# Comparison between molecular dynamics and Monte Carlo simulations of an ordering process in a binary alloy

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Ordering in a binary alloy is studied by means of a molecular-dynamics (MD) algorithm which allows to reach the domain growth regime. Results are compared with Monte Carlo simulations using a realistic vacancy-atom (MC-VA) mechanism. At low temperatures fast growth with a dynamical exponent $x>1/2$ is found for MD and MC-VA. The study of a nonequilibrium ordering process with the two methods shows the importance of the nonhomogeneity of the excitations in the system for determining its macroscopic kinetics. [S0163-1829(99)05717-3]

In the study of out of equilibrium relaxation phenomena two processes are considered as prototypes. Both correspond to the evolution of a solid $AB$ binary alloy quenched from a high-temperature disordered phase to a temperature below a phase transition. The first case is the growth of ordered domains [nonconserved order parameter (NCOP)] and the second is the phase separation problem [conserved order parameter (COP)]. There is general agreement,[1] in the fact, that in both cases the mean size of the domains $R$ grows, during the late stages of the evolution, following a power law. Such laws $[R(t)\sim t^x]$ are characterized by the growth exponent $x$ that takes the value $x_{\mathrm{NCOP}}=1/2$ (Allen-Cahn law[2]) for the nonconserved case and $x_{\mathrm{COP}}=1/3$ (Lifshitz-Slyozov law[3]) for the conserved case. These values are considered to be universal. They have been corroborated by theoretical arguments, numerical analysis of Langevin equations and Monte Carlo (MC) simulations of lattice systems.[1] In this report we focus on the NCOP case.

The MC simulation of relaxation processes is based on the hypothesis that the evolution of the system can be described by a master equation characterized by a transition probability matrix $\mathcal{W}(\zeta\rightarrow\eta)$ joining two microstates of the system.[4] This matrix should fulfill a global balance condition in order to ensure the evolution towards equilibrium. The transition probability matrix is generally split (Metropolis algorithm) into two probability matrices $\mathcal{W}(\zeta\rightarrow\eta)=\mathcal{P}(\zeta\rightarrow\eta)\times\mathcal{A}(\zeta\rightarrow\eta)$: a proposal probability matrix $\mathcal{P}(\zeta\rightarrow\eta)$ and an acceptation probability matrix $\mathcal{A}(\zeta\rightarrow\eta)$. Requiring that $\mathcal{A}$ fulfills a detailed balance and $\mathcal{P}$ is symmetric $[\mathcal{P}(\zeta\rightarrow\eta)=\mathcal{P}(\eta\rightarrow\zeta)]$ is enough to warrant the global balance conditions. Most nonequilibrium MC simulations of ordering processes in alloys have been carried out using coarse-grained lattice models. The atomic species $A$ and $B$ are represented by pseudospin variables $S_i=\pm 1$ on a rigid lattice. The concentration of the two species is kept fixed and the interaction between the atoms is modeled by an Ising Hamiltonian $H=J\Sigma_{ij}S_iS_j$, where the sum extends over all nearest-neigbors (NN) pairs and $J>0$ is the interaction energy. Usually $J$ is considered to be the unit of energy. Standard simulations use the atom-atom exchange dynamics (MC-AA), with a proposal probability $\mathcal{P}(\zeta\rightarrow\eta)$ consisting in the trial of neighboring atom-atom exchanges homogeneously on the lattice, and a standard acceptation probability like $\mathcal{A}(\zeta\rightarrow\eta)=\min(1,\exp-\Delta H/k_BT)$ where $T$ is the temperature, $k_B$ is Boltzmann's constant, and $\Delta H$ is the energy difference between the states $\eta$ and $\zeta$. For a lattice with $N$ sites, the time unit called a MC step (mcs), is defined as $N$ proposals of atom-atom exchanges, independently of its acceptation ratio. Such a definition is based on the assumption that a system out of equilibrium, in contact with a heat bath, is excited (exchange proposals) with a rate constant in time and homogeneous in space. These standard simulations lead, for the NCOP case and in the absence of defects, to $x=0.5$.[5]

