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Density-functional approach for superionic conductors: effects of host-lattice deformations

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Abstract. By means of classical density-functional theory we study the density distribution of mobile Ag^+ ions in α -AgI-type superionic conductors, taking into account the thermal fluctuations in the anion host lattice. Our model is based on an expansion of the 'external' potential $v(\mathbf{r})$ acting on the cation-component up to second order in the displacements of anions, the latter being regarded as Einstein oscillators. Calculated density profiles are compared with molecular-dynamics simulations. For α -AgI the agreement is almost quantitative. In the case of β - Ag_2S the inclusion of anion vibrations leads to significant corrections in the temperature-dependent profiles.

1. Introduction

The quantitative understanding of structural and electrical properties of solid ionic conductors in terms of interionic forces is an important problem in both materials science and statistical physics, which has so far only been solved in special cases. Most of the previous studies are based on the molecular dynamics technique (for a review see for example Vashishta 1986, Gillan 1983). On the other hand, it has recently been shown that the equilibrium density distribution $\rho(\mathbf{r})$ of the diffusing component in certain superionic conductors can be calculated from interionic potentials in a rather simple way by means of density-functional methods (Roman and Dieterich 1986, Billi *et al* 1988). The physical interest in that quantity is due to the fact that it provides a certain link between structural and transport properties. In fact, knowledge of the distribution $\rho(\mathbf{r})$ implies information on conduction pathways and on effective potential barriers entering the transport process (Boughaleb and Ratner 1989, Thomas and Dieterich 1986). In those density-functional calculations it turned out that a second-order expansion of the contribution of interactions to the free energy functional with respect to density-inhomogeneities leads to an acceptable representation of the experimentally measured density-profiles. It also accounts for the increasing importance of Ag^+ - Ag^+ correlations in the series of BCC materials α -AgI, β - Ag_3SI and β - Ag_2S . That type of approximation has also been tested before (Roman and Dieterich 1985) by comparison with the exactly solvable case of an inhomogeneous one-dimensional fluid of hard-core particles (Percus 1976).

Density-functional investigations for α -AgI-type materials performed so far imply the assumption of a rigid anion cage, which reduces the problem to calculating the

cation density in the presence of a static cage potential with the symmetry of the lattice. In principle, however, applying that method to the coupled system of cations and anions in superionic conductors would require a two-component formulation. In this paper we pursue this direction and extend our previous treatment by including host lattice deformations in the simplest possible way. Since we are basically interested in high-temperature properties, i.e. in temperatures larger than the Debye temperature, we disregard any detailed lattice-dynamical aspects and simply represent the anions as Einstein oscillators. Clearly, the inclusion of anion displacements is closely related to the problem of screening within the inhomogeneous, correlated cation-fluid. In fact it turns out that a proper treatment of screening is crucial in obtaining even the correct order of magnitude of density changes due to cage-potential perturbations. By using a second-order expansion in the anionic displacements we obtain the density $\rho(\mathbf{r})$ in the form

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r})\left(1 + \frac{1}{2}\langle u_X^2 \rangle \Delta(\mathbf{r})\right) \quad (1)$$

where $\rho_0(\mathbf{r})$ is the result for a rigid anion cage. The quantity $\langle u_X^2 \rangle$ denotes the mean-square displacement of anions which is the only parameter of the present model. The function $\Delta(\mathbf{r})$ is calculated from the same interionic potentials that have been employed in previous molecular dynamics (MD) studies (Vashishta and Rahman 1978, Vashishta *et al* 1985) and also in our previous calculations of $\rho_0(\mathbf{r})$. It turns out that inclusion of host lattice deformations does improve the overall agreement of the calculated density profiles with MD studies, in particular with respect to their temperature dependence.

In section 2 we outline the method and describe some additional details of our previous work within the rigid lattice approximation. Then in section 3 we turn to the problem of a deformable lattice and derive the self-consistency equations for the first-order and second-order changes in density relative to $\rho_0(\mathbf{r})$. These are solved numerically for the case of α -AgI and β -Ag₂S. We conclude with some final comments in section 4.

2. Density-functional theory: rigid-lattice approximation

Let us consider a superionic conductor such as α -AgI. It is composed of two subsystems: the Ag⁺ ions which constitute the mobile component responsible for the high ionic conductivity of the system, and the I⁻ ions which form a BCC lattice structure. Early structural investigations of α -AgI by Strock *et al* (1934) have suggested that Ag⁺ ions are randomly distributed over some crystallographic locations in the unit cube as shown in figure 1. From more recent diffraction experiments Cava *et al* (1980) have determined the distribution of mobile ions in terms of the one-particle density $\rho(\mathbf{r})$ which is a periodic function with the periodicity of the lattice. Clearly, due to short-range repulsive forces, $\rho(\mathbf{r}) \rightarrow 0$ near an iodine ion. On the other hand, $\rho(\mathbf{r})$ is appreciably delocalized along certain channels, which are interpreted as the dominant conduction paths. These are the t-M-t and the t-C-t paths (see figure 1) in the cases of α -AgI and β -Ag₂S, respectively.

