

Direct Computation of the Superionic Conductivity in CaF_2 by Constant-Temperature Equilibrium and Nonequilibrium Molecular Dynamics

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 Europhys. Lett. 8 599

(<http://iopscience.iop.org/0295-5075/8/7/003>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 195.251.197.81

The article was downloaded on 12/04/2012 at 09:28

Please note that [terms and conditions apply](#).

Direct Computation of the Superionic Conductivity in CaF_2 by Constant-Temperature Equilibrium and Nonequilibrium Molecular Dynamics.

G. A. EVANGELAKIS(*)(**) and V. PONTIKIS(*)

(*) *Centre d'Etudes Nucléaires de Saclay*

Section de Recherches de Métallurgie Physique, 91191 Gif-sur-Yvette Cedex, France

(**) *University of Ioannina, Physics Department*

Applied Physics Laboratory, 45110 Ioannina, Greece

(received 12 December 1988; accepted in final form 20 January 1989)

PACS. 05.90 – Other topics in statistical physics and thermodynamics.

PACS. 66.30D – Theory of diffusion and ionic conduction in solids.

Abstract. – We present the results of the first direct calculation of the superionic conductivity of CaF_2 , using constant temperature equilibrium and nonequilibrium molecular dynamics in the linear response regime based on a rigid-ion potential. We found $\sigma = (5.1 \pm 0.2)$ mho/cm at $T = 1700 \text{ K} \approx T_{\text{melting}}$, in good agreement with available experimental data and that the response of the system remains linear under external forces up to $F = 10^7 \text{ eV/cm}$. The Haven's ratio, resulting from independent computations of conductivity and diffusivity at this temperature, $H = 0.34 \pm 0.05$, suggests that the anionic sublattice is still crystalline and that mass transport and ionic conduction are not due to a simple vacancy or interstitialcy mechanism for which higher H values are expected.

Superionic conductors with the fluorite structure have been extensively studied in recent years both experimentally and theoretically [1-3]. Neutron scattering investigations established the existence of an increasing anionic sublattice disorder on increasing the temperature above a critical value T_c [4, 5], associated to a broad specific-heat anomaly [6]. Concurrently, the anionic diffusivity, D [7], and the conductivity, σ [8], reach liquidlike values comparable to those obtained for molten salts [9]. This behaviour is attributed to the onset of an order-disorder transition suppressed before completion by the increasing repulsion between defects when their concentration increases [10]. The oversimplified explanation of the origin of liquidlike diffusivity and conductivity values according to which this behaviour is due to a «melted» anionic lattice has been discarded, since equilibrium molecular dynamics (EMD) calculations demonstrated that it remains crystalline up to T_m despite the high thermal disorder [11-13]. This conclusion is based on a detailed analysis of EMD trajectories, which showed that diffusion occurs via a hopping mechanism. MD investigation of the solid-state thermodynamic properties is usually restricted to those dynamical properties which do not involve mass transport. Indeed diffusion cannot occur in MD systems, which are of infinite extension via the usual periodic boundary conditions,

since sources of point defects such as dislocations, surfaces or grain boundaries are absent and the formation energy of interstitials is too high to allow the creation of such defects at the time scale of MD simulations. From this standpoint superionic conductors are peculiar among crystalline solids, since the anionic sublattice disorder above T_c allows detectable diffusion by MD. In CaF_2 ($T_c \approx 1430$ K), the calculated fluorine diffusion coefficient is in satisfactory agreement with the experimental data, extrapolated at the same temperature [13], since these are available only below $T = 0.8T_m$ [7] and MD computations are performed at temperatures near to T_m , in order to circumvent space and time limitations of computer simulations [14]. However, the superionic conductivity, σ , has never been computed directly. To evaluate σ one uses EMD diffusion data and the Nernst-Einstein relation, assuming a value $H = D_t$, $D = 1$ for the Haven's ratio, where D_t is the tracer diffusion coefficient and D corresponds to the diffusivity the ions would have, if they were moving randomly and completely free [13, 15].

In this letter we present the results of a direct computation of the superionic conductivity in CaF_2 by both, EMD and nonequilibrium molecular dynamics (NEMD) in the linear response regime, at constant temperature. The two methods lead to practically identical results in fair good agreement with the experiment. In addition we determined Haven's, $H = 0.34 \pm 0.05$, by determining separately the values of conductivity and diffusivity.

