Correlations in the Motion of Particles in α-AgI: A Molecular-Dynamics Study

W. Schommers

*Kernforschungszentrum Karlsruhe, Institut für Angewandte Kernphysik, D-7500
Karlsruhe, Federal Republic of Germany*

I have performed molecular-dynamics calculations for α-AgI at 563 K using a realistic
pair potential and a model system of 256 particles. I investigated the influence of I⁻ ions
on single-particle motion in the Ag⁺ subsystem. In addition, I showed that correlations
between different ions must be distinctly reflected in frequency-dependent conductivity.

α-AgI is a representative member of the class
of superionic conductors. The silver subsystem
of α-AgI is highly disordered and shows strongly
anharmonic behavior. This appears from the pro-
nounced quasielastic peak in the scattering law
experimentally observed[1] and the extremely high
mobility of the silver ions; the value of the diffu-
sion constant[2] ($D \cong 2.1 \times 10^{-5}$ cm²/sec) is compa-
rable to that of liquids (e.g., argon[3] and rubidi-
um[4]). Molecular-dynamics (MD) calculations are
important in studying many-particle systems with
strong anharmonicities, such as superionic con-
ductors, since anharmonicity is treated without
approximations.

In contrast to some analytic approaches[5,6] re-
cently employed, this method allows one to study
the particle motions more generally: It is pos-
sible to study in detail the influence of the I⁻ ions
on the motion of the Ag⁺ ions, and one is then
able to learn something about correlations be-
tween *different* ions; such correlations are re-
flected in the frequency-dependent conductivity.

MD calculations for α-AgI at 563 K were per-
formed for the following model system: $N = 256$
ions (Ag⁺ and I⁻) were arranged in a cubical box
such that its structure corresponds to that of
α-AgI (see Strock[7] and Hoshina[7]). To avoid sur-
face effects, periodic boundary conditions were
imposed on the system. For the interaction be-
tween the jth I⁻ ion and another ion i (Ag⁺ or I⁻)
I have chosen the form

$$v_j^{\text{I}^-}(r_{ij}) = A_{ij}\exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) + \frac{e_i e_i}{r_{ij}} + c(\vec{r}_j - \vec{r}_j^{\text{E}})^2, \quad (1)$$

and for the jth Ag⁺ ion I use

$$v_j^{\text{Ag}^+}(r_{ij}) = A_{ij}\exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) + \frac{e_i e_i}{r_{ij}}, \quad (2)$$

where e_i is the charge of the ith ion; $\vec{r}_j$ is the ac-
tual position of the I⁻ ion and $\vec{r}_j^{\text{E}}$ its equilibrium
position, r_{ij} is the relative distance between the
particles i and j, and c is a spring constant. The

first term of Eqs. (1) and (2) is the Born-Mayer
repulsion potential and the second term represents
the Coulomb potential. The long-range nature of
the Coulomb interaction makes it necessary to
perform Ewald summations in order to get the
correct Coulomb contributions to the potential en-
ergy and the force acting on an ion. To describe
well the behavior of the iodine ions, a harmonic
term [third term of Eq. (1)] had to be introduced.
MD calculations without consideration of the har-
monic term showed that the iodine ions leave their
equilibrium positions r_j^{E}; this can be shown by
the MD results for the structure factor and the
Debye-Waller factor, which are not in agreement
with the respective data obtained experimentally.
The harmonic term of Eq. (1) might be due to co-
valent binding effects between the ions.