Let us now outline the calculation of the equilibrium density $\rho_0(\mathbf{r})$ of the fluid-like component under the assumption that host lattice ions are held fixed in their lattice positions. The problem is thus reduced to study the equilibrium properties

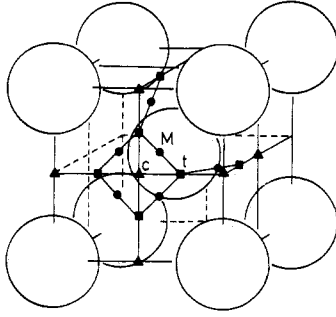


Figure 1. Structure of superionic α -AgI. The large circles are iodine ions in a BCC array. Two Ag^+ ions are distributed at random over 42 crystallographic locations in the unit cube: 12 t (tetrahedral) sites (■), 24 M (three-fold coordinated) sites (●), and 6 C (octahedral) sites (▲), (after Strook 1934). The Ag^+ ions preferentially occupy the t-sites where the potential energy attains its minimum.

of a non-uniform classical one-component fluid. This can be achieved within the classical version of density-functional theory (DFT), originally introduced to study the inhomogeneous electron gas (Hohenberg and Kohn 1964). The starting point of the classical DFT is the thermodynamic potential as a functional of the density $\rho(\mathbf{r})$ (Mermin 1965, Evans 1979, Baus 1987). For our purposes it is convenient to study the grand free-energy functional $\Omega[\rho]$,

$$\Omega[\rho] = \int d^3r v(\mathbf{r})\rho(\mathbf{r}) + F[\rho] - \mu \int d^3r \rho(\mathbf{r}) \quad (2)$$

where $v(\mathbf{r})$ is the external potential, $F[\rho]$ the free energy functional and μ the chemical potential. Within DFT, the equilibrium density $\rho(\mathbf{r})$ is obtained by minimising (2) with respect to ρ . At the minimum, Ω reduces to the grand potential and $F[\rho]$ coincides with the 'intrinsic' Helmholtz free energy of the system.

To proceed further we write $F[\rho]$ as

$$F[\rho] = \beta^{-1} \int d^3r \rho(\mathbf{r})(\log(\Lambda^3 \rho(\mathbf{r})) - 1) + \Phi_{\text{int}}[\rho] \quad (3)$$

where we have separated the ideal gas term from the interaction part $\Phi_{\text{int}}[\rho]$ of F . Here $\beta^{-1} = k_{\text{B}}T$ and $\Lambda = h/(2\pi m k_{\text{B}}T)^{1/2}$. The exact form of $\Phi_{\text{int}}[\rho]$ is not known in general and we need to resort to some approximation. To this end, we expand $\Phi_{\text{int}}[\rho]$ in powers of $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_{\text{R}}$, where ρ_{R} is the density of a uniform reference fluid. The value of ρ_{R} can be taken equal to the average density $\bar{\rho}$ of mobile ions in the unit cell, which is an input parameter of the theory. Keeping terms up to second order in $\Delta\rho$, the following approximate expression for $\Phi_{\text{int}}[\rho]$ is obtained (see e.g. Evans 1979),

$$\begin{aligned} \Phi_{\text{int}}[\rho] \simeq & \Phi_{\text{int}}[\bar{\rho}] + \int d^3r \Delta\rho(\mathbf{r}) \left(\frac{\delta\Phi_{\text{int}}[\rho]}{\delta\rho} \right)_{\bar{\rho}} - \frac{1}{2\beta} \iint d^3r d^3r' C_0(\mathbf{r} - \mathbf{r}', \bar{\rho}) \\ & \times \Delta\rho(\mathbf{r})\Delta\rho(\mathbf{r}') \end{aligned} \quad (4)$$

where

$$C_0(\mathbf{r} - \mathbf{r}', \bar{\rho}) = -\beta \left(\frac{\delta^2\Phi_{\text{int}}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \right)_{\bar{\rho}} \quad (5)$$

is the direct correlation function of the uniform reference fluid, which is assumed to be known. Using (2) and (3), the equilibrium density satisfies the exact equation

$$\log \rho(\mathbf{r}) = -\log \Lambda^3 + \beta(\mu - v(\mathbf{r})) - \beta \frac{\delta \Phi_{\text{int}}[\rho]}{\delta \rho}. \quad (6)$$

The last term in (6) can be evaluated with the help of (4). Thus,

$$\frac{\delta \Phi_{\text{int}}[\rho]}{\delta \rho} \simeq \left(\frac{\delta \Phi_{\text{int}}[\rho]}{\delta \rho} \right)_{\bar{\rho}} - \beta^{-1} \int d^3 r' C_0(\mathbf{r} - \mathbf{r}', \bar{\rho}) \Delta \rho(\mathbf{r}'). \quad (7)$$

Applying (6) to the uniform reference state with zero potential, we obtain

$$\left(\frac{\delta \Phi_{\text{int}}[\rho]}{\delta \rho} \right)_{\bar{\rho}} = \bar{\mu} - \beta^{-1} \log(\Lambda^3 \bar{\rho}) \quad (8)$$

where $\bar{\mu}$ is the chemical potential of the reference state. Now we insert (7) and (8) into (6) to obtain

$$\rho(\mathbf{r}) = \rho_0 \exp[-\beta v(\mathbf{r}) + \int d^3 r' C_0(\mathbf{r} - \mathbf{r}', \bar{\rho})(\rho(\mathbf{r}') - \bar{\rho})] \quad (9)$$

where $\rho_0 = \bar{\rho} \exp[\beta(\mu - \bar{\mu})]$. The value of $(\mu - \bar{\mu})$ can be obtained within the present theory by requiring that the average density determined from (9) be consistent with the input value $\bar{\rho}$.

