like arrangement.

Possible calculations along these lines for fast ion conductors are mentioned in Section VI below.

IV. THE MOTION OF F⁻ IONS IN CaF₂

As has already been mentioned, the potential function of the system is the primary input required for molecular dynamics studies. For most materials of interest in fast ion conduction it will be quite difficult to construct particle interaction schemes of sufficient simplicity for use in computer models. However, for a material like CaF₂, in view of the work already available in the literature, it is a simple matter to set up a molecular dynamics calculation.

Kim and Gordon [5] have given, in tabulated form, the short range part of the three interactions. On adding the appropriate Coulombic part one gets the full interaction for any pair.

As regards the manner of incorporating Coulomb interactions, there is a considerable body of literature on the use of Ewald summations in molecular dynamics calculations. In principle, for a charge neutral unit cell of arbitrary complexity, the Coulomb potential of the infinite crystal can be written as $\sum_i \sum_{j > i} f(r_{ij})$; the sum over i and $j > i$ is from 1 to N where N is the total number of ions in the charge neutral unit cell; $f(r)$ is a function of the vector r and it is built up of part real space and part reciprocal space summations both of which are rapidly convergent. The necessity of using Ewald summations in dealing with charged particles makes molecular dynamics calculations with charged systems much more time consuming than similar calculations with short range interactions only. The review by Sangster and Dixon [1] gives a very useful account of the problems involved.

There has been a large amount of molecular dynamics work on solid and molten ionic materials (see Sangster and Dixon [1]). In almost all the materials studied the cations and the anions carry unit charge and have comparable sizes. Obviously under such conditions the cations and the anions cannot show qualitative asymmetry in their dynamical and structural behavior. In CaF₂ there is an obvious asymmetry between the Ca⁺⁺'s and the F⁻'s and therefore it is not excluded that they may (and do) exhibit qualitatively different behavior at appropriate temperatures. However it is not obvious that the Kim-Gordon [5] potential scheme is capable of showing this qualitative difference.

Molecular dynamics calculations on CaF₂ using the Kim-Gordon scheme showed [6], for the first time, that this manner of studying liquids and solids is also a powerful potential tool in the field of fast ion conduction. In the following paragraphs a brief summary of the work on CaF₂ will be given.

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At 1600 K and 2.525 gcm⁻³ CaF₂ is close to its melting point; these conditions were chosen as the optimal conditions for a molecular dynamics calculation. The calculations were started with all ions at positions corresponding to the normal fluorite structure. The 108 Ca⁺⁺ and 216 F⁻ ions fit into a cube of length 17.7 Å. At 1600 K the motion of the two types of ions is remarkably different as seen from Fig. 2.

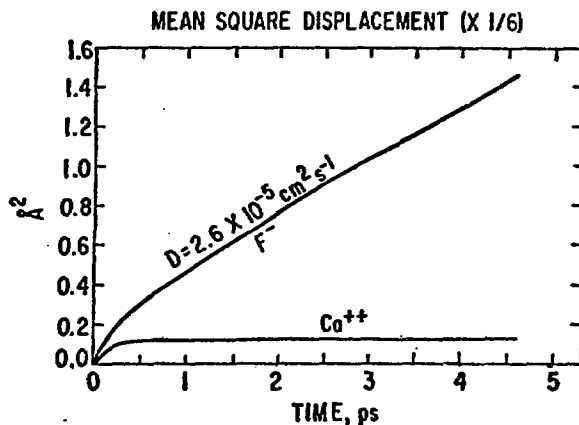


Fig. 2. $\langle x^2 \rangle / 6$ for Ca⁺⁺ and F⁻ in CaF₂. The thermal cloud of Ca⁺⁺ is 0.12 Å wide. F⁻ have a self-diffusion constant $2.6 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$. $T = 1590 \text{ K}$, $\rho = 2.525 \text{ gcm}^{-3}$.

It will be appropriate at this point to emphasize two possible points of view because their difference cannot be overlooked. One is to pursue the analysis of the dynamics generated on the computer to learn about the complex correlations that are present in that dynamics. The other is to ask how close the computer system is to CaF₂ as found in laboratory experiments. A little of both these points of view will be presented in the following.