Recently the more realistic vacancy-atom exchange dynamics (MC-VA) has been proposed for the study of such growth processes:[6–11] a very small amount of vacancies is introduced in the system, almost not affecting its equilibrium properties. For such a low concentration of vacancies the system can still be modeled by an Ising Hamiltonian with $S_i=\{-1,0,1\}$ representing $A$ atoms, vacancies, or $B$ atoms, respectively. Only neighboring atom-vacancy exchanges are proposed and accepted according to a standard $\mathcal{A}$ matrix. Vacancies are allowed to ''jump'' to NN positions but a small amount of vacancy jumps to next-nearest neighbors (NNN) positions is needed in order to prevent trapping phenomena.[7] A parameter $Q$ (the fraction of proposed jumps to NN) characterizes the vacancy mobility. The time unit (mcs) is also defined as $N$ vacancy jump proposals, which now turn out to be *inhomogeneously* distributed since the vacancy walks are highly correlated with the current order existing in the system.[7] For the case of NCOP it is well established that the MC-VA algorithm increases the growth exponent towards a value $x>1/2$.[7,8] Its exact value is not universal but depends on the system dimensionality and temperature. The physical reason for this acceleration is that the vacancies stay most of the time on the interfacial regions, avoiding the already ordered bulk. The inclusion of this mechanism in the Allen-Cahn theory renders a large growth exponent.[11] The exponent decreases towards the value 1/2 for temperatures approaching the critical ordering temperature $T_c$ since fluctuations make the vacancy paths more and more homogeneous.

 

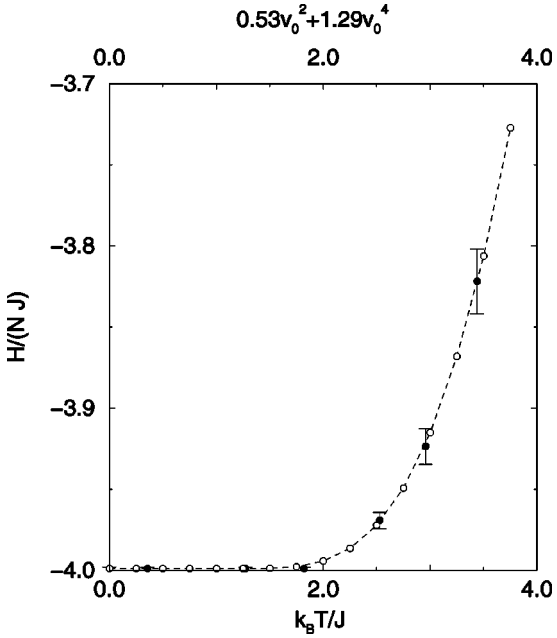


FIG. 1. Comparison of the equilibrium ordering energy obtained by MC-VA and MD simulations. MC-VA data (open circles) is plotted as a function of $k_BT/J$ (bottom scale) while MD data (black dots) is plotted as a function of $0.53v_0^2+1.29v_0^4$ (top scale).

The above discrepancy between the MC-AA simulations ($x=1/2$) and the MC-VA mechanism ($x>1/2$) at low temperatures leads to the following question: during the relaxation towards equilibrium, are the excitations in the system homogeneous or, are they correlated with the existing order? Experiments[8] have always been carried out at temperatures $0.8<T/T_c<1$, too close to $T_c$ to elucidate if the value of the exponent increases above 1/2, and confirm the existence of such inhomogeneous excitations in the system. Moreover a deeper insight into the discrepancy leads to the conclusion that the MC time scale is ill-defined and that such simulations cannot solve the question. The validity of the obtained exponents and the possible comparison with experimental results relies on the hypothesis that the ratio between mcs and the ''real'' time, is constant during the domain growth regime. The fundamental doubt can only be solved by performing MD of the same process, in which time has a real physical meaning.

The MD simulation of an order-disorder process in a 3d system, long enough to observe the domain growth regime, is a great challenge. A large system is needed in order to observe growing domains not affected by the finite size of the system and simulations have to be performed for a long enough time to overcome energy barriers and reach the growth regime. For this purpose we have designed a MD strategy which is used to obtain results in Figs. 1, 2, and 4. We consider a stoichiometric alloy with $N=2\times16^3-1$ atoms, periodic boundary conditions, and interacting through a pair potential. The system is set up with the two species randomly distributed on a bcc lattice, except for one lattice site on which a vacancy will be introduced. This gives a vacancy concentration of $1.2\times10^{-4}$ which is a reasonable value for an alloy after a quench from high temperature.[12] Constant energy MD using the ''velocity Verlet'' integration algorithm[13] is performed only on a cell with 90 atoms centered on the vacancy site. The rest of the system is considered to be equilibrated with positions centered on the exact lattice sites and velocities Gaussian distributed. The variance of this distribution $v_0$ is the parameter that controls the temperature of the system. After the first relaxation, the atoms surrounding the vacancy start to jump into the empty Wigner-Seitz cell. Every time such a jump occurs the center of the simulation cell is displaced to the new vacancy position. Simulations have been performed at temperatures for which fluctuation amplitudes are low enough to prevent the problems associated with the localization of the vacancy: at all times all the Wigner-Seitz cells of the bcc lattice are occupied by a single atom except that of the vacancy. Atom-atom exchanges are not prohibited but none has been observed. This MD algorithm, in the absence of vacancy jumps, keeps the energy constant inside the simulation cell. At every vacancy jump there is an energy exchange with the surrounding atoms through the kinetic energy difference between the entering and leaving particles and the change in the interactions with the particles outside the simulation cell. Therefore the evolution of the full system is similar to that of a canonical system. This MD scheme may, in principle, be applied to many kinds of potential for the study of vacancy mediated phenomena in solids at low temperature.

