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Correlation and Spectral Properties of Individual Particles of Molecular Crystals with Isolated Point Imperfections

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The analogue of the dynamical equations for a crystal lattice is used to calculate the momenta time correlation functions and vibrational spectral densities of individual particles in heavy rare gas solids with defects. Some peculiarities in the behaviour of particles near a vacancy and light or heavy substitutional imperfections are discussed.

На основе аналога динамических уравнений кристаллической решетки вычислены временные корреляционные функции импульсов и спектральные плотности колебаний частиц в отвердевших благородных газах при наличии в них дефектов. Обсуждаются некоторые особенности в поведении частиц кристалла вблизи вакансии и легкой или тяжелой примеси замещения.

1. Introduction

Many important properties of solids are connected with the presence of defects in them. The distinctions in the dynamic behaviour of particles with respect to their distances from a defect were pointed out in the pioneer works of Lifshits [1, 2]. Defects violate the translational invariance of the crystal lattice and the collective behaviour of particles in a solid is manifested in their individual characteristics in different ways.

The time correlation functions (TCFs) and their Fourier transforms are the most important characteristics of the collective properties of a crystal. In case of a perfect crystal the momentum autocorrelation function (MACF) of a particle is the same for all particles of the crystal, and in the harmonic approximation its Fourier transform determines the spectral density of vibrations of the crystal. In the presence of imperfections the MACF contains information about the collective properties of the system and at the same time reflects individual peculiarities of the particle behaviour.

Methods of the statistical mechanics allow the localization of particles near the lattice points to be used effectively and simultaneously the nonlinearity of intermolecular interactions to be taken into account. The self-consistent phonon theory [3, 4] is an example of such an approach. Another statistical procedure based on the system of self-consistent integral equations for the conditional distribution functions [5] was proposed in [6, 7]. This procedure provides relatively easy consideration of both perfect and imperfect crystals [8, 9].

2. The Constitutive Equations

The problem of calculation of TCFs can be reduced to the investigation of the time behaviour of the special dynamical functions B_N determined in phase space of the

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system of N particles,

$$C(t) \equiv \langle A(0) B(t) \rangle = \int_{\Gamma_N} A(0) B_N(t) d\Gamma_N, \quad (1)$$

$$\frac{\partial B_N(t)}{\partial t} + iL_N B_N(t) = 0, \quad B_N(0) = B D_N^{(0)}. \quad (2)$$

Equation (1) defines the TCF of A and B which are functions of the dynamical variables (coordinates \mathbf{q} and momenta \mathbf{p} of particles of the system); Γ_N , L_N are the phase space and the Liouville operator of the system; $D_N^{(0)}$ is the equilibrium Gibbs distribution function; angular brackets $\langle \dots \rangle$ mean the equilibrium averaging.

The reduced dynamical functions

$$b_n = \int_{\Gamma_{N-n}} B_N d\Gamma_{N-n} \quad (3)$$

and the system of integro-differential equations for them can be then generated. Their representation in terms of special orthogonal polynomials (Hermitian polynomials in momentum space) and truncation at the lowest order results in a system of ordinary differential equations, which is formally the same as the equations of motion in the harmonic theory of the crystal lattice. In case of a perfect crystal the system of equations which defines the momentum TCFs has the form

$$\ddot{\hat{\varphi}}(i; t) + \omega^2 \hat{\varphi}(i; t) = \sum_{j \neq i} \hat{C}_{ij} \cdot \hat{\varphi}(j; t), \quad (4)$$

$$\hat{\varphi}(1; 0) = \hat{\mathbf{E}}, \quad \hat{\varphi}(i \neq 1; 0) = 0, \quad \dot{\hat{\varphi}}(i; 0) = 0, \quad (5)$$

$$\omega^2 = \frac{1}{3} \sum_{j \neq i} \hat{C}_{ij} : \hat{\mathbf{E}}, \quad \hat{C}_{ij} = \left\langle \frac{\partial^2 \Phi_{ij}}{\partial \mathbf{q}_i \partial \mathbf{q}_i} \right\rangle, \quad (6)$$

$$\hat{\varphi}(1; t) = \langle \mathbf{p}_1(0) \mathbf{p}_1(t) \rangle / \langle p^2 \rangle, \quad \hat{\varphi}(i; t) = \langle \mathbf{p}_1(0) \mathbf{p}_i(t) \rangle / \langle p^2 \rangle, \quad (7)$$

$\hat{\mathbf{E}}$ is a unit matrix. The contribution of the elder polynomials is discussed in [13].