Equation (9) is a non-linear integral equation for $\rho(\mathbf{r})$ which we solve self-consistently such that $\rho(\mathbf{r}) \rightarrow \bar{\rho}$, $\mu \rightarrow \bar{\mu}$ if $v(\mathbf{r}) \rightarrow 0$. Clearly, if $\beta|v(\mathbf{r})| \ll 1$ for all \mathbf{r} , then $\Delta \rho(\mathbf{r})$ is easily obtained from linear response theory. This, however, is not the case for a superionic conductor and the full non-linearity of (9) needs to be taken into account.

The range of validity of (9) in cases $\beta|v(\mathbf{r})| > 1$ has been tested against an exactly solvable model (Percus 1976) of a one-dimensional system of hard-core particles subject to a periodic potential (Roman and Dieterich 1985). There we have found that (9) works reasonably well even in cases of fairly large potential strengths. From this we conclude that (9) should almost quantitatively account for density variations in α -AgI-type ionic conductors at least in the regions of interest close to the conduction paths.

In order to solve for $\rho(\mathbf{r})$ we first transform the integral in (9) into a sum over reciprocal lattice vectors \mathbf{G} of the host-lattice. We thus have

$$\rho(\mathbf{r}) = \rho_0 \exp\left(-\beta v(\mathbf{r}) + \sum_{\mathbf{G} \neq 0} \rho_{\mathbf{G}} C_0(\mathbf{G}, \bar{\rho}) e^{i\mathbf{G} \cdot \mathbf{r}}\right) \quad (10)$$

with Fourier coefficients $\rho_{\mathbf{G}}$ of the density and the Fourier transform $C_0(\mathbf{k}, \bar{\rho})$ of the direct correlation function, evaluated at $\mathbf{k} = \mathbf{G}$. Note that the term $\mathbf{G} = 0$ does not appear in (10).

The lattice potential $v(\mathbf{r})$ is determined by the interaction between mobile and host-lattice ions. Assuming effective pairwise potentials and denoting by \mathbf{R}_k the lattice positions of counter ions X, we write

$$v(\mathbf{r}) = \sum_k V_{\text{AgX}}(|\mathbf{r} - \mathbf{R}_k|) \quad (11)$$

and

$$V_{\text{AgX}}(\mathbf{r}) = -Z_+ Z_X \frac{e^2}{r} + \frac{H_{+X}}{r^n} - \frac{1}{2}(\alpha_+ Z_X^2 + \alpha_X Z_+^2) \frac{e^2}{r^4}. \quad (12)$$

Here Z_+ , Z_X are effective ionic charges, $H_{+X} = A_X(\sigma_+ + \sigma_X)^n$ where A_X is a constant, σ_+ , σ_X are effective ionic diameters, and α_+ , α_X are effective polarizabilities of the ions. The units of length and energy are Å and $e^2 \text{Å}^{-1} = 14.4 \text{ eV}$, respectively. The Coulomb contribution in (11) is obtained using the Ewald method and requires the formal introduction of a neutralizing uniform background of positive charge. This positive background is however compensated by a negative uniform background required for the solution of the direct correlation function as discussed next.

We specify now the direct correlation function $C_0(\mathbf{r} - \mathbf{r}', \bar{\rho})$ to be used in (10). Since one expects the Coulomb interaction between Ag^+ ions to be the dominant one, we choose as a model for the uniform Ag^+ fluid the classical one-component plasma (COCP). The COCP is a system of identical point charges embedded in a rigid neutralizing background and is characterized by the dimensionless plasma parameter $\Gamma = \beta Z_+^2 e^2 / d$, where $d = (4\pi\bar{\rho}/3)^{-1/3}$. Analytical results for the direct correlation function of the COCP have been obtained within the rescaled mean spherical approximation (MSA) (Gillan 1974, see also Chaturvedi *et al* 1981). The MSA predictions for the structure of the COCP (e.g. the radial distribution function $g(r)$) agree well with computer simulation data at high values of Γ (> 10), where the strong Coulomb repulsion prevents particles from approaching each other closely. The plasma parameters corresponding to the superionic conductors $\alpha\text{-AgI}$ and $\beta\text{-Ag}_2\text{S}$ studied in this work fall in the high- Γ regime as displayed in table 1. We also note that for these Γ -values the effective hard core-diameter in the rescaled MSA is larger than the ionic diameter σ_+ , which a posteriori justifies the application of the COCP to the system of cations.

Table 1. Values of the input parameters used in the present work for $\alpha\text{-AgI}$ and $\beta\text{-Ag}_2\text{S}$. a denotes the lattice constant, T the temperature, s the number of Ag^+ ions in the unit cell and Γ the COCP parameter. For other parameters see equation (12). (Data for $\alpha\text{-AgI}$ from Vashishta and Rahman 1978, for $\beta\text{-Ag}_2\text{S}$ from Vashishta *et al* 1985.)