Determination of the model parameters.—For
the three parameters ρ_{ij} I have made the follow-
ing simplifying assumption:

$$\rho_{++} = \rho_{--} = \rho_{+-} = \rho, \quad (3)$$

and ρ was chosen to be 0.33 Å (see Flygare and
Huggins[8] and Drexel[9]). In order to determine the
constants A_{ij} I have used Barker's definitions for
the hard-sphere radius[10]:

$$2r_c = \int_0^\infty dr\{1 - \exp[-v_0(r)/k_{\text{B}}T]\}, \quad (4)$$

where $v_0(r)$ is the Born-Mayer repulsion potential.
The hard-sphere radii for Ag⁺ and I⁻ are given in
Ref. 8 (Ag⁺, $r_c = 0.9$ Å; I⁻, $r_c = 1.75$ Å). From
this and Eq. (4) we obtained $A_{++} = 2.34 \times 10^{-11}$ erg,
$A_{--} = 4.04 \times 10^{-9}$ erg, and $A_{+-} = 3.07 \times 10^{-10}$ erg.
The spring constant c was fitted to the experimen-
tally determined mean displacement $\langle r^2(t \to \infty)\rangle^{1/2}$
= 0.385 Å, which is given by the Debye-Waller fac-
tor.[11] My MD result for $\langle r^2(t \to \infty)\rangle^{1/2}$ is 0.373 Å.
This value is in agreement (within the error lim-
its) with that obtained experimentally.

To test our *vibrating-ion model* (the I⁻ ions are
vibrating), I have computed the structure factor

$S(\vec{k})$ for the silver subsystem. $S(\vec{k})$ is given by[12]

$$S(\vec{k}) = \langle \rho(\vec{k})\rho*(\vec{k})\rangle, \qquad (5)$$

where

$$\rho(\vec{k}) = N_{\mathrm{Ag}^+}{}^{-1/2} \sum_{i=1}^{N_{\mathrm{Ag}^+}} \exp(i\vec{k}\cdot\vec{r}_i), \qquad (6)$$

where $\vec{k}$ is the wave vector and N_{Ag^+} the number of Ag^+ ions. In Fig. 1(a), $S(\vec{k})$ is shown for 0.8 $\text{Å}^{-1} \le k \le 3.0 \ \text{Å}^{-1}$. There is close agreement between the MD results and the experimental results of Fuess, Funke, and Kalus.[12]

The diffusion constant D of the Ag^+ ions is given by the slope of the linear part of the mean-square displacement $\langle r^2(t)\rangle$ [see Fig. 1(b)]:

$$\lim_{t \to \infty} \langle r^2(t)\rangle = 6Dt + \text{const.} \qquad (7)$$

From this, one finds the diffusion constant to be $2.15 \times 10^{-5} \ \text{cm}^2/\text{sec}$. This value is also very close to that obtained experimentally[2] $(2.1 \times 10^{-5} \ \text{cm}^2/\text{sec})$. The results for $S(k)$ and D indicate that we can consider this vibrating-ion model for α-AgI to be quite realistic.

One purpose of the calculations presented here is to investigate how the motion of the I^- ions is reflected in the structure and the dynamics of the silver subsystem. Therefore, I made an additional MD calculation for a rigid-lattice model (all the I^- ions are at rest). For such a system we also computed $S(k)$, $\langle r^2(t)\rangle$, and the normalized velocity autocorrelation function

$$\Psi_{\mathrm{Ag}^+}(t) = \langle\vec{u}(0)\cdot\vec{u}(t)\rangle/\langle u^2(0)\rangle, \qquad (8)$$

where $\vec{u}(t)$ is the velocity of an Ag^+ ion of the ensemble. The results are shown in Fig. 1. It can be seen that the position of the main peak of $S(k)$ is shifted to small wave vectors k. This implies that the mean distance between next silver neighbors is larger than in the case of the vibrating-ion model. The behavior of $\langle r^2(t)\rangle$ [see Fig. 1(b)] indicates that there is very little diffusion of Ag^+ ions in the rigid-lattice model. This is supported by the velocity autocorrelation function $\Psi_{\mathrm{Ag}^+}(t)$ [see Fig. 1(c)]. The oscillations of $\Psi_{\mathrm{Ag}^+}(t)$ can be interpreted as oscillations of a given Ag^+ ion in a cage formed by the I^- lattice—the Ag^+ ion does not leave the cage. On the other hand, in the case of the vibrating-ion model, $\Psi_{\mathrm{Ag}^+}(t)$ has only a long negative tail—after backscattering within the cage, the Ag^+ ions leave it (diffusion).