The most essential distinction of these equations from those in the dynamical theory of the crystal lattice is that the analogue of the dynamical matrix \hat{C}_{ij} is defined by the mean value of the second derivative of the intermolecular potential Φ_{ij} . The conditional distribution functions [5] are used in (6) for averaging. So, the matrix \hat{C}_{ij} reflects the nonlinearity of the intermolecular potential and is a function of the thermodynamic parameters, the temperature T , and the volume V of the system.

Further, an isolated point defect is supposed to exist in the lattice point d . The tensor $\hat{C}_{id}^{(d)}$ characterizes the effective interaction between the defect and the particle of the matrix near the lattice point i . Indeed, its properties differ from those of \hat{C}_{ij} , which characterizes the interaction between the particles i and j of the matrix. The system of the constitutive equations has the form

$$\ddot{\hat{\varphi}}(i; t) + (\omega^2 \hat{\mathbf{E}} - \hat{C}_{id} + \hat{C}_{id}^{(d)}) \cdot \hat{\varphi}(i; t) = \sum_{j \neq i} \hat{C}_{ij} \cdot \hat{\varphi}(j; t); \quad i \neq d, \quad (8)$$

$$\ddot{\hat{\varphi}}(d; t) + \frac{m}{m_d} \omega_d^2 \hat{\varphi}(d; t) = \sum_{j \neq d} \hat{C}_{jd}^{(d)} \cdot \hat{\varphi}(j; t); \quad \omega_d^2 = \frac{1}{3} \sum_{j \neq d} \hat{C}_{jd}^{(d)} : \hat{\mathbf{E}}. \quad (9)$$

The symbol (*) at the sum in the right-hand side of (8) indicates that the summand at $j = d$ should be multiplied by the ratio m/m_d and \hat{C}_{id} should be replaced by $\hat{C}_{id}^{(d)}$ in it; m and m_d are masses of a matrix particle and the defect, respectively. If a vacancy appears as a defect ($d = v$), $\hat{C}_{iv}^{(d)} = 0$ and (9) should be omitted.

In order to receive the momentum TCFs, a particle of the matrix or the defect at time $t = 0$ is excited (see, e.g., (5)). Different TCFs (like (7)) can be received from time integration of the system (8), (9).

All the above equations are written in a dimensionless form. The mass m , the energy ε , and space σ parameters of a two-parameter intermolecular interaction potential (Lennard-Jones potential, for example) between particles of the matrix are chosen as the scale parameters. The time scale is defined as

$$\tau = \sigma \sqrt{\frac{m}{\varepsilon}}. \quad (10)$$

Integration with respect to time of equations (8), (9) could be performed without the use of the spectral representation, which is supposed to be a more natural way in the problem of calculating the TCFs. The methods of time integration for such systems were developed earlier [7]. The system (8), (9) is reduced to equations with respect to invariants of the tensors $\hat{\phi}$, and Verlet's algorithm [10] of the second order in time step is used. The presence of defects in a crystal makes the tensor $\langle \mathbf{p}_i \mathbf{p}_k \rangle$ asymmetrical, and this peculiarity should be taken into account when the tensors $\hat{\phi}$ are represented in terms of their invariants.

3. Results and Discussion

The results of computations of MACF are shown in Fig. 2 to 5. The Lennard-Jones potential was used, $T = \varepsilon/k_B$, $\nu = V/N = 0.98\sigma^3$. The time step was taken equal to 0.01τ . The frequencies are given in units of τ^{-1} . The appropriate tensors for second and fourth neighbours of the defect are represented by their diagonal elements in the system of principal axes. The axis n is directed to the defect, k lies in the plane (100), and l is perpendicular to n and k (Fig. 1). The k and l directions are not equivalent. In the k direction the particle has a nearest neighbour while in the l direction a second neighbour.