	AgI	Ag ₂ S
a (Å)	5.086	4.858
T (K)	430	464
s	2	4
Z_+	0.6	0.45
Z_X	0.6	0.9
σ_+ (Å)	0.63	0.61
σ_X (Å)	2.2	2.1
α_+ (Å ³)	0	0
α_X (Å ³)	6.52	6.52
n	7	7
A_X ($e^2 \text{Å}^{-1}$)	0.01231	0.01502
Γ	55.9	38.4

The next step towards the solution of (10) consists in using a simple and accurate parametrization of $\rho(\mathbf{r})$ for the purpose of evaluating its Fourier coefficients ρ_G . A useful representation of the density is in terms of Gaussians, centred at suitable positions in the unit cube, since in this case the Fourier coefficients can be calculated

analytically. The minimum number of Gaussians and their positions required to obtain an accurate representation of $\rho(\mathbf{r})$ can be deduced by studying the 'bare' density $\rho_B(\mathbf{r}) = \rho_0 \exp(-\beta v(\mathbf{r}))$, which provides input values for the Gaussian parameters. For α -AgI and β -Ag₂S we locate Gaussians at the t-, M- and C-sites (see figure 1). The amplitudes and widths of the Gaussians are readjusted at every iteration step, while their positions remain constant. On the contrary, in β -Ag₃SI, appreciable shifts of the t- and M-sites have to be taken into account (Billi *et al* 1988). The final solution for $\rho(\mathbf{r})$ is obtained by iterating (10) up to self-consistency.

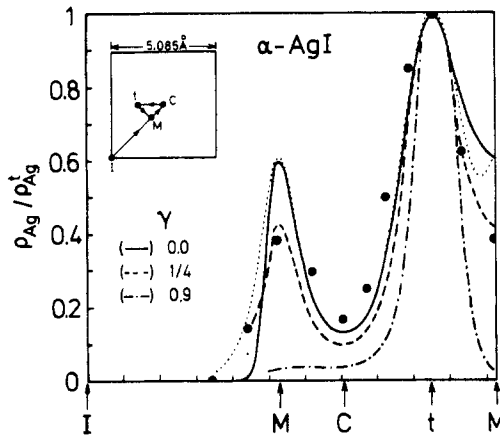


Figure 2. Density profile of Ag^+ ions in α -AgI at $T = 430$ K. The full curve corresponds to the density in the rigid lattice approximation obtained from (10), the dotted curve to its Gaussian representation and the points to molecular dynamics calculations of Vashishta and Rahman (1978). The path along which the density is calculated is shown in the inset. Corrections due to host lattice deformations (see section 3) are shown for different parameters γ . Broken curve, $\gamma = \frac{1}{4}$; chain curve, $\gamma = 0.9$.

Results for the density $\rho(\mathbf{r})$ of Ag^+ ions in α -AgI at $T = 430$ K are shown in figure 2, where we compare the density obtained from (10) (full curve) with the corresponding Gaussian approximation (dotted curve). These results show that the Gaussians provide a rather good representation of the density. Clearly, from figure 2, the maximum of $\rho(\mathbf{r})$ occurs at the t-sites, while the M-sites become saddle points and the C-sites points of local minima of $\rho(\mathbf{r})$. In other words, we find that the main Ag^+ -diffusion paths are along t-M-t channels where the density is largest. This is in perfect qualitative agreement with molecular dynamics simulations by Vashishta and Rahman (1978) and with experiments by Cava *et al* (1977). It should be emphasized that in α -AgI the final self-consistent density $\rho(\mathbf{r})$ does not differ significantly from the bare density $\rho_B(\mathbf{r})$ (Billi *et al* 1988). The situation is different for β -Ag₂S since there are four cations in the BCC unit cell and cation-cation correlations are expected to be more important than in α -AgI. Indeed, while the bare densities of both substances are quite similar, the Ag^+ - Ag^+ interactions in β -Ag₂S modify drastically the resulting density and lead to a new structure of the conduction paths (Roman and Dieterich 1986)—see also figure 5 later.

3. Effects of host-lattice deformations

So far we have described a density-functional theory for superionic conductors within the rigid lattice approximation. In reality, however, the positions of anions are subject to thermal fluctuations which are coupled to each other via pair-potentials V_{XX} and which are also coupled to the Ag^+ -motion. In order to gain some insight into this problem we study the effect of cage deformations on the equilibrium density $\rho(\mathbf{r})$ of mobile ions by expanding it up to second order in the anion displacements \mathbf{u}_k . To do this we consider a simplified model in which the anions are treated as Einstein oscillators.

Let us start from the expression for the one-particle distribution function which is written as

$$\rho(\mathbf{r}) = \frac{N!}{(N-1)! Z_N} \int d^3r_2 \cdots d^3r_N d^3u_1 \cdots d^3u_N \exp[-\beta V(\mathbf{r}_1, \dots, \mathbf{u}_N)] \quad (13)$$

where Z_N is the configurational integral and V the total potential energy of the system as function of cation positions \mathbf{r}_i and displacements \mathbf{u}_k of anions from their regular sites \mathbf{R}_k . In the case under consideration, the potential energy reads

$$V(\mathbf{r}_1, \dots, \mathbf{u}_N) = \sum_{i < j} V_{AgAg}(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{i,k} V_{AgX}(|\mathbf{r}_i - \mathbf{R}_k - \mathbf{u}_k|) + \sum_k \frac{\alpha}{2} \mathbf{u}_k^2. \quad (14)$$

The first term in (14) accounts for the interaction between Ag^+ ions and the second represents the Ag^+ -X interaction, see equation (12). The last term represents a local harmonic potential acting on the anions, where α is a parameter.