The results for $S(k)$, $\langle r^2(t)\rangle$, and $\Psi_{\mathrm{Ag}^+}(t)$ show that the movements of the I^- ions cannot be neglected in describing the silver subsystem. However, to describe $\Psi_{\mathrm{Ag}^+}(t)$ analytically, the rigid-
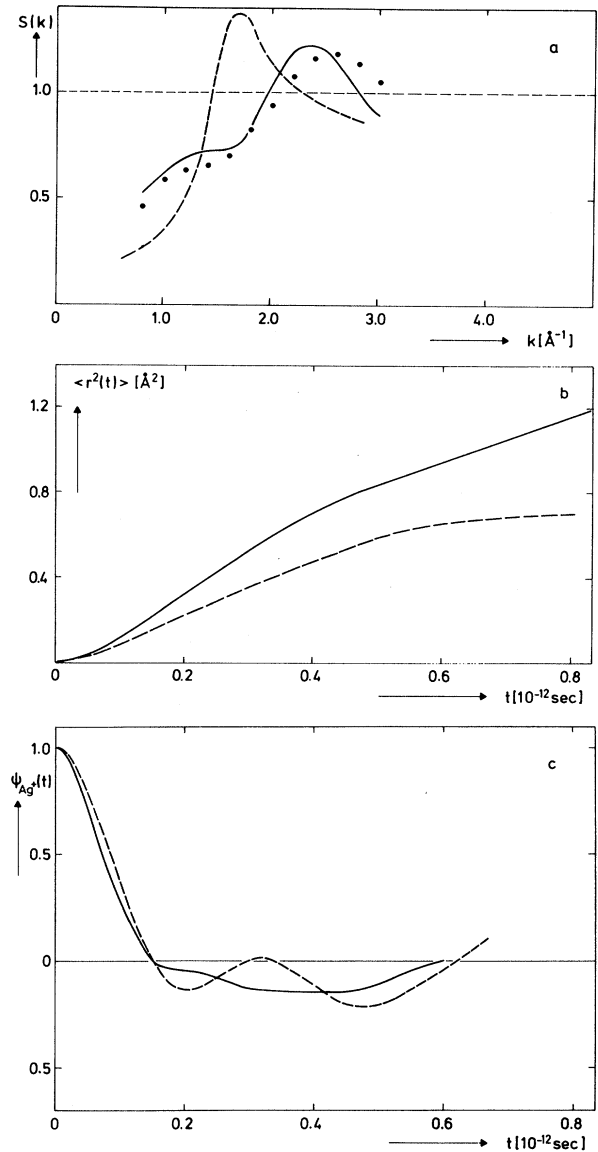

FIG. 1. Results for the Ag^+ subsystem. (a) Structure factor: dotted line, from experiment; solid line, from MD calculations for the vibrating-ion model; dashed line, from MD calculations for the rigid-lattice model. (b) Mean-square displacement $\langle r^2(t)\rangle$: solid line, MD results from the vibrating-ion model; dashed line, MD results from the rigid-lattice model. (c) Velocity autocorrelation function $\Psi_{\mathrm{Ag}^+}(t)$: solid line, MD results from the vibrating-ion model; dashed line, MD results from the rigid-lattice model.

lattice model should be a good starting point.[5] Furthermore, it can be concluded from the behavior of $\Psi_{\mathrm{Ag}^+}(t)$ and $\langle r^2(t)\rangle$ that the single-particle motion in the Ag^+ subsystem of α-AgI is similar to that in monoatomic liquids (e.g., argon[3] and rubidium[4]).