The results for the particle which is a nearest neighbour of a vacancy can be found in Fig. 2a (MACF) and b (its Fourier transform). The behaviour of components k and l is similar and resembles the behaviour of the MACF of a particle in a perfect crystal, especially in a not very large period of time (see [7, 11] for comparison). On the contrary the n -component shows some essential features, the most important of which are the disappearance of the first maximum and irregular rapid damping. In the spectrum of the n -component the high-frequency peak is absent and the low-frequency one becomes more pronounced (in comparison with the perfect crystal spectrum). Symbol Σ indicates the spectrum obtained as an average over n -, k -, and

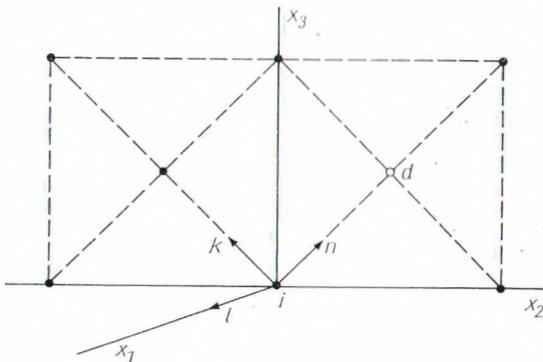


Fig. 1. The coordinate system; d defect, i its nearest neighbour

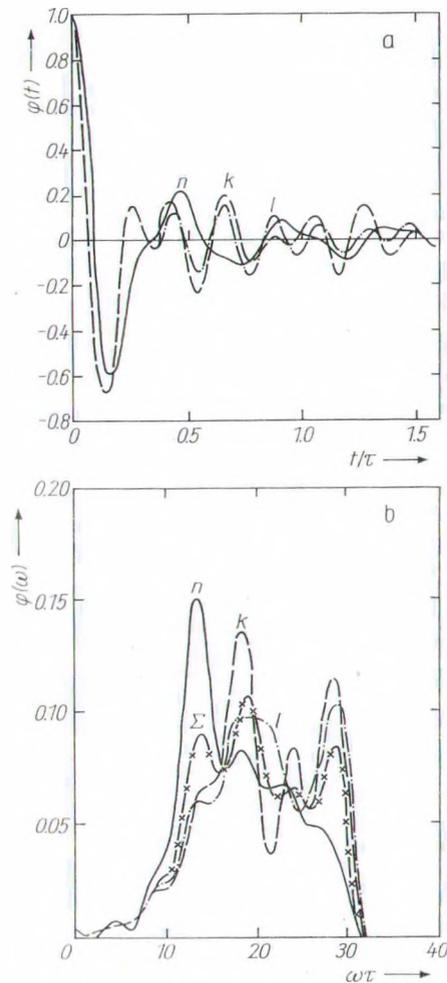


Fig. 2

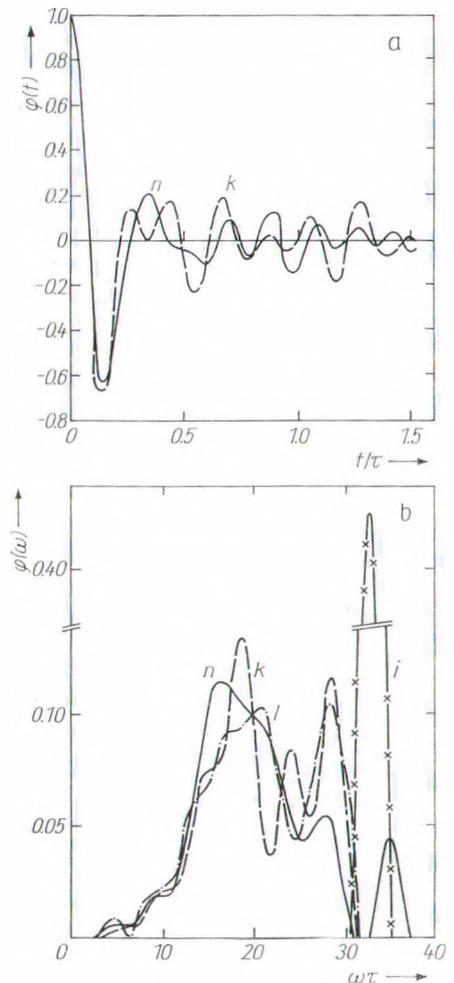


Fig. 3

Fig. 2. a) MAF and b) its Fourier transform for a nearest neighbour of a vacancy

Fig. 3. a) MAF and b) its Fourier transform for a nearest neighbour of a light substitutional imperfection

l-components. This spectrum has a rather poor structure which demonstrates an approximately uniform frequency distribution over a wide spectral range. One can notice the splitting of the low-frequency maximum into two peaks caused by interference of *n*- and *k*-, *l*-components. For the MAFs and their Fourier transforms of the fourth neighbour of a vacancy only some quantitative differences from those of a perfect crystal remain.