By using (14), equation (13) can be cast into the more convenient form:

$$\rho(\mathbf{r}) = \frac{1}{A} \int d^3u_1 \cdots d^3u_N \rho(\mathbf{r}, \mathbf{u}_1, \dots, \mathbf{u}_N) \exp\left(-\sum_{k=1}^N \frac{\beta \alpha \mathbf{u}_k^2}{2}\right) \quad (15)$$

where $A = (2\pi/\beta\alpha)^{3N/2}$ and $\rho(\mathbf{r}, \mathbf{u}_1, \dots, \mathbf{u}_N)$ denotes the density of cations for given displacements $\mathbf{u}_1, \dots, \mathbf{u}_N$. To solve (15) we consider a perturbation expansion of $\rho(\mathbf{r}, \mathbf{u}_1, \dots, \mathbf{u}_N)$ up to second order around its value for $\mathbf{u}_k = 0$, which is justified if α is sufficiently large

$$\rho(\mathbf{r}, \mathbf{u}_1, \dots, \mathbf{u}_N) \simeq \rho(\mathbf{r}, 0) + \sum_k \left(\frac{\partial \rho}{\partial \mathbf{u}_k}\right)_0 \cdot \mathbf{u}_k + \frac{1}{2} \sum_{k,l} \left(\frac{\partial^2 \rho}{\partial \mathbf{u}_k \partial \mathbf{u}_l}\right)_0 \mathbf{u}_k \mathbf{u}_l. \quad (16)$$

The derivatives in (16) can be computed from a corresponding expansion of (9). For the first and second derivatives of $\rho(\mathbf{r})$ we find

$$\left(\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_k}\right)_0 = \rho_0(\mathbf{r}) \left[(-\beta \nabla_{\mathbf{u}_k} V(\mathbf{r} - \mathbf{R}_k - \mathbf{u}_k))_0 + \int d^3r' C_0(\mathbf{r} - \mathbf{r}') \left(\frac{\partial \rho(\mathbf{r}')}{\partial \mathbf{u}_k}\right)_0 \right] \quad (17)$$

and

$$\begin{aligned} \left(\frac{\partial^2 \rho(\mathbf{r})}{\partial \mathbf{u}_k^2}\right)_0 &= \rho_0(\mathbf{r}) \left[\left(\frac{1}{\rho(\mathbf{r})} \frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_k}\right)_0^2 - [\beta \nabla_{\mathbf{u}_k}^2 V(\mathbf{r} - \mathbf{R}_k - \mathbf{u}_k)]_0 \right. \\ &\quad \left. + \int d^3r' C_0(\mathbf{r} - \mathbf{r}') \left(\frac{\partial^2 \rho(\mathbf{r}')}{\partial \mathbf{u}_k^2}\right)_0 \right] \end{aligned} \quad (18)$$

where $\rho_0(\mathbf{r}) = \rho(\mathbf{r}, 0)$ denotes the density for the rigid lattice case and $V \equiv V_{\text{AgX}}$.

Note that in these equations the unknown quantities $(\partial\rho/\partial\mathbf{u}_k)_0$ and $(\partial^2\rho/\partial\mathbf{u}_k^2)_0$ are still implicit and must be calculated self-consistently. Physically, the first term in (17) represents the unscreened linear response of the system to the external perturbation $v' = \beta\nabla_{\mathbf{u}_k}v$, while the second term accounts for the screening of v' due to Ag^+-Ag^+ correlations. Similarly, equation (18) can be regarded as the screened quadratic response to anion displacements. In the latter we have considered derivatives $(\partial^2\rho/\partial\mathbf{u}_k\partial\mathbf{u}_l)_0$ for $k=l$ since these are the only second-order terms which survive in (16) after integrating in (15). From that equation we now obtain

$$\rho(\mathbf{r}) \simeq \rho_0(\mathbf{r})(1 + \frac{1}{2}\langle u_{\mathbf{x}}^2 \rangle \Delta(\mathbf{r})) \quad (19)$$

with $\langle u_{\mathbf{x}}^2 \rangle = 3/\beta\alpha$ and

$$\Delta(\mathbf{r}) = \rho_0^{-1}(\mathbf{r}) \sum_k (\nabla_{\mathbf{u}_k}^2 \rho)_0. \quad (20)$$

Obviously, $\Delta(\mathbf{r})$ is periodic since the sum extends over all sites \mathbf{k} of the anion lattice.

Let us turn now to the problem of solving (17) and (18). Clearly, it is enough to consider only the displacement, along one given direction, of a *single* anion (thus keeping the others at their equilibrium positions), since host-lattice ions are assumed to vibrate isotropically and independently of each other. The complete expression (19) can be easily calculated from the solution of a single anion by straightforward symmetry considerations.

Next, it is convenient to write (17) and (18), respectively, as

$$f_1(\mathbf{r}) = \left(-\beta \frac{\partial}{\partial u_x} V(\mathbf{r} - \mathbf{u}_x) \right)_0 + \int d^3r' C_0(\mathbf{r} - \mathbf{r}') \rho_0(\mathbf{r}') f_1(\mathbf{r}') \quad (21)$$

and

$$f_2(\mathbf{r}) = (f_1(\mathbf{r}))^2 - \left(\beta \frac{\partial^2}{\partial u_x^2} V(\mathbf{r} - \mathbf{u}_x) \right)_0 + \int d^3r' C_0(\mathbf{r} - \mathbf{r}') \rho_0(\mathbf{r}') f_2(\mathbf{r}') \quad (22)$$