Do there exist correlations between the velocities of different ions? This question is important because those correlations would be reflected in the frequency-dependent conductivity $\sigma(\omega)$. $\sigma(\omega)$ is fully determined by the current-current correlation function[14]

$$\varphi_{AgI}(t) = \frac{1}{e^2}\left\langle \sum_{i=1}^{N} e_i \vec{u}_i(0) \cdot \sum_{j=1}^{N} e_j \vec{u}_j(t) \right\rangle. \qquad (9)$$

The subscript AgI denotes that the sum has to be taken over all ions (Ag^+ and I^-) of the system. If there are no correlations between $\vec{u}_i(t)$ and $\vec{u}_j(t)$, for $i \neq j$, $\Psi_{AgI}(t)$ is given by the corresponding autocorrelation function [e.g., in the frame of the rigid-lattice model[5,6] by $\Psi_{Ag^+}(t)$]. All correlation functions discussed below have been calculated within the framework of the vibrating-ion model.

I first compare the current-current correlation function $\varphi_{Ag^+}(t)$ with the autocorrelation function $\Psi_{Ag^+}(t)$ for the silver subsystem at $t = 0$. For

$$\frac{\varphi_{Ag^+}(0)}{N_{Ag^+}\langle u(0)^2\rangle}$$

$$= 1 + \left\langle \frac{1}{N_{Ag^+}} \sum_{\substack{i,j \\ i \neq j}} \vec{u}_i(0) \cdot \vec{u}_j(0) \right\rangle / \langle u(0)^2\rangle, \qquad (10)$$

I have obtained the value of 0.35. This means that there are relatively strong systematic correlations between the velocities of different ions, which are described by the second term of Eq. (10). In the case of monoatomic liquids, those correlations do not occur. A way to show such correlation effects experimentally is to measure the second moment of the scattering law $S(k, \omega)$.[12] This was done by Suck[15] for a monoatomic liquid (rubidium). His measurements show that there are no systematic correlations between the velocities of different atoms in liquid rubidium. The same measurements should be made for α-AgI.

As already mentioned by Hansen and McDonald,[16] the effect of correlations between the velocities of different ions reflects the tendency for local charge equilibrium to be maintained.

Figure 2 shows $\varphi_{Ag^+}(t)$ as a function of time. $\varphi_{Ag^+}(t)$ and $\Psi_{Ag^+}(t)$ agree well for $0 \leqslant t \leqslant 10^{-13}$ sec. For times greater than 10^{-13} sec there is no point of similarity between the two curves. Furthermore, Fig. 2(a) presents the current-current correlation function $\varphi_{AgI}(t)$ and its autocorrelation function $\Psi_{AgI}(t)$ for the whole system. Although $\Psi_{AgI}(t)$ is different from $\Psi_{Ag^+}(t)$, the time dependence of the normalized functions $\varphi_{AgI}(t)$ and $\varphi_{Ag^+}(t)$ are similar to each other. However,
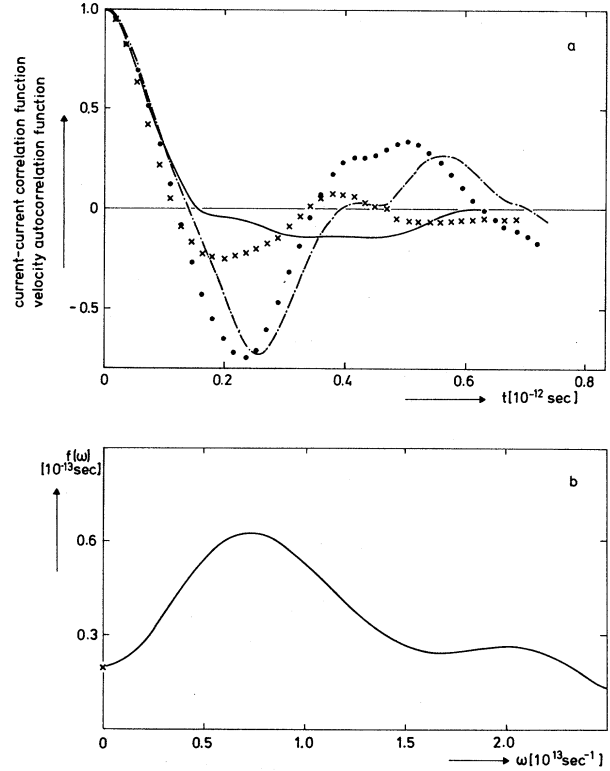