Similar peculiarities in the behaviour of the *n*-component of the MAF of a particle which is a nearest neighbour of a light substitutional imperfection can be found in Fig. 3a, b (^{40}Ar in the matrix of ^{86}Kr). In addition to these, there are local oscillations with frequencies beyond the major spectral range in the spectrum of the *n*-component in Fig. 3b. Their fraction is appreciably lower as compared with the imperfection

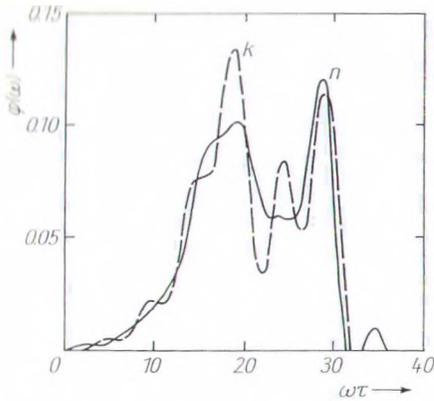


Fig. 4. Spectral density for a fourth neighbour of a light substitutional impurity

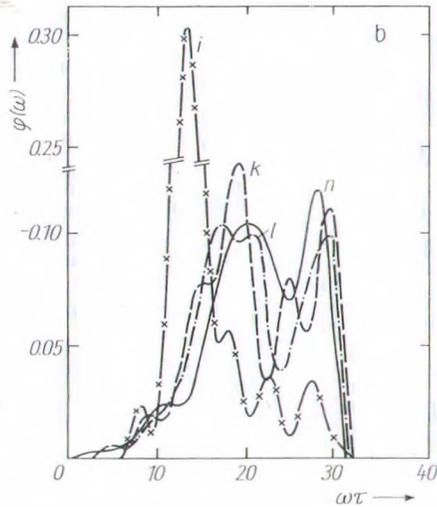
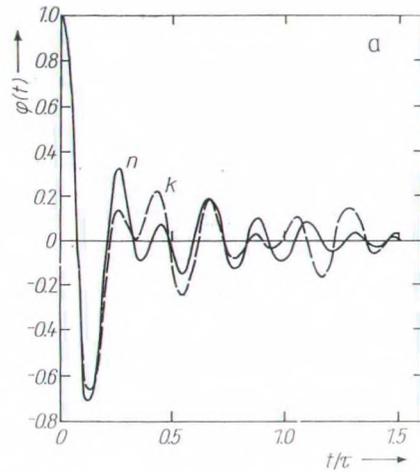


Fig. 5. a) MACF and b) its Fourier transform for a nearest neighbour of a heavy substitutional impurity

spectrum indicated by *i* in Fig. 3b, and it rapidly decreases with the particle distance from the defect (Fig. 4). It is useful to note that the drawings in Fig. 2b demonstrate the absence of the local frequencies in the spectrum of a crystal with isolated vacancies and this statement is in agreement with the recent publication [12].

In case of a heavy substitutional imperfections (Fig. 5, ^{86}Kr in the matrix of ^{40}Ar) the frequencies of a nearest neighbour of the defect are redistributed in the low-frequency range of the spectrum. There is no visible evidence for the quasiresonance frequencies in the spectrum, while the quasiresonance peak forms to a considerable extent the spectrum of the defect (curve *i* in Fig. 5b).

Some general properties in the behaviour of particles in the vicinity of a point defect could be noted. The TCFs decrease more rapidly than those in a perfect crystal. The most important dynamic characteristics of the defect manifest themselves, to a certain extent, in the behaviour of its neighbours. The influence of the defect strongly depends on the distance of the particle from the defect and becomes negligible after some lattice spacings.

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