Molecular-dynamics computer simulation of crystal growth and melting in Al$_{50}$Ni$_{50}$

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Abstract – The melting and crystallization of Al$_{50}$Ni$_{50}$ are studied by means of molecular-dynamics computer simulations, using a potential of the embedded atom type to model the interactions between the particles. Systems in a slab geometry are simulated where the B2 phase of AlNi in the middle of an elongated simulation box is separated by two planar interfaces from the liquid phase, thereby considering the (100) crystal orientation. By determining the temperature dependence of the interface velocity, an accurate estimate of the melting temperature is provided. The value $k = 0.0025$ m/s/K for the kinetic growth coefficient is found. This value is about two orders of magnitude smaller than that found in recent simulation studies of one-component metals. The classical Wilson-Frenkel model is not able to describe the crystal growth kinetics on a quantitative level. We argue that this is due to the neglect of diffusion processes in the liquid-crystal interface.

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Introduction. – The classical model for crystallization from the melt is the one proposed by Wilson [1] and Frenkel [2]. It considers crystal growth as an activated process, controlled by the mass transport in the liquid. However, various studies using molecular-dynamics (MD) computer simulation have shown that the Wilson-Frenkel scenario is not applicable to a large class of materials. Especially in pure metals, growth kinetics is much faster than expected for an activated diffusion-limited mechanism [3–15]. In this case, rearrangements in the liquid structure are not required to provide the formation of crystalline layers. This may explain why one-component metals are not glass-forming systems in general. On the other hand, binary metallic alloys are known as glass-forming systems, provided that heterogeneous nucleation can be avoided. Indeed, these systems exhibit in general a much slower growth kinetics than pure metals. Recent studies have demonstrated that the MD simulation technique is well suited to elucidate the crystallization kinetics in binary alloys [16–22]. But these studies show also that the growth kinetics in binary mixtures is more complicated than in the one-component counterparts.

One of the open questions is to what extent the Wilson-Frenkel picture is valid for two-component metals. This question is addressed in the following.

In this work, the crystal growth kinetics of the binary alloy Al$_{50}$Ni$_{50}$ is investigated by MD simulation. The experimental melting temperature for this system is at 1920 K where it exhibits a first-order phase transition from a liquid to an intermetallic B2 phase. Very recently, the crystal growth velocity for this congruent melting transition has been measured by Reutzel et al. [23] using an electromagnetic levitation technique under reduced gravity conditions in combination with a high-speed camera. At an undercooling of about 60 K, growth velocities of the order of 0.1 m/s were found. This value is about two orders of magnitude smaller than that found for pure metals at comparable undercoolings, indicating that Al$_{50}$Ni$_{50}$ may be the prototype of a system with a diffusion-limited growth mechanism [24].

The MD simulation allows for an accurate determination of the melting temperature, kinetic growth coefficients, and transport coefficients such as self- and interdiffusion constants. These information are required
to check the validity of the Wilson-Frenkel model of crystal growth. As we shall see below the kinetic growth coefficient, as estimated by our simulation for the (100) orientation of the crystal, is indeed much smaller than that found for simple metals. Thereby, the growth velocities are in good agreement with those measured in the aforementioned experiment by Reutzel et al. [23]. However, we demonstrate that the Wilson-Frenkel model is not able to describe the crystal growth kinetics in Al$_{50}$Ni$_{50}$ on a quantitative level, at least for plausible choices of the various free parameters appearing in the theory. This indicates the need of microscopic theories on the various aspects of crystal growth kinetics. By computing diffusion profiles for an inhomogeneous crystal-liquid system at coexistence, we show explicitly that such theories have to take into account diffusion processes in the crystal-liquid interface region.