FIG. 2. (a) Current-current correlation functions and velocity autocorrelation functions: solid line, $\Psi_{Ag^+}(t)$; crosses, $\Psi_{AgI}(t)$; dash-dotted line, $\varphi_{AgI}(t)/\varphi_{AgI}(0)$; dotted line, $\varphi_{Ag^+}(t)/\varphi_{Ag^+}(0)$. (b) Frequency spectrum for the silver subsystem. The cross at $\omega = 0$ is the experimental result obtained from the diffusion constant. The two maxima of the frequency-dependent conductivity (see Ref. 18) seem to be reflected in $f(\omega)$.

this is not valid for the absolute values of both functions, since their values differ at $t = 0$ [$\varphi_{AgI}(0)/\varphi_{Ag^+}(0) = 4$]. Therefore, in order to determine the frequency-dependent conductivity $\sigma(\omega)$, the knowledge of $\varphi_{AgI}(t)$ is necessary; $\sigma(\omega)$ cannot be approximated by $\varphi_{Ag^+}(t)$ and $\Psi_{Ag^+}(t)$ alone. It should be mentioned that the statistical errors of the current-current correlation functions are large. A determination of these functions with high accuracy and an enlarged time region is now under way.

As can be seen from Fig. 2(a), the decay with time of $\varphi_{Ag^+}(t)$, $\varphi_{AgI}(t)$, and $\Psi_{AgI}(t)$ is slow. To obtain their Fourier transform, we have to know these functions for much longer times than were calculated. Only the data for $\Psi_{Ag^+}(t)$ are sufficiently complete for calculation of its Fourier transform.

The Fourier transform of the velocity autocor-

relation function yields a frequency spectrum $f(\omega)$ which in the case of the harmonic solid is the frequency spectrum of the normal modes. The frequency spectrum for the silver subsystem is, by definition,

$$f(\omega) = (2/\pi) \int_0^\infty \Psi_{Ag^+}(t') \cos\omega t' \, dt', \tag{11}$$

where $f(\omega)$ is normalized to unity. $f(\omega)$ is where in Fig. 2(b). In principle, $f(\omega)$ can be measured by inelastic neutron scattering experiments.[17] A rough estimation of the position of the main peak of $\sigma(\omega)$ from $\varphi_{AgI}(t)$ leads to 81 cm^{-1}. The experimentally observed value[18] is 90 cm^{-1}.

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Jahn-Teller Effect in an Orbital Triplet Coupled to Both E_g and T_{2g} Modes of Vibration: Experimental Evidence for the Coexistence of Tetragonal and Trigonal Minima

Le Si Dang, R. Romestein, and Y. Merle d'Aubigné

Laboratoire de Spectrométrie Physique,* Université Scientifique et Médicale de Grenoble, 38041 Grenoble-Cédex, France

and

A. Fukuda

Tokyo Institute of Technology, Department of Textile and Polymeric Materials, Meguro-Ku, Tokyo 152, Japan

We have observed magnetic resonance in the $^3T_{1u}$ excited levels of Ga$^+$ in KBr using an optical detection technique. The A_T and A_X emissions take place from excited states which display tetragonal and trigonal symmetries respectively. A model assuming nearly equal linear coupling to E_g and T_{2g} modes and an additional bilinear coupling to totally symmetric modes, A_{1g}, accounts for the available data: magnetic resonance spectra, and temperature and pressure dependence of the optical spectra.

Characteristic phenomena caused by the Jahn-Teller effect have been observed in (KI:Tl$^+$)-type phosphors.[1] The luminescent center is of O_h symmetry in its ground state (s^2) and has simple unrelaxed excited states (sp): $^3T_{1u}$ and $^1T_{1u}$. Öpik

and Pryce[2] studied the linear Jahn-Teller effect in $^3T_{1u}$ and $^1T_{1u}$ states and concluded that either of the tetragonal or trigonal distortion, but not both, will occur. Actually, however, excitation of $^3T_{1u}$ through the A absorption band generally