where $f_1(\mathbf{r}) = \rho_0(\mathbf{r})^{-1} \partial\rho/\partial u_x$ and $f_2(\mathbf{r}) = \rho_0(\mathbf{r})^{-1} \partial^2\rho/\partial u_x^2$. Here we have considered the displacement along the x direction of the anion at the origin ($\mathbf{R}_{\mathbf{k}} = 0$). Note that f_1, f_2 are *not* periodic. An approximate solution for f_1 and f_2 can be obtained by writing $\rho_0(\mathbf{r})$ in (21) and (22) as a sum of delta-functions, $\rho_0(\mathbf{r}) = \sum_{i=1}^N \rho_i \delta(\mathbf{r} - \mathbf{r}_i)$. The amplitudes ρ_i and positions \mathbf{r}_i can be deduced from the Gaussian representation of $\rho_0(\mathbf{r})$ in section 2. Thus (21) is transformed into a system of N linear equations with N unknowns, $f_1(\mathbf{r}_i)$. In a final step one uses the values of $f_1(\mathbf{r}_i)$ on the right-hand side of (21) to get $f_1(\mathbf{r})$ for arbitrary \mathbf{r} . The same procedure is then applied to solve (22) for $f_2(\mathbf{r})$.

3.1. Results for $\alpha\text{-AgI}$

We have solved (21) and (22) numerically for a BCC lattice with $(2 \times 2 \times 2)$ unit cubes, such that the iodine ion under consideration is surrounded by the 8 cubes. It turns out (see below) that such small system size suffices for our present purposes. Results for the first derivative of $\rho_0(\mathbf{r})$, equation (21), obtained for $\alpha\text{-AgI}$ at $T = 430$ K are plotted in figure 3. The broken curve represents the first term in (21), while the full curve

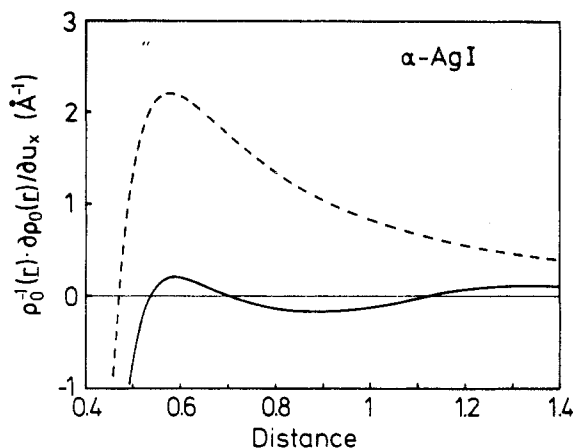


Figure 3. First derivative of the density $\rho(\mathbf{r})$ for α -AgI with respect to a displacement u_x of an iodine ion located as in figure 2. The broken curve is the bare force multiplied by β , $-\beta\partial v/\partial u_x$, and the full curve the self-consistent screened 'force' (equation (21)), plotted as a function of the distance from the iodine ion along the diagonal I-M-C-M-I.

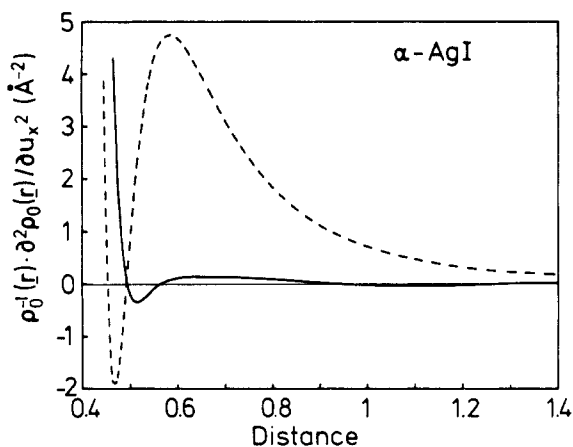


Figure 4. Same as in figure 3 for the second derivative of $\rho(\mathbf{r})$ with respect to u_x . The broken curve is the bare result, $(\beta\partial v/\partial u_x)^2 - \beta\partial^2 v/\partial u_x^2$, and the full curve the self-consistent result, equation (22).

gives the final self-consistent solution for $f_1(\mathbf{r})$. A drastic reduction of the external perturbation $-\beta\partial v/\partial u_x$ due to screening effects is evident. For small distances the short-range repulsion from the displaced iodine ion leads to a pronounced depletion in the Ag^+ density which is followed by an oscillatory behaviour at larger distances. The latter is reminiscent of the characteristic behaviour of the pair-correlation function between unlike ions in binary charged fluids (March and Tosi 1976).

Using these results for $f_1(\mathbf{r})$, we have obtained $f_2(\mathbf{r})$, equation (22), as shown in figure 4. Clearly, the unscreened result $f_2(\mathbf{r}) = (\beta\partial v/\partial u_x)^2 - \beta\partial^2 v/\partial u_x^2$ overestimates the effect of anion vibrations. Thus, the inclusion of correlations between fluid particles becomes essential in the calculation of lattice deformation effects on the density of Ag^+

ions. These results show, on the other hand, that $f_2(\mathbf{r})$ vanishes sufficiently fast with distance r from the iodine ion and justifies *a posteriori* the use of small system size.