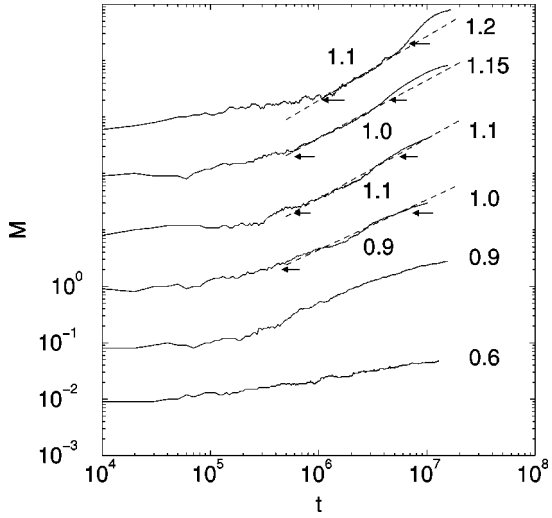


FIG. 2. Evolution of $M(t)$ obtained by MD, for different values of $v_0$ which correspond to $k_BT/J=0.36$, 1.28, 1.82, 2.53, 2.94, 3.44. Data correspond to averages over 16 runs. Dashed lines show the fitted power laws in the region indicated by arrows. The fitted exponents are indicated with the numbers below each dashed line. Curves are shifted one decade each in order to clarify the picture.

In order to favor nn and even nnn atoms to jump into the vacancy cell we have choosen a Morse potential given by $V_{\alpha\beta}(r)=4\epsilon_{\alpha\beta}e^{-D_{\alpha\beta}(r-\sigma_{\alpha\beta})}[e^{-D_{\alpha\beta}(r-\sigma_{\alpha\beta})}-1]$, with $\alpha\beta=AA,AB,BB$. In this work we have restricted to the study of a symmetric alloy (i.e., $m_A=m_B$, $\epsilon_{AA}=\epsilon_{BB}$, $\sigma_{AA}=\sigma_{BB}$ and $D_{AA}=D_{BB}$). We have worked with reduced units so that the unit of mass is $m_A=m_B=1$, the unit of length is the bcc lattice parameter $d=1$, and the unit of energy is $\epsilon_{AA}=\epsilon_{BB}=1$. The other parameters are: $\epsilon_{AB}=2$, $\sigma_{AA}=\sigma_{BB}=\sigma_{AB}=2/3$, $D_{AA}=D_{BB}=2.0794$, and $D_{AB}=5.1986$. With these parameters, the minimum of the pair potential is located at a distance $d$ for $AA$ and $BB$ pairs and at $0.8d$ for $AB$ pairs. One may compare these values with a fit of such a Morse potential to Cu-Zn:[14] concerning the symmetry assumption,

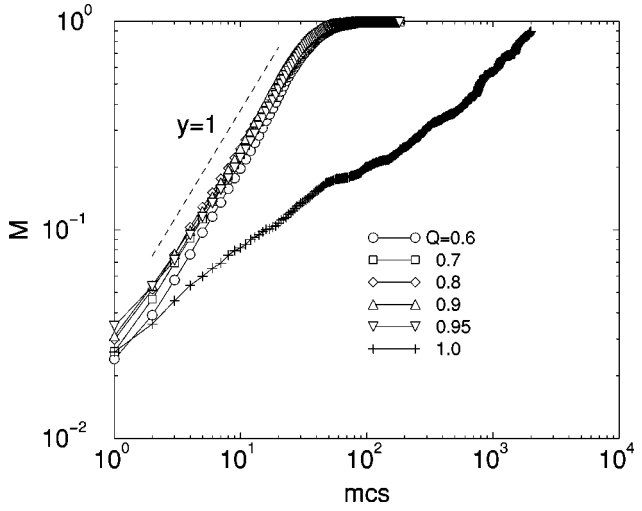


FIG. 3. Evolution of the order parameter $M(t)$ obtained by MC-VA, for $k_BT/J=1.82$. The different curves have been obtained with different values of the parameter $Q$. Data correspond to an average of $\sim 30$ runs. The dashed line shows the behavior of $M(t)\sim t$.