**Details of the simulation.** – To investigate the crystallization of Al$_{50}$Ni$_{50}$ from the melt, we have done extensive molecular-dynamics computer simulations. The interactions between the atoms were modelled by a potential of the embedded atom type, proposed by Mishin et al. [25]. Recent studies have shown that this potential gives a realistic description of the diffusion dynamics in Al-Ni melts [26,27]. The simulations were done at constant pressure ($p_{\text{ext}} = 0$). For this, an algorithm proposed by Andersen was used, setting the mass of the piston to 0.0027 u [28]. Temperature was kept constant by coupling the system at every 100 steps to a stochastic heat bath. The equations of motion were integrated with the velocity form of the Verlet algorithm [29] with a time step of 1 fs.

At each temperature in the range 1600 K $\geq T \geq$ 1200 K, 12 independent samples with solid-liquid interfaces were prepared. To this end, the B2 phase of Al$_{50}$Ni$_{50}$ was equilibrated at the target temperature for 1 ns. The simulations were done for a system of $N = 3072$ particles ($N_{\text{Al}} = N_{\text{Ni}} = 1536$) in an elongated simulation box of size $L \times L \times L_z$ (with $L_z = 3 \times L$), considering the (100) direction of the crystal. Periodic boundary conditions were employed in all three spatial directions. Having relaxed the crystal sample, one third of the particles in the middle of the box were fixed and the rest of the system was melted during 500 ps at $T = 3000$ K. Then, the whole system was annealed at the target temperature for another 500 ps, before we started the production runs over 1 ns in the $NpT$ ensemble. A snapshot of the system with two interfaces at $T = 1500$ K is shown in fig. 1. We did also 20 independent microcanonical runs of the crystal-liquid system at the coexistence temperature $T = 1520$ K (see below), starting from fully equilibrated samples. These runs, each of them over 1 ns, was used to study the diffusion dynamics in the crystal-liquid interface region.

In addition, simulations of liquid samples were performed at the temperatures $T = 1200$ K, 1300 K, 1400 K, 1500 K, 1600 K, 1800 K, and 2000 K, in order to determine self-diffusion coefficients as well as the

Fig. 1: Snapshot of a simulated configuration with two crystal-melt interfaces of the system Al$_{50}$Ni$_{50}$ at the temperature $T = 1500$ K. Al and Ni atoms are shown as black and white spheres, respectively.
interdiffusion coefficient (see below). In this case, systems of 2000 particles were placed in a cubic simulation box. At each temperature, equilibration runs over 1 ns were done in the NpT ensemble, followed by microcanonical production runs over 23 ns.

Results. – As described in the previous section, samples in an elongated simulation box were prepared as starting configurations where the crystal in the middle is surrounded by the liquid phase on both sides, separated by two interfaces (see fig. 1). The behavior of these samples depends strongly on the temperature at which they are simulated. While below the melting temperature \( T_m \), the crystal will grow (as shown in fig. 2), it will melt above \( T_m \). From the simulation, the velocity \( v_I \) with which the liquid-crystal interface moves can be determined. At \( T = T_m \), the interface velocity \( v_I \) vanishes. Thus, by extrapolation \( v_I \to 0 \) the melting temperature \( T_m \) can be estimated. In the following, we show that this procedure yields a rather accurate estimate of \( T_m \). Then, we demonstrate that the crystal growth mechanism in \( \text{Al}_{50}\text{Ni}_{50} \) can be elucidated by investigating the diffusion dynamics in the liquid phase and in the crystal-liquid interface region.

Figure 2 displays the partial number density profiles \( \rho(z) \) of Al and Ni at \( T = 1460 \) K along the \( z \)-direction, \( i.e. \) perpendicular to the solid-liquid interfaces. The lower profiles in fig. 2 correspond to the starting configuration, while the second and the third ones correspond to \( t = 560 \) ps and \( 994 \) ps. Note that in fig. 2 the \( z \) coordinate is scaled by the factor \( 2/L_z \), placing \( z = 0 \) in the middle of the simulation box. Whereas the crystal structure leads to pronounced peaks in \( \rho(z) \), a constant density is observed for the liquid regions along the \( z \)-direction, as expected. We can also infer from fig. 2 that the intermetallic B2 phase (here in (100) orientation) exhibits a pronounced chemical ordering, characterized by the alternate sequence of Al and Ni layers. This indicates that, different from one-component metals, the crystal growth kinetics relies on local rearrangements in the liquid structure. Thus, one may expect that diffusive transport is required to bring the atoms of each species to a suitable site in the B2 crystal.