The simulations are performed on a system of 324 particles (108 cations and 216 anions) interacting through the following rigid-ion potential:

$$\phi(r_{ij}) = \frac{Q_i Q_j}{r_{ij}} + A_{ij} \exp \left[-\frac{r_{ij}}{\rho_{ij}} \right] - \frac{C_{ij}}{r_{ij}^6}, \quad (1)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, Q_i , Q_j are, respectively, the mutual distance and the charges of ions i and j , $A_{++} = C_{++} = C_{+-} = 0$, $A_{--} = 1808$ eV, $\rho_{--} = 0.293$ Å, $C_{--} = 109.1$ eV · Å⁶, $A_{+-} = 674.3$ eV, $\rho_{+-} = 0.336$ Å [13]. The Ewald summation is used for the calculation of the Coulombic contribution to the potential energy and forces. The system is prepared at $T = 1700$ K, a temperature in the superionic conductivity region near the experimental melting point $T_m \approx 1691$ K [16] and atmospheric pressure using the Nosé-Andersen (NPT) EMD method [17, 18]. The equilibrium lattice constant, $a = 0.56716$ nm, is thereby obtained. By quenching the liquid we verified that at this temperature the crystal is the stable phase for our system. Indeed, recrystallization occurs after 10^4 time steps annealing as indicated by the progressive apparition of the crystal characteristic peaks on the pair correlation function profiles [19]. Starting from an equilibrium configuration the calculation is continued in the (NVT) ensemble (Nosé thermostat [17]) and external forces, simulating the presence of an electric field, are applied to the ions along the X-direction. The equations of motion are integrated with periodic boundary conditions using a fifth-order predictor-corrector algorithm [20] and a timestep $\delta t_1 = 2 \cdot 10^{-15}$ s for the EMD and NEMD computations and forces $F \leq 10^{-5}$ eV/cm. For larger values of the external force $\delta t_2 = 5 \cdot 10^{-17}$ s is used.

By a standard result of linear response theory [21] the mean induced electrical current in the presence of an external force is related to the equilibrium autocorrelation function of the appropriate dynamical variable. In the present case the specific conductivity is given by

$$\sigma = \lim_{t \rightarrow \infty} \left(\frac{e \langle J_x^Q(t) \rangle}{VF_x} \right) = \frac{e^2}{k_B T} \int_0^\infty \langle J(t) J(0) \rangle dt, \quad (2)$$

where

$$J_x^Q(t) = \sum Q_i v_{ix}(t) \quad (3)$$

is the induced electrical current, k_B is the Boltzmann constant, e and Q_i are, respectively, the elementary charge and the charge of ion i , $v_{ix}(t)$ is the x -component of the velocity of particle i , V is the volume of the simulation box, F_x is the external force and brackets indicate ensemble averages. The left-hand side of eq. (2), valid in the limit of small perturbations, would provide in principle an independent check of EMD σ values (right-hand side of eq. (2)) using NEMD.

Unfortunately large statistical errors affect the values of σ thereby obtained, thus making such a verification impossible. Moreover, the equilibrium computations of σ require a large amount of statistics. A method to circumvent this difficulty is provided by the so-called «subtraction technique» [22] which proceeds as follows: trajectories of the particles are generated twice, starting from the same initial equilibrium configuration, both by EMD and with the external perturbation by NEMD runs. The response of the system in the presence of the external field is obtained as a function of time by calculating the difference of the current in the perturbed and the unperturbed trajectories, averaged over many segments. The applicability of this technique is restricted to the study of physical phenomena with short relaxation times [22]. Indeed for ergodic systems the trajectories will depart exponentially from each other when time increases [23]. The success of the method is due to the strong correlation, on a time interval limited in extension, between the perturbed and unperturbed trajectories. By subtracting the corresponding currents, fluctuations cancel out and the desired signal emerges free of noise. Following the procedure adopted in ref. [24], we divided an unperturbed trajectory into contiguous segments of 1000 time steps each, this time interval being larger than the typical relaxation time of the autocorrelation functions of the electrical current and the ion velocities [19]. Figure 1a) displays the results obtained for averages over 50 and 200 segments, respectively. The «plateau» value, expected after $\Delta t = 50 \delta t_1$, which corresponds to the stationary electrical current and gives through the left-hand side of eq. (2) the specific conductivity, is clearly affected by

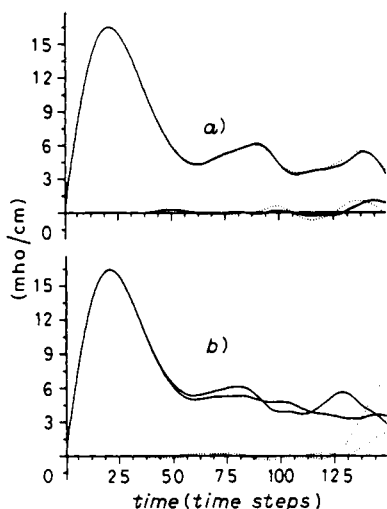


Fig. 1. - Superionic conductivity at $T = 1700$ K computed by the subtraction technique using an external force $F = 10^5$ eV/cm. a) Full lines: 200 segments average, dotted lines: 50 segments average. b) Averages over 40 and 260 segments using random initial configurations for the perturbed and the unperturbed trajectories (see text). Upper curves: system response along the X-axis, parallel to the applied force. Lower curves: system response along the Y-axis providing an estimate of the correlation in time between the perturbed and unperturbed trajectories. Time is expressed in time steps, δt_1 units.

