

## Kinetic correlation effects in binary alloys

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We derive analytical expressions for the relaxation time of disordered binary alloys, which quantify the influence of correlations on the relaxation behavior of the concentration wave amplitudes within a linear kinetic theory. The main characteristic of our model is that it does not limit the effective radius of atomic interaction and correlations in the system. Lattice displacements caused by atomic size mismatch are naturally contained in the formalism. The results are applied to an ordering model system. Using two iterations of the recently developed correlation correction algorithm, we show that only a highly accurate correlation function allows one to predict the most stable modes of the fluctuation spectrum.

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Static properties of the fluctuation spectrum in binary system are readily accessible experimentally via the diffuse scattering of x-rays or neutrons as well as theoretically via first-principles calculations. It is more challenging to describe experimentally observed kinetic properties such as the lifetime of the fluctuations,<sup>1</sup> transient structures,<sup>2</sup> and ordering and decomposition processes.<sup>3-9</sup> Kinetic properties are also accessible by simulations techniques, such as Monte Carlo.<sup>10,11</sup> Nevertheless, qualitative trends can be deduced from discrete kinetic theories.<sup>3,8,12,13</sup> However, microscopic analytical approaches involve assumptions for the free energy, which is the key quantity in these theories. The simplest approximation for the free energy is the mean-field approximation which does in general not describe the fluctuation spectrum of real systems. In the present Brief Report, we overcome this problem by calculating the free energy with our recently developed correlation correction algorithm (CCA) and applying it within a linear  $k$ -space kinetic theory. This accurate and rapidly converging iterative algorithm allows us to derive quantitative expressions for the lifetime of the fluctuations in a binary crystalline system  $A$ - $B$ . As a case study, we investigate in detail the relaxation behavior of the fluctuations in a model ordering system.<sup>14</sup>

In the following, we consider the redistribution of the  $A$  atoms. The nonequilibrium single-site probability to find an  $A$  atom on the lattice site  $\mathbf{R}$  at time  $t$  is denoted as  $P_{\mathbf{R}}(t)$ . The probability to find an atom of type  $B$  is then given by the conservation requirement,

$$c = \frac{1}{N} \sum_{\mathbf{R}} P_{\mathbf{R}}, \quad (1)$$

where  $c$  denotes the concentration of  $A$  atoms. During the thermally activated redistribution of atoms over the lattice sites of the crystal, the Onsager equation for the diffusive relaxation of the nonequilibrium single-site probabilities is given by<sup>3-5,15</sup>

$$\frac{dP_{\mathbf{R}}(t)}{dt} = \sum_{\mathbf{R}'} \frac{L_{\mathbf{R}-\mathbf{R}'}}{k_B T} c(1-c) \frac{\delta \tilde{F}}{\delta P_{\mathbf{R}'}(t)}, \quad (2)$$

where the kinetic coefficient  $L_{\mathbf{R}-\mathbf{R}'}$  denotes the probability for an atomic jump from the position  $\mathbf{R}$  to the position  $\mathbf{R}'$

per time unit. The summation in Eq. (2) is carried out over all sites of the alloy.

$\frac{\delta \tilde{F}}{\delta P_{\mathbf{R}'}(t)}$  denotes a thermodynamic force, which drives the system towards thermodynamic equilibrium.

In the following, we assume that the alloy is in the disordered state with remaining short-range order correlations. Introducing the Fourier transforms,

$$P_{\mathbf{R}} = c + \sum_{\mathbf{k}} \delta P_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}} \quad (3)$$

and

$$L_{\mathbf{R}} = N^{-1} \sum_{\mathbf{k}} L_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}}, \quad (4)$$

we derive from Eq. (2) the linearized  $\mathbf{k}$ -space kinetic equation,

$$\frac{d\delta P_{\mathbf{k}}(t)}{dt} = \frac{L_{\mathbf{k}}}{k_B T N} c(1-c) \frac{\delta^2 \tilde{F}}{\delta P_{\mathbf{k}} \delta P_{-\mathbf{k}}} \delta P_{\mathbf{k}}(t). \quad (5)$$

The solution can be written in the form

$$\delta P_{\mathbf{k}}(t) = \delta P_{\mathbf{k}}(0) \exp\left(-\frac{t}{\tau_{\mathbf{k}}}\right), \quad (6)$$

where  $\delta P_{\mathbf{k}}(0)$  is defined by the initial conditions at  $t=0$ , and the relaxation time  $\tau_{\mathbf{k}}$  given by

$$\tau_{\mathbf{k}} = -\frac{\varepsilon_{\mathbf{k}}}{c(1-c)L_{\mathbf{k}}}. \quad (7)$$