As one can further see in fig. 2, the crystal is growing at \( T = 1460 \) K. Thus, this temperature is below the melting temperature of our \( \text{Al}_{50}\text{Ni}_{50} \) model.

Since the density of the crystalline B2 phase is higher than that of the liquid phase, the total volume of the system decreases at temperatures \( T < T_m \), whereas it increases above \( T_m \). Figure 3 shows the time dependence of the volume per particle, \( V_p \), for different temperatures between 1400 K and 1600 K. From this plot, one can infer that the melting temperature is between 1500 K and 1530 K. Also shown in fig. 3 are examples of linear fits of the form \( f(t) = A - V_p t \). Such linear growth laws are expected for steady-state growth of planar interfaces [7]. We use these fits to determine the change of the volume \( V \) per unit of time. The deviations from the linear behavior at short times reveal that the growth (or melting) of the crystal is not yet in a steady-state regime [7]. At high temperatures, we see a complete melting of the crystal and thus the volume \( V_p \) reaches a constant at long times corresponding to the specific volume of the liquid phase. Prior to this, the melting of the crystal is faster than in the linear steady-state regime. In this intermediate regime the crystal has shrunk to such small dimensions that we see essentially the interaction between the two interfaces in
The inset shows the interface velocity as a function of undercooling \( \Delta T \) increases linearly up to an undercooling of about 30 K.

The simulation box and thus strong deviations from steady-state growth are observed.

From the volume change \( \dot{V}_p \), the velocity \( v_I \), with which the liquid-crystal interfaces move, can be estimated as follows:

\[
v_I = \frac{\dot{V}_p}{2N_l(V_c - V_l)d}
\]

(1)

Here, the product \( N_l(V_c - V_l) \) quantifies the increase of the volume caused by the addition of a crystalline layer (with \( N_l \) the average number of particles in a layer, and \( V_c \) and \( V_l \) the specific volumes of the crystal and the liquid phase, respectively). The length \( d \) is the spacing between crystalline layers.

Figure 4 displays the interface velocity \( v_I \) as a function of temperature. We see that \( v_I \) vanishes around 1520 K and thus this temperature is the estimate for the melting temperature, \( T_m \), of our simulation model. Note that the experimental value for \( T_m \) is around 1920 K and so our simulation underestimates the experimental value by about 20%. Around \( T_m \), the simulation data for \( v_I \) can be fitted by the linear law \( v_I = k(T_m - T) \) where the fit parameter \( k \) is the so-called kinetic coefficient. The fit, that is shown in fig. 4, yields the value \( k = 0.0025 \text{ m/s/K} \). This value is about two orders of magnitude smaller than the typical values for kinetic coefficients that have been found in simulations of one-component metals [9–11,30].

The inset in fig. 4 shows the interface velocity as a function of undercooling \( \Delta T = T_m - T \). We see that \( v_I \) increases linearly up to an undercooling of about 30 K. At \( \Delta T \approx 180 \text{ K} \), the interface velocity reaches a maximum value of about 0.15 m/s. Note that at small undercoolings our simulation data are in good agreement with recent experimental data on \( \text{Al}_{50}\text{Ni}_{50} \), measured under reduced gravity conditions during a parabolic flight campaign [23]. Also shown in the inset of fig. 4 is the quantity \( 2v_I/(D_{NI} + D_{Al}) \), with \( D_{NI} \) and \( D_{Al} \) the self-diffusion constants of Ni and Al, respectively. The self-diffusion constants will be discussed in detail below. Here, we note that the maximum in \( v_I \) disappears when one divides this quantity by the averaged self-diffusion coefficient. Thus, the occurrence of a maximum in \( v_I(\Delta T) \) is due to the slowing-down of diffusion processes with decreasing temperature.