which we have taken in order to simplify the problem, it should be noted that the masses of Cu and Zn are, indeed, very similar. The ratio $\epsilon_{\mathrm{CuZn}}/\epsilon_{\mathrm{CuCu}}$ is also very close to 2, but from the fit one obtains that $\epsilon_{\mathrm{CuCu}}\sim 9\epsilon_{\mathrm{ZnZn}}$. The values found for $D_{\alpha\beta}$ are not very far from the fitted $D_{\mathrm{CuCu}}=1.865$, $D_{\mathrm{ZnZn}}=2.84$, and $D_{\mathrm{CuZn}}=6.545$, and our values of $\sigma_{\alpha\beta}$ are also relatively close to $\sigma_{\mathrm{CuCu}}/d=0.544$, $\sigma_{\mathrm{ZnZn}}/d=0.6657$, and $\sigma_{\mathrm{CuZn}}/d=0.7858$. A potential cutoff at $r/d=3.0$ has been considered to simplify the force computation. Realistic values for $m_A$, $d$, and $\epsilon_{AA}$ lead to a unit of time $\sqrt{m_Ad^2/\epsilon_{AA}}\sim 5\times 10^{-13}s$. Trajectories have been integrated with a time step $\Delta t=0.02$. The longest runs we have performed lasted for $2\times 10^7$ steps ($\sim 0.2$ $\mu$s). Vacancy jumps occur typically every $\sim 10^3$ steps ($\sim 10^{-11}$ s). Since we are interested in comparing the ordering process taking place in the full system with MC simulations, we have monitored the evolution of the order parameter defined as $M=\Sigma_i S_i\mathrm{sgn}(i)/N$, where $i$ sweeps all the lattice positions of the bcc structure, $S_i=1,-1$ indicates if a Wigner-Seitz cell is occupied by an $A$ or a $B$ atom, respectively, and $\mathrm{sgn}(i)$ is $\pm 1$ alternatively on the two interpenetrated simple cubic sublattices forming the bcc structure. In a $3d$ system exhibiting scaling, during the domain growth regime, the evolution of $M$ should satisfy: $M(t)\sim t^y$ with $y=\frac{3}{2}x$.[15] We have also measured the ordering energy $H(t)$ and its equilibrium average $\langle H\rangle_{\mathrm{MD}}$. The excess of this ordering energy $\Delta H(t)=H(t)-\langle H\rangle_{\mathrm{MD}}$ should evolve according to $\Delta H\sim t^{-x}$. Nevertheless, this last equation is based on the assumption that all the excess energy is contained in the interfaces. This is only true at very long times when the bulk of the domains is fully ordered. Such long times may not be attained with the system sizes simulated here. For this reason, our study mainly focuses on the evolution of $M(t)$.

In order to compare MD and MC results we have first established the equivalence between the temperature $k_BT/J$ and the parameter $v_0$. To do that, we have performed MD simulations starting with an ordered system with different values of $v_0$. For values of $v_0<1.0$ equilibration is difficult, but for higher values one can fit an exponential relaxation

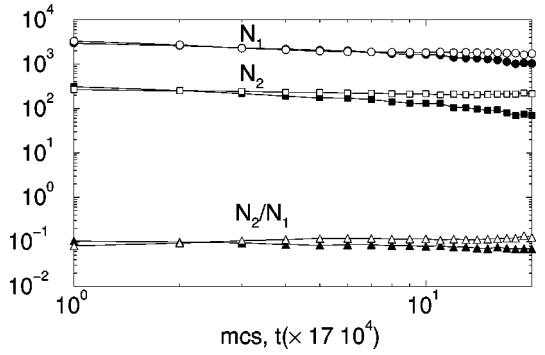


FIG. 4. Time evolutions of $N_1$, $N_2$, and its ratio $N_2/N_1$. Black symbols correspond to MD data (counts every $\Delta t=17\ 10^4$) with $v_0=1.0$. Open symbols correspond to MC-VA (counts each mcs) with $Q=0.95$ and $k_BT/J=1.82$.