The quantity  $\varepsilon_{\mathbf{k}}$  has the exact form of a correlation function,<sup>5,6,15</sup>

$$\varepsilon_{\mathbf{k}} = k_B T N \left( \frac{\partial^2 F_{fl}}{\partial \delta P_{\mathbf{k}} \partial \delta P_{-\mathbf{k}} \big|_{\{\delta P_{\mathbf{k}}\}=0}} \right)^{-1}, \quad (8)$$

and introduces a dispersion to the relaxation time  $\tau_{\mathbf{k}}$ . The kinetic coefficients  $L_{\mathbf{k}}$  read<sup>15</sup>

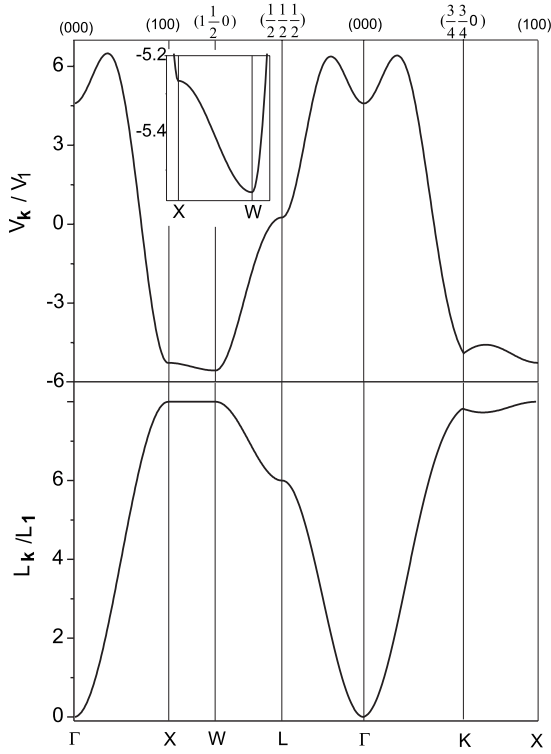


FIG. 1.  $V_{\mathbf{k}}/|V_1|$  and  $L_{\mathbf{k}}/L_1$  as a function of the wave vector along a number of high-symmetry directions in the first Brillouin zone.

$$L_{\mathbf{k}} = - \sum_{\rho} \sum_{\mathbf{R}_{\rho}} L_{\mathbf{R}_{\rho}} (1 - e^{-i\mathbf{k}\mathbf{R}_{\rho}}) = -2 \sum_{\rho} \sum_{\mathbf{R}_{\rho}} L_{\mathbf{R}_{\rho}} \sin^2 \frac{1}{2} \mathbf{k}\mathbf{R}_{\rho}, \quad (9)$$

where the summation is carried over coordination shells  $\rho = 1, 2, \dots$  and vectors  $\mathbf{R}_{\rho}$  for each coordination shell.

The value  $L_{\mathbf{R}_1}$  in the first coordination shell can be extracted from experimental diffusion coefficients.<sup>15</sup> Taking into account only the first coordination shell, the kinetic coefficient can then be rewritten as

$$L_{\mathbf{k}} = -2L_1 \sum_{\mathbf{R}_1} \sin^2 \frac{1}{2} \mathbf{k}\mathbf{R}_1, \quad (10)$$

where  $\mathbf{R}_1$  denotes the lattice sites in the first coordination shell.

It follows directly from Eq. (7), that  $\tau_{\mathbf{k}}$  is increasing for stronger correlations  $\varepsilon_{\mathbf{k}}$  in the system, i.e., strong short-range order correlations slow down the relaxation process. The accuracy of the calculated relaxation time depends crucially on the exact knowledge of the correlation function. It is therefore mandatory to determine the dispersion of the correlation function by the most accurate model.

In the following, we employ the recently developed CCA<sup>16,17</sup> for the calculation of the correlation function, which provides, in particular, accurate analytic expressions for the correlation function. Starting with a mean-field expression for the free energy, which implies a Gaussian distribution of the fluctuation amplitudes, the CCA allows us to calculate corrections to the correlation function  $\varepsilon_{\mathbf{k}}$  using an exact thermodynamic integration for the correlation correction to the free energy. Applying this scheme iteratively, we have shown that the correlation function  $\varepsilon_{\mathbf{k}}$  converges rapidly and exhibits high numerical accuracy over wide temperature and concentration intervals.<sup>16,17</sup>