The correction term in (19) is now obtained by a rapidly convergent summation over contributions from nearby anions. Figure 2 includes the final density for different choices of the anion mean-square displacement, which for convenience is written as $\langle u_I^2 \rangle = \gamma \langle u_I^2 \rangle_{\text{exp}}$. Here $\langle u_I^2 \rangle_{\text{exp}} = 0.099 \text{ \AA}^2$ denotes the experimental value deduced from measurements of the Debye-Waller factor by Cava *et al* (1977). The full curve $\gamma = 0$ corresponds to the rigid anion approximation discussed before. As seen from the figure, our model is not fully compatible with these experiments as it does not allow us to use $\gamma = 1$. In fact, away from the t-sites this choice would imply the correction in (1) to be of order unity, which is definitely outside the range of validity of the expansion (16). This shortcoming of our model may lie in our assumption of a local harmonic potential acting on I^- ions. This assumption is expected to introduce more severe constraints on the Ag^+ -distribution than one would have in the case of a complete lattice-dynamical model based on pair-wise forces. In our treatment we should therefore use $\langle u_I^2 \rangle < \langle u_I^2 \rangle_{\text{exp}}$. In fact, using $\gamma = \frac{1}{4}$ we obtain remarkable agreement with the MD studies by Vashishta and Rahman (1978). As is apparent from the figure, the lattice displacements tend to localize the Ag^+ fluid around the t-sites and suppress the densities near M and C. Essentially, this is because uncorrelated, spherically symmetric displacements will, on average, reduce the effective free space available for the Ag^+ ions, an effect which is larger near M and C than near t.

3.2. Results for $\beta\text{-Ag}_2\text{S}$

In a manner similar to that used for $\alpha\text{-AgI}$, we have solved (21) and (22) for $\beta\text{-Ag}_2\text{S}$ within $(2 \times 2 \times 2)$ unit cubes of the BCC lattice. This material is particularly interesting in the present context because experimental results at the Ag^+ -density at different temperatures are available.

Calculations of the function $\Delta(\mathbf{r})$ indicate that host-lattice displacements favour the Ag^+ -occupancy around the t-sites, where the density has its maximum, as found for $\alpha\text{-AgI}$. In contrast to $\alpha\text{-AgI}$, there is now a strong positive correction around the M-sites. Close to the C-sites $\Delta(\mathbf{r})$ remains negative.

The final density $\rho(\mathbf{r})$ in $\beta\text{-Ag}_2\text{S}$ is plotted in figure 5 for two different temperatures. While the density $\rho(\mathbf{r})$ in the case of a rigid lattice tends to display a relative maximum around a C-site, with a small dimple between the C-sites and t-sites, the corrected density shows instead a local minimum at C. This result is in qualitative agreement with molecular dynamics simulations (Vashishta *et al* 1985). It is apparent from figure 5(a), however, that already the density $\rho_0(\mathbf{r})$ calculated within the rigid lattice approximation overestimates the localization of Ag^+ ions around the t-sites, as compared with molecular dynamics simulations. This result cannot be improved by simply taking into account host-lattice ion vibrations as independent oscillators, since the density becomes more localized around the t-sites as explained above (subsection 3.1). Nonetheless, the present approximation has the merit that it modifies the rigid-lattice density $\rho_0(\mathbf{r})$ such that the correct local structure of $\rho(\mathbf{r})$ is obtained (see e.g. figure 5).

These local effects can be more accurately appreciated in figure 6 where we have plotted the normalized values of $\rho_i(T)/\rho_i(T_0)$, for $i = t, \text{M}$ and C , as a function of temperature. We see that already $\rho_0(\mathbf{r})$, for the rigid-lattice case, displays behaviours of $\rho_{\text{M}}(T)$ and $\rho_{\text{t}}(T)$ in qualitative agreement with molecular dynamics simulations (inset, figure 6). The quantity $\rho_{\text{C}}(T)$, however, shows an opposite trend compared

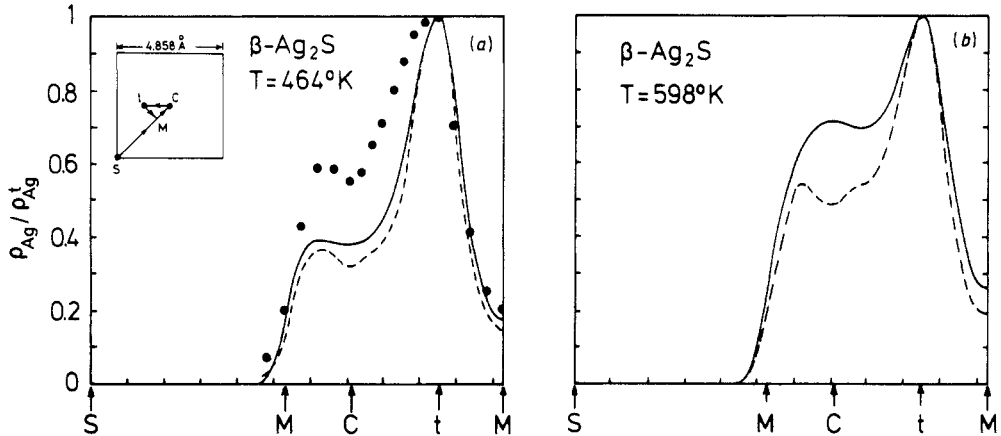


Figure 5. Density of Ag^+ ions in $\beta\text{-Ag}_2\text{S}$ at different temperatures with corrections due to host-lattice deformations, (a) $T = 464$ K and (b) 598 K. In both cases the full curves correspond to $\rho_0(\mathbf{r})(\gamma = 0)$ and the broken curves to $\rho(\mathbf{r})$ including deformation corrections with $\gamma = \frac{1}{4}$. The points in (a) are from molecular dynamics calculations of Vashishta *et al* (1985). Here we have used $\langle u_S^2 \rangle_{\text{exp}} = 0.054 \text{ \AA}^2$ for $T = 464$ K and 0.091 \AA^2 for $T = 598$ K, from Cava *et al* (1980). The path along which the density is calculated is shown in the inset of (a).