On a qualitative level, the behavior of \( v_I(\Delta T) \) can be understood in the framework of the Wilson-Frenkel model. The model relates the interface velocity to the difference between the rate at which the atoms join the crystal and the rate at which they leave the crystal. As a result the following formula for \( v_I \) is obtained [30]:

\[
v_I = A_{\text{kin}} \left[ 1 - \exp \left( -\frac{\Delta g}{k_B T} \right) \right] \]

(2)

with \( A_{\text{kin}} \) a kinetic prefactor, \( k_B \) the Boltzmann constant and \( \Delta g \) the free-energy difference between the liquid and crystal phase. Close to coexistence, the free-energy difference \( \Delta g \) is proportional to \( \Delta T \), and the exponential function in eq. (2) can be approximated, such that \( 1 - \exp(-\Delta g/k_B T) \approx \Delta g/k_B T = \lambda (\Delta T) \), with \( l \) the latent heat of the liquid-to-solid transition. Furthermore, the kinetic prefactor \( A_{\text{kin}} \) can be expressed in terms of the diffusion coefficient \( D \) of the liquid. Eventually, at small \( \Delta T \) the expression for \( v_I \) can be written as [30]

\[
v_I = k_{\text{WF}} \Delta T \quad \text{with} \quad k_{\text{WF}} = \frac{6fD}{\Lambda^2} \frac{l}{k_B T T_m},
\]

(3)

where \( f \) represents the fraction of collisions with the crystal that contribute to the growth of the crystal. The parameter \( \Lambda \) corresponds to an elementary diffusive jump distance of particles in the liquid [30]. Note that it is assumed in the derivation of eq. (3) that the diffusion constant can be expressed by an Arrhenius law,

\[
D = D_0 \exp \left( -\frac{Q}{k_B T} \right) \quad \text{with} \quad D_0 = \frac{1}{6}\Lambda^2 \nu
\]

(4)

with \( Q \) an activation energy associated with the diffusion of the atoms in the liquid and \( \nu \) a frequency of the order of the Debye frequency.

In order to check whether the Wilson-Frenkel formula for the kinetic coefficient \( k_{\text{WF}} \) in eq. (3) yields quantitative agreement with the value \( k = 0.0025 \text{ m/s/K} \) for \( \text{Al}_{50}\text{Ni}_{50} \) (see above), we have computed the temperature dependence of self- and interdiffusion coefficients around \( T_m = 1520 \text{ K} \). Whereas the self-diffusion constant \( D_0 \) is the transport coefficient for tagged particle diffusion of atoms of type \( \alpha \) (here \( \alpha = \text{Al}, \text{Ni} \)), the interdiffusion coefficient \( D_{AB} \) describes diffusive transport due to concentration...
fluctuations among the different components. The self-diffusion constants \(D_\alpha\) have been computed from the long-time limit of the corresponding mean-squared displacements. The interdiffusion coefficient is given by \(D_{AB} = \Phi L\), where \(\Phi\) is the so-called thermodynamic factor and \(L\) is the Onsager coefficient. The thermodynamic factor expresses the thermodynamic forces to homogenize the mixture with respect to concentration fluctuations. We have calculated this quantity from the \(q \to 0\) limit of the inverse concentration-concentration structure factor (see ref. [27]). The Onsager coefficient \(L\) contains all the kinetic contributions to \(D_{AB}\) and can be determined from a generalized mean-squared displacement describing the centre-of-mass motion of one species. For details of the calculation of \(L\) and \(\Phi\), we refer the reader to