Within the first iteration of the CCA, the relaxation time is given by Eqs. (7) and (10),

$$\tau_{\mathbf{k}}^{(1)} = \left[ 2L_1 \sum_{\mathbf{R}_1} \sin^2 \frac{1}{2} \mathbf{k}\mathbf{R}_1 \right]^{-1} \times \left[ 1 + (V_{\mathbf{k}} + \lambda) \frac{c(1-c)}{k_B T} \right]^{-1}, \quad (11)$$

where the explicit form of the correlation function  $\varepsilon_{\mathbf{k}}^{(1)}$  has been taken from Eq. (54) in Ref. 17, where  $V_{\mathbf{k}}$  denotes the Fourier components of the atomic interactions. The atomic interactions contain both the chemical and the strain-induced parts of the interactions.<sup>15,18</sup> The actual value of the Lagrangian multiplier  $\lambda$  is obtained numerically from the normalization condition

$$N^{-1} \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} = c(1-c), \quad (12)$$

resulting in

$$\frac{1}{N} \sum_{\mathbf{k}} \frac{1}{1 + \frac{c(1-c)}{k_B T} (V_{\mathbf{k}} + \lambda)} = 1, \quad (13)$$

which holds even in the presence of atomic jumps. For  $\lambda = 0$ , we recover the Krivoglaz-Clapp-Moss expression.<sup>3-5</sup>

Within the more accurate second iteration of the CCA, the relaxation time defined by Eq. (7) can be written in the form

$$\tau_{\mathbf{k}}^{(2)} = \left[ 2L_1 \sum_{\mathbf{R}_1} \sin^2 \frac{1}{2} \mathbf{k}\mathbf{R}_1 \right]^{-1} \left\{ 1 + (V_{\mathbf{k}} + \lambda) \frac{c(1-c)}{k_B T} - \frac{c(1-c)}{k_B T N} \sum_{\mathbf{q}} \left[ \frac{V_{\mathbf{q}} + \lambda}{1 + \frac{c(1-c)(V_{\mathbf{q}} + \lambda)}{k_B T}} \right] \right. \\ \left. - \frac{(1-2c)^2 c(1-c)}{2(k_B T)^2 N} \sum_{\mathbf{q}} \left[ \frac{(V_{\mathbf{q}} + \lambda)(V_{\mathbf{k}-\mathbf{q}} + \lambda)}{1 + \frac{c(1-c)(V_{\mathbf{q}} + \lambda)}{k_B T}} \right] \left[ \frac{1}{1 + \frac{c(1-c)(V_{\mathbf{k}-\mathbf{q}} + \lambda)}{k_B T}} \right] \right\}^{-1}, \quad (14)$$

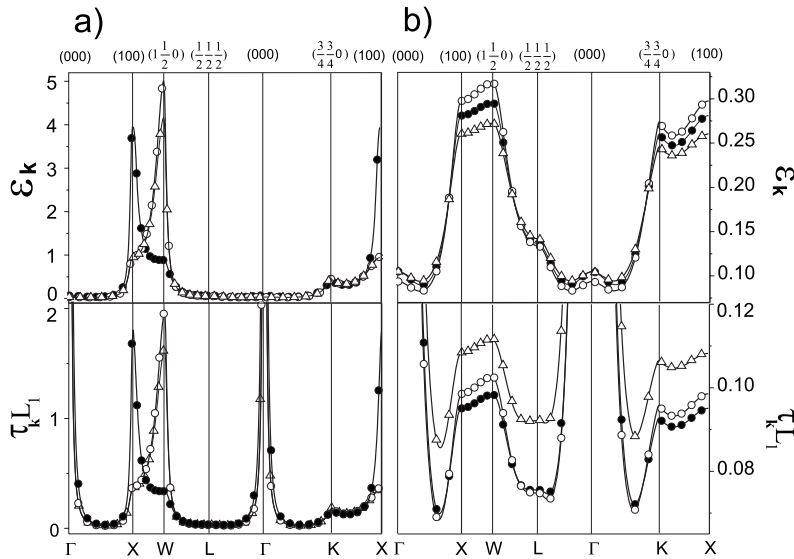


FIG. 2. Correlation function  $\epsilon_{\mathbf{k}}$  and relaxation time  $\tau_{\mathbf{k}}L_1$  as a function of the wave vector along a number of high-symmetry directions in the first Brillouin zone close to the spinodal temperature, (a) at  $T \approx 1.1T_{sp}$  and (b) at  $T \approx 2T_{sp}$ . The results of the first (open circles) and second iteration (filled circles) of the CCA are compared to the Krivoglaz-Clapp-Moss approximation (triangles).

which is the key result of this study. Here the correlation function  $\epsilon_{\mathbf{k}}^{(2)}$  has been taken from Eqs. (77), (78), and (75) in Ref. 17. The Lagrangian multiplier is obtained from the same normalization condition [Eq. (12)] applied to the correlation function  $\epsilon_{\mathbf{k}}^{(2)}$ .