oscillations whose amplitude is not reduced when improving the statistics. This behaviour can be understood if one refers to the microscopic origin of electrical current in our system. Indeed, the current is due to the motion of fluorine anions in the well crystalline, up to T_m , cation sublattice by a hopping mechanism [11-13] and not by a continuous motion as in molten salts for which this method has been successfully employed [24]. The accuracy of our computations depends therefore on the efficiency of the sampling of the different hopping conduction events occurring in the system and of the average delay separating them. Accordingly, we proceeded as follows: a number of statistically independent starting configurations, equal to the number of desired segments, has been prepared by choosing at random the initial ion velocities and performing equilibration EMD runs which lasted 4000 time steps. The resulting final configuration is then used as the starting point for the given perturbed and unperturbed segment. The results obtained using this procedure are shown in fig. 1b) for averages over 40 and 260 segments, respectively. The «plateau» corresponds to the stationary current value and is practically free from statistical noise for the higher statistics average. The resulting specific conductivity value, $\sigma = (5.1 \pm 0.2) \text{ mho} \cdot \text{cm}^{-1}$ is in satisfactory agreement with the extrapolation of the experimental data up to $T = 1700 \text{ K}$, $\sigma_{\text{exp}} = 3.1 \text{ mho} \cdot \text{cm}^{-1}$ [25].

An equilibrium computation of σ can also be performed using the Green-Kubo formula (right-hand side of eq. (2)). When the average value of the equilibrium current autocorrelation function [19] is computed using statistically independent equilibrium trajectory segments, thanks to the procedure described above, its time integral leads to conductivity value identical to that obtained from the NEMD computations. It is worth emphasizing that the Green-Kubo integral of the current autocorrelation function averaged over a unique equilibrium trajectory of 10^6 timesteps results into an unreliable σ value for the reason discussed above.

The linearity of the system response has also been explored as a function of the external force for perturbation values ranging from 10 eV/cm up to 10^7 eV/cm . A linear response is obtained over this whole range. On increasing the external force the average current increases significantly up to values which can be extracted from the statistical noise without the use of the subtraction technique. Figure 2 displays the results obtained at $F = 10^7 \text{ eV/cm}$ on averaging the system response over 40 statistically independent trajectory

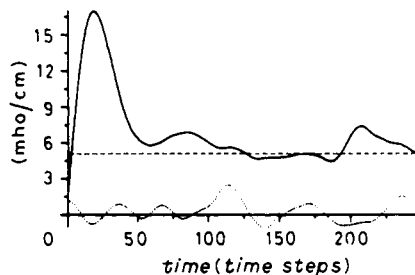


Fig. 2. - System response obtained without the subtraction technique at $F = 10^7 \text{ eV/cm}$. Full line: direction parallel to the external force, dotted line: direction normal to the external force, dashed line: conductivity value obtained by the subtraction technique. Time is expressed in time steps, δt_1 units.

segments. These have been obtained using the aforementioned procedure. Unlike the subtraction technique, the mean induced current is now computed on a much longer time scale. The resulting conductivity $\sigma = 5.8 \pm 0.8$, despite the poor statistics, is in fair good agreement with that given by the subtraction technique. Table I illustrates the computa-

tional effort required to obtain the conductivity by EMD and NEMD. The subtraction technique is the less time consuming and should be preferred when short relaxation time phenomena are under study. The exceedingly large amount of computations needed for NEMD with high perturbations, in order to obtain statistical averages comparable with those achieved when using the subtraction technique (260 segments), explains the reason for which only 40 segments have been used in that case.

TABLE I. - *Computational effort required per segment, to determine the conductivity by the three methods used in the present work, expressed in number of iterations for the integration of the equations of motion, δt_1 and δt_2 are the time steps we used (see text). A, B and C correspond, respectively, to NEMD using the subtraction technique, the equilibrium Green-Kubo and NEMD without the subtraction technique computations.*

	A	B	C
Equilibrium starting configuration	4000 (δt_1)	4000 (δt_1)	4000 (δt_1)
Computation of τ	2×150 (δt_1)	> 400 (δt_1)	40×150 (δt_2)
Total for one segment	4300	> 4400	10 000

The anion diffusion coefficient, D^- , is obtained by computing the mean square displacement of anions as a function of time

$$D^- = \lim_{t \rightarrow \infty} \frac{\langle \delta r^2 \rangle}{6t}. \tag{4}$$

We found $D^- = 3.72 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, a value in reasonable agreement with the extrapolation of available experimental data at the temperature of the simulation $D^- = 5.77 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ [7]. Cations do not contribute to diffusion up to the highest temperature we studied, $T = 1700 \text{ K}$. The independently determined diffusion coefficient and conductivity of the anions allow one to compute the Haven ratio. We found $H = 0.34 \pm 0.05$ a value which indicates that the mechanisms underlying diffusion and conductivity are more complex than the vacancy ($H = 0.65$) or the interstitialcy ($H = 0.75$) mechanism [15]. This conclusion is also in agreement with recent EMD work on CaF_2 and superionic perovskites [26, 27] for which diffusion was observed to occur mainly by a ring exchange mechanism.