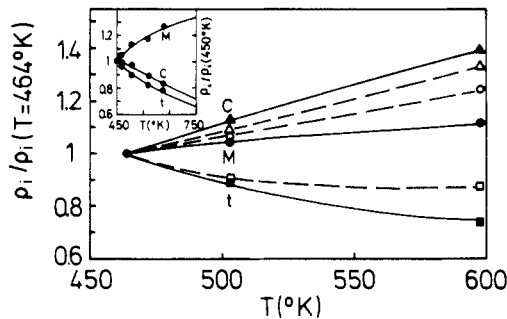


Figure 6. Temperature dependence of the normalized Ag^+ density in $\beta\text{-Ag}_2\text{S}$. Plotted values $\rho_i(T)/\rho_i(T_0)$ for $i = t$ (\blacksquare), M (\bullet) and C (\blacktriangle) with $T_0 = 464$ K. The full symbols are from $\rho_0(\mathbf{r})(\gamma = 0)$ and the open symbols for $\rho(\mathbf{r})$ with deformation corrections ($\gamma = \frac{1}{4}$). The curves are drawn as a guide. Inset: the molecular dynamics results of Vashishta *et al* (1985).

with the simulations. The inclusion of host-lattice vibrations improves the situation in the sense that its temperature dependence now becomes weaker. For $\rho_M(T)$ and $\rho_t(T)$ also a better agreement with the results of simulations is obtained after correcting for the host-lattice vibrations.

4. Summary and concluding remarks

In this work we use classical density-functional theory (CDFT) for calculating the one-particle density $\rho(\mathbf{r})$ of mobile ions in the superionic materials $\alpha\text{-AgI}$ and $\beta\text{-Ag}_2\text{S}$. In a first approximation, the counterions, which form a crystal structure, are assumed

to remain fixed at their lattice positions. Within this rigid-lattice approximation, the calculated density $\rho(\mathbf{r})$ of Ag^+ ions in α -AgI and β - Ag_2S is in good agreement with molecular dynamics simulations and experiments for temperatures close to the superionic transition temperature T_S . It should be emphasized that the CDFT allows us to describe quantitatively the effect of increasing the strength of $\text{Ag}^+ - \text{Ag}^+$ correlations in these systems. In the case of α -AgI, with two Ag^+ ions per unit cell, we find that $\text{Ag}^+ - \text{Ag}^+$ correlations do not play an important role in determining the density profile, and $\rho(\mathbf{r})$ is given essentially by the potential $v(\mathbf{r})$ due to the interaction between unlike ions. However, in β - Ag_2S where four Ag^+ ions per unit cell are present, the shape of $\rho(\mathbf{r})$ is qualitatively different from that obtained in α -AgI, although the bare potentials $v(\mathbf{r})$ are similar in both substances.

Although the rigid lattice approximation provides us with a simple and rather successful scheme to evaluate density profiles, its applicability appears to be limited to temperatures close to the transition temperature T_S . The reason for this is expected to be the increasing importance of host-lattice deformations as the temperature is raised. In order to take that aspect into account we treated a model where host-lattice ions are regarded as Einstein oscillators. Their mean-square displacement $\langle u_X^2 \rangle$ is treated as a parameter such that $\langle u_X^2 \rangle = \gamma \langle u_X^2 \rangle_{\text{exp}}$, where γ is a constant independent of temperature. The temperature dependence of the calculated density profiles turns out to be improved considerably as compared with the rigid lattice approximation. However, in order to obtain the desired overall magnitude of the correction term in (1), we have to choose $\gamma \simeq \frac{1}{4}$ which means that $\langle u_X^2 \rangle$ has to be taken considerably smaller than the experimental value $\langle u_X^2 \rangle_{\text{exp}}$. This deficiency may be due to our assumption of local restoring forces for the I^- ions, as discussed in subsection 3.1.

Nevertheless, one has to note that the unscreened response of the Ag^+ system to host lattice deformations would overestimate the function $\Delta(\mathbf{r})$ (see equation (1)) by an order of magnitude and would thus lead to unphysical results. A careful treatment of screening effects, as provided by the CFDT, see equations (21) and (22), is essential to obtain the correct order of magnitude of the relative density change $\frac{1}{2} \langle u_X^2 \rangle \Delta(\mathbf{r})$. In that respect our present approach is to be regarded as satisfactory.

The incorporation into the theory of the deformation effects discussed above produces the desired result for α -AgI, where the bare density $\rho_0(\mathbf{r})$ is too large as compared with experiments and molecular dynamics simulations. For β - Ag_2S the departure of the calculated $\rho(\mathbf{r})$ from the simulation results increases slightly. Nonetheless, the anion vibration effects considered here definitely reduce the discrepancy between theory and simulation even in β - Ag_2S when one looks at the local structure in $\rho(\mathbf{r})$ and at its temperature dependence.

The present simplified treatment of host-lattice deformations should be complemented by including a kind of feedback mechanism by which Ag^+ ions could react against the oscillations of host-lattice ions. The problem should then be treated as a two-component system in which the density of both components is obtained simultaneously from a CDFT, similarly as currently done for example in the theory of freezing of molten salts.

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