The relaxation time obtained in the second iteration is determined not only by the interatomic interactions with the dominant wave vector  $\mathbf{k}$  but also by all the other modes with the wave vectors  $\mathbf{q}$ , which contribute to the value of the correlation function  $\epsilon_{\mathbf{k}}^{(2)}$ .

In many cases, the wave vector which denotes the maximum of the correlation function  $\epsilon_{\mathbf{k}}$  coincides with the wave vector for which the atomic interactions  $V_{\mathbf{k}}$  exhibit a minimum. Nevertheless, in general, these two vectors can be different<sup>14,19</sup> which directly affects the relaxation time.

In order to numerically investigate the possibility of such effects, we consider a model alloy with normalized atomic interactions in five coordination shells  $V_1=1$ ,  $V_2=-0.255$ ,  $V_3=-0.188$ ,  $V_4=-0.106$ , and  $V_5=-0.004$  in a face centered

cubic crystal lattice.<sup>19</sup> These particular atomic interaction coefficients specify an ordering system.

In Fig. 1, we show the form of the functions  $V_{\mathbf{k}}/|V_1|$  and  $L_{\mathbf{k}}/L_1$  ( $L_1$ —kinetic coefficient in the first coordination shell) in a reduced Brillouin zone scheme at fixed concentration  $c$

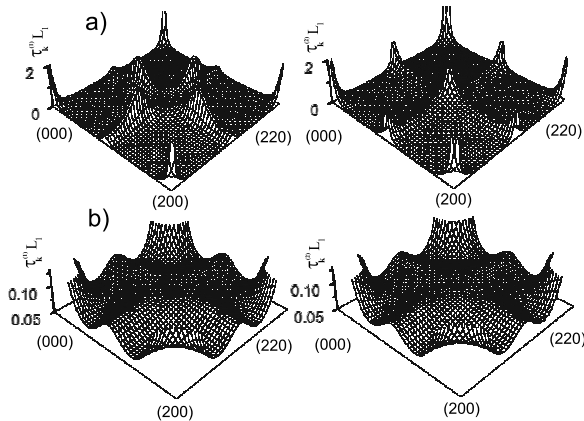


FIG. 3.  $\tau_{\mathbf{k}}^{(1,2)}L_1$  in the  $(hk0)$  plane close to the phase transition temperature (a) at  $T \approx 1.1T_{sp}$  and (b) at  $T \approx 2T_{sp}$ .

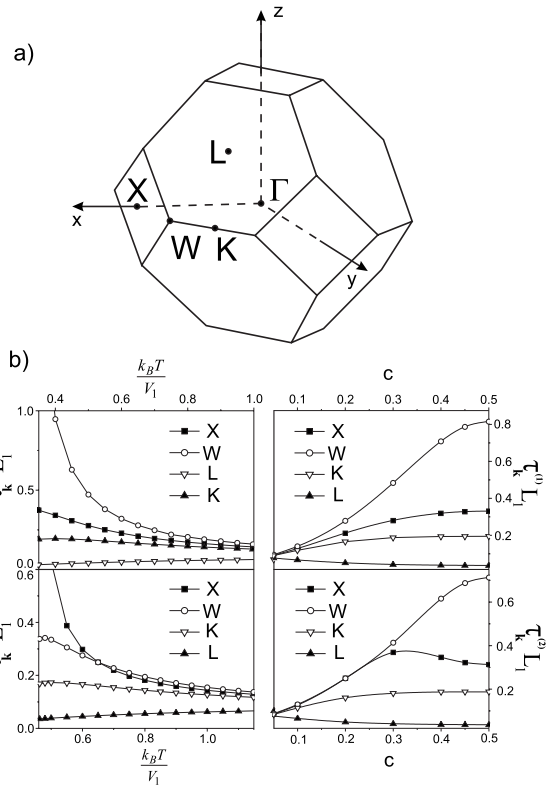


FIG. 4. (a) Sketch of the first Brillouin zone, indicating all high-symmetry points. (b)  $\tau_{\mathbf{k}}^{(1,2)}L_1$  as a function of temperature ( $c=0.2$ ) and concentration ( $T \approx 1.1T_{sp}$ ) in the high-symmetry points  $X(001)$ ,  $W(1/2, 1, 0)$ ,  $L(1/2, 1/2, 1/2)$ , and  $K(3/4, 3/4, 0)$  of the first Brillouin zone

$=0.2$ . Regions in  $\mathbf{k}$  space where  $V_{\mathbf{k}}/|V_1|$  is large correspond to regions where  $L_{\mathbf{k}}/L_1$  is small. This implies that the relaxation time favors a dominant mode of the short-range order correlations. The full dispersion of the relaxation time is, of course, also affected by the dispersion of the kinetic coefficient, which is most pronounced in the vicinity of the  $\Gamma$  point.