Finally, it is worth noting that although linear response theory is of widespread use for the calculation of transport coefficients in liquids, it cannot be used for mass transport and conductivity computations in crystalline solids since these phenomena are highly nonlinear. Superionic conductors are peculiar from this standpoint, as has been shown for the first time in the present study. The anionic sublattice disorder leads in these systems to a linear behaviour of the induced electrical current over a wide range of values of the external field, the system being still crystalline up to the melting point.

* * *

We are indebted to M. GILLAN for fruitful discussions and to G. CICCOTTI for his useful suggestions. GAE is grateful to the Physics Department of the University of Ioannina (Greece) for financial support during a study leave.

REFERENCES

- [1] VASHISTA P., MUNDY J. N. and SHENOY J. K. (Editors), *Proceedings of the International Conference on Fast Ion Transport in Solids, Lake Geneva* (North-Holland, Amsterdam) 1979.
- [2] SALAMON M. B. (Editor), *Topics in Current Physics: Physics of Superionic Conductors* (Springer, Berlin) 1975.
- [3] PERRAM J. W. (Editor), *The Physics of Superionic Conductors and Electrode Materials*, NATO ASI, Odense (Plenum Press, New York, N.Y.) 1983.
- [4] THOMAS M. W., *Chem. Phys. Lett.*, **40** (1975) 111.
- [5] DICKENS M. H., HAYES W., HUTCHINGS M. T. and SMITH C., *J. Phys. C*, **15** (1982) 4043.
- [6] SCHRÖTER W. and NÖLTING J., *J. Phys. (Paris)*, **41** (1980) C6-20.
- [7] MATZKE H., *J. Math. Sci.*, **5** (1970) 831.
- [8] OBERSCHMIDT J. and LAZARUS D., *Phys. Rev. B*, **21** (1980) 5823.
- [9] YOUNG R. E. and O'CONNELL J. P., *Ind. Eng. Chem. Fundam.*, **10** (1971) 418.
- [10] CATLOW C. R. A., COMINS J. D., GERMANO F., HARLEY A. and HAYES W., *J. Phys. C*, **11** (1978) 3197.
- [11] RAHMAN A., *J. Chem. Phys.*, **65** (1976) 11.
- [12] JACUCCI G. and RAHMAN A., *J. Chem. Phys.*, **69** (1978) 4117.
- [13] GILLAN M. and DIXON M., *J. Phys. C*, **6** (1980) 41.
- [14] PONTIKIS V., *Round table: Perspective in Materials Science in Molecular-Dynamics Simulation of Statistical-Mechanical Systems*, in *Proceedings of the International School of Physics «Enrico Fermi»*, Course XCVII, edited by G. CICCOTTI and W. G. HOOVER (North-Holland, Amsterdam) 1986, p. 562.
- [15] COMPAAN K. and HAVEN Y., *Trans. Faraday Soc.*, **54** (1958) 1498 and references therein.
- [16] NAYLOR B. F., *J. Am. Chem. Soc.*, **67** (1945) 150.
- [17] NOSÉ S., *J. Chem. Phys.*, **81** (1984) 511.
- [18] ANDERSEN H., *Mol. Phys.*, **72** (1980) 2384.
- [19] EVANGELAKIS G. A. and PONTIKIS V., in preparation.
- [20] NORDSIECK A., *Math. Comput.*, **16** (1962) 22.
- [21] KUBO R., *Rep. Prog. Phys.*, **29** (1966) 255.
- [22] CICCOTTI G. and JACUCCI G., *Phys. Rev. Lett.*, **35** (1975) 12.
- [23] STODDARD S. D. and FORD J., *Phys. Rev. A*, **8** (1974) 1504.
- [24] CICCOTTI G., JACUCCI G. and McDONALD I. R., *Phys. Rev. A*, **13** (1976) 426.
- [25] BARSIS E. and TAYLOR J. A., *Chem. Phys.*, **45** (1966) 1154.
- [26] DOAN N. V. and ADDA Y., *Philos. Mag.*, **56** (1987) 269.
- [27] KAPUSTA B. and GUILLOPÉ M., *Philos. Mag.*, **58** (1988) 809.