$\langle H\rangle_{\mathrm{MD}}-H(t)\sim e^{-t/\tau}$ to the ordering energy evolution. Thus, we obtain the dependence of the equilibrium ordering energy $\langle H\rangle_{\mathrm{MD}}$ with $v_0^2$. Besides, we have performed MC-VA simulations as explained elsewhere.[7,8] We have used a system with the same size in order to be equally affected by finite size. Equilibrium energies $\langle H\rangle_{\mathrm{MC}}$ have been obtained as a function of temperature. The comparison of both curves allows us to obtain the correspondence between $v_0$ and $k_BT/J$ which is well accounted for by the equation $k_BT/J=0.53v_0^2+1.29v_0^4$ as can be seen in Fig. 1. Thus we have established an equivalence between the equilibrium data from MD and MC (MC-AA and MC-VA give almost equal results concerning equilibrium[7]).

Next, we study the kinetic evolution starting from the disordered lattice with $A$ and $B$ atoms occupying random positions. Figure 2 shows the time evolution of $M$ obtained by MD simulations for different values of $v_0$. After an initial transient period, growth of ordered domains starts with a clear increase of the order parameter. Algebraic growth of $M(t)$ can be observed in almost 1.5 decades. Figure 3 shows, as an example, the evolution of the order parameter obtained by MC-VA simulation, for $k_BT/J=1.82$. The curves correspond to different values of the parameter $Q$ which controls the amount of vacancy jumps proposed to NN positions. Provided that $Q$ is different from 1 (some NNN jumps are allowed) it does not affect substantially the behavior of the system. In order to fit power-law behaviors $M(t)\sim t^y$ we have only considered the data into the regions (indicated by arrows in Fig. 2) with $0.02<M<0.2$ in which the system is clearly ordering but still domains are small enough to avoid finite-size effects. The fits to MD data (also plotted in Fig. 2) are performed only to simulations corresponding to $v_0\geqslant 1$. The two low-temperature cases are affected by metastability problems (due to the existence of high barriers one will need many more statistics to have good averages). The fitted $y$ exponents are consistent with $y=1.0\pm 0.1$ giving $x=0.75\pm 0.07$. For the MC data (Fig. 3) we have represented, for comparison, the behavior corresponding to $y=1.0$. Therefore, we conclude that both methods MD and MC-VA give, within accuracy, the same growth exponent $x$ with a value larger than the $x=0.5$ obtained from Allen-Cahn theory and MC-AA simulations. The consistency of the results obtained by both methods suggests that there exists, in the domain growth regime, a proportionality between the MC-VA step

and the ''real'' MD time. To gain insight into this proportionality and find the equivalence between the unit of time in MD and MC-VA we have studied the number of accepted jumps of the vacancy to NN ($N_1$) and NNN ($N_2$) positions and the corresponding ratio ($N_2/N_1$). Figure 4 shows the results corresponding to MD simulations with $v_0=1.0$ together with the MC-VA data corresponding to the equivalent temperature $k_BT/J=1.82$ and with $Q=0.95$. The ratio $N_2/N_1$ is quite constant for MD and also for MC-VA up to $\sim 20$ mcs. The value of $Q$ has been selected in order to overlap as much as possible the ratio $N_2/N_1$ obtained by the two methods. Although $Q$ does not affect the behavior of $M(t)$, it changes the value of $N_2/N_1$. The accounting of accepted jumps $N_1$ and $N_2$ has been done every mcs for MC-VA and every $\Delta t=17\ 10^4$ for MD. This $\Delta t$ has been fitted to reproduce the initial values of $N_1$ and $N_2$. Therefore, this $\Delta t$ gives an estimation of the ''duration'' of a mcs of the MC-VA algorithm.

In conclusion, MD simulation of the order-disorder growth process in a binary alloy shows, in agreement with MC-VA results, that at low temperature the excitations in the system are inhomogeneous and correlated with the existing order. Such inhomogeneous excitations give a growth exponent higher than 1/2. This is in contradiction with results obtained by standard MC-AA simulations, which give an exponent equal to 1/2 at all temperatures, as predicted by Allen-Cahn theory. Comparing MC-VA and MD data, we have obtained the numerical equivalence between both time scales ($1\ \text{mcs} \simeq 17\times 10^4$ MD steps $\sim 85\times 10^{-9} s$).

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