According to Eq. (7) and taking into account atomic jumps in the first coordination shell only ( $L_1 > 0$ ,  $L_s = 0$ ,  $s \geq 2$ ), we calculated the dispersion of the relaxation time  $\tau_{\mathbf{k}}L_1$  within the first and the second iteration of the CCA.

Numerical results along the high-symmetry directions for the correlation function  $\varepsilon_{\mathbf{k}}$  and for the relaxation time  $\tau_{\mathbf{k}}L_1$  are shown in Fig. 2 at  $T \approx 1.1T_{sp}$  ( $T_{sp} = 0.347|V_1|/k_B$  for the first iteration,  $T_{sp} = 0.463|V_1|/k_B$  for the second iteration of the CCA, and  $T_{sp} = 0.903|V_1|/k_B$  for the Krivoglaz-Clapp-Moss approximation of the correlation function) and  $T \approx 2T_{sp}$ .

The correlation functions exhibit distinct maxima within the Brillouin zone. It is interesting to note that the position of the maximum in the correlation function shifts from the  $W$  point in the first iteration to the  $X$  point in the second iteration, implying a shift of the most stable mode in the correlation function.<sup>20</sup> The relaxation time peaks very strongly at the  $\Gamma$  point, which implies that the fully separated  $A$  and  $B$  crystals have the longest lifetime. The interplay of the dispersion of both the kinetic coefficient and the correlation function gives rise to a strongly decreased lifetime of the fluctuations with wave vectors around the  $\Gamma$  point (see the minimum between the  $\Gamma$  and the  $X$  point in Fig. 2). Numerical results for the relaxation time  $\tau_{\mathbf{k}}^{(1,2)}L_1$  in the  $(hk0)$  plane are shown in Fig. 3.

In the first iteration, the minimum position of the function  $V_{\mathbf{k}}$  coincides with the maximum position of  $\tau_{\mathbf{k}}^{(1)}L_1$  at the  $W$

point close at  $T \approx 1.1T_{sp}$ , while the second iteration shifts the maximum position of  $\tau_{\mathbf{k}}^{(2)}L_1$  to the  $X$  point. This shift disappears at higher temperatures ( $T \approx 2T_{sp}$ ).

Using Eqs. (11) and (14), it is now possible to analyze the temperature and concentration dependence of the relaxation time of the most stable modes in the correlation function in more detail. Figure 4 shows the results for four different high symmetry modes in the first and second iterations. In the first iteration,  $\tau_{\mathbf{k}}^{(1)}L_1$  is a monotonous function of temperature and concentration. In the more accurate second iteration, the scenario is changed. The most stable mode in the correlation function changes from the  $X$  point at low temperature to the  $W$  point at high temperature. In addition,  $\tau_{\mathbf{k}}^{(2)}L_1$  shows a non-monotonous concentration behavior at the high-symmetry point  $W$ . Such intricate details of the relaxation behavior of the concentration waves, i.e., the fluctuations in the system, are accessible only with a detailed and accurate knowledge of the correlation function  $\varepsilon_{\mathbf{k}}$ . In our scheme,  $\varepsilon_{\mathbf{k}}$  is provided by the CCA, which has been shown to converge within two iterations. The second iteration gives a full and accurate account of the dispersion law of the fluctuations in agreement with calculations within the cluster variation method and Monte Carlo simulations.<sup>17,20</sup> Our results also demonstrate that a simple mean-field model cannot predict correctly the fluctuations with the longest lifetime, i.e., the most stable modes in the fluctuation spectrum.

The lifetime of atomic scale fluctuations can be accessed by x-ray photon correlation spectroscopy.<sup>21</sup> The flux of coherent photons from current synchrotron x-ray sources is, however, not sufficient to measure the lifetime of atomic scale fluctuation. With the advent of the next generation high brilliance synchrotron radiation sources, such as PETRA III (DESY, Hamburg), these measurements can be performed readily.

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