The three pair correlation functions are shown in Fig. 3. The distances of the F⁻'s from the octahedral sites of the Ca⁺⁺ fcc structure (generated by the time averaged positions of the Ca⁺⁺ ions) generates the fourth "pair" correlation in Fig. 3; the broad first peak in this "pair" correlation is due to the fact that the F⁻ motion, while it temporarily resides at the fluorite sites, has a large Debye-Waller cloud; in Ref. 6 this broad first peak was erroneously interpreted as the occupation by F⁻'s of the O-sites. Proper analysis (see Ref. 7,8) shows that only a small fraction of F⁻'s can actually be said to have left their sites to reside at the O-site.

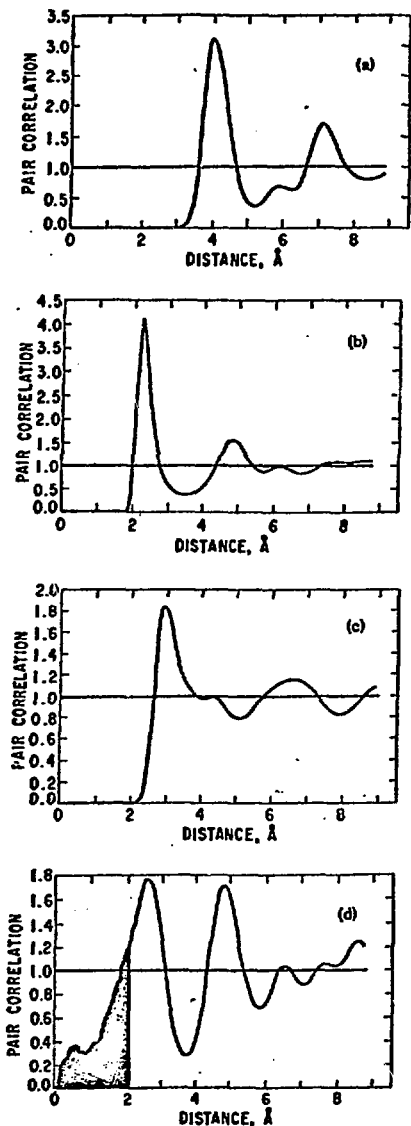


Fig. 3. (a) Pair correlation between Ca^{2+} ions. The populations under the three peaks are 12, 6, 24, respectively, the Ca^{2+} 's preserve the face centered cubic lattice structure throughout the molecular dynamics run. (b) Pair correlation between Ca^{2+} and F^- ions. The populations under the first peak is 8; the peaks appear at positions expected in the fluorite lattice. (c) Pair correlation between F^- ions. It indicates that the F^- ions have considerable disorder in their mutual arrangements. However, the shoulder and the second peak still correspond to positions in the fluorite structure. (d) Pair

correlation between the octahedral site (of the Ca^{2+} fcc lattice) and the F^- ions; it shows a population of one under the shaded region. Thus half the anions appear in regions unoccupied in a fluorite lattice but they do not reside at the O-sites.

It is to be noted that the pair correlations give no direct indication as to the nature of the dynamics of the two types of ions. It is the behavior of the mean square displacement which gives direct evidence of the fact that the F^- 's are mobile while the Ca^{2+} 's are not.

On the basis of very detailed analysis of the motion of F^- ions by Dixon and Gillan [7] and by Jacucci and Rahman [8] it is quite clear that these ions perform their diffusive motion by jumps which are mostly (80%) in the 100 direction. This result can be deduced by simply "looking" at the motion of F^- 's in space and time; however, a more sophisticated description of diffusion is given by its Fourier analysis. Let $\underline{d}(t)$ denote the displacement of an F^- in time interval t and \underline{k} be the wave vector of interest for the Fourier analysis. Then $F_S(\underline{k}, t)$ defined in Section II in terms of \underline{d} and \underline{k} gives us a complete picture of the diffusion process for wave vector \underline{k} . (In the jargon of neutron inelastic scattering theory and experiments F_S is the so called "self part" of the "intermediate scattering function"; in favorable circumstances, with such experiments one can observe the frequency transform of this function). Our interest in F_S lies in the fact that simple mathematical models can be constructed for F_S . One such model is that of Chudley and Elliott [9] and it was shown by Jacucci and Rahman [8] that in spite of the oversimplifications in the model of Chudley and Elliott it gives a very satisfactory account of the molecular dynamics data. This is somewhat discouraging in the sense that extremely accurate $F_S(\underline{k}, t)$ will be needed to judge and to test models of jump diffusion which introduce more sophistication into the description than has been done in the Chudley-Elliott model. It has been shown in Ref. 8 that the jump model gives a satisfactory fit with the molecular dynamics $F_S(\underline{k}, t)$ on taking 6.27 ps as the residence time, 80% probability of jumping in the 100 direction and 20% in the 110 direction. Trajectory analysis in the manner of Refs. 7 and 8 confirms this and also shows that the motion can be analyzed in terms of the generation and annihilation of anti Frenkel pairs.

V. TEMPERATURE AND DENSITY DEPENDENCE OF DIFFUSION IN CaF_2

The temperature dependence of the diffusion

constant at two different densities is shown in Fig. 4. The result is an essentially linear dependence on temperature at each density but a rather dramatic change with density. At 1450 K and 2.8 gcm^{-3} the diffusion is barely noticeable whereas at that temperature and 2.525 gcm^{-3} it is an easily observable diffusion constant $\sim 2 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$.

For finite budget molecular dynamics a diffusion constant of $\sim 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ is most favorable and $10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ can be investigated at considerable expense. The experimental information on diffusion in CaF_2 is that of Matzke [10] taken between 600 K and 1200 K, giving a fit with the formula $50 \times \exp(-23210/T^\circ\text{K}) \text{ cm}^2 \text{ sec}^{-1}$. Extrapolated beyond 1200 K this formula gives the steeply rising curve shown in Fig. 4. Experimental results in the region of temperature of interest to molecular dynamics are therefore badly needed.

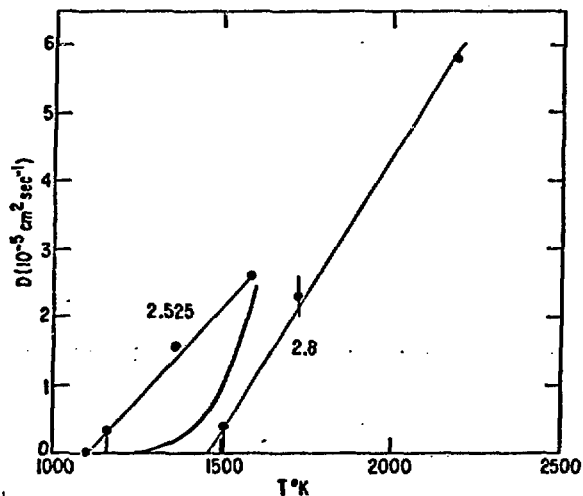


Fig. 4. Constant of self-diffusion of F^- at two densities as a function of temperature. Laboratory results of Matzke [10] are shown as the steeply rising exponential.

The conclusion we can draw from Fig. 4 is that a detailed comparison of the calculated and experimental values of the diffusion constant in CaF_2 cannot be made at present. Firstly experimental results in the temperature range of interest are not available. Secondly a potential function scheme will have to be constructed which gives the correct equation of state for CaF_2 before a comparison with experimental diffusion constants can be made. The Kim-Gordon [5] potential gives a large negative pressure [6] at 2.525 gcm^{-3} and temperatures shown in Fig. 4. This is as

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expected since this density is lower than the density of the solid at the melting point; it is also expected then that the constant of self-diffusion will be much larger than at the normal density [11] of the solid at the same temperature. However at 2.8 gcm^{-3} and 1650°K , the calculations still give a negative pressure ($pV/NKT \ll -1$) but the diffusion is much slower than that indicated by the values extrapolated out of Matzke's experimental range.

VI. CONCLUDING REMARKS

1. One of the challenges for molecular dynamics in the field of fast ion conductors will be to start from the molten state and on cooling to observe first the crystallization of one ionic other species and on further cooling the arrest of the species in the interspaces of the already frozen structure. In monatomic systems such changes of phase have been observed by calculation and some results have been presented here for illustration.

2. In materials like Kim-Gordon- CaF_2 considerable molecular dynamics data is already available regarding the nature of jump motion of the F^- ions and regarding the temperature and density dependence of the constant of self-diffusion. This can be used with profit for developing a theoretical understanding of structure and dynamics in CaF_2 type systems.

3. An effort will have to be made to invent a new interaction potential scheme for CaF_2 which will give a good description of the thermodynamics of the real material and at the same time of the transport of F^- ions in that system. This is lacking at present. In the meantime hopefully experimental values of transport coefficients near melting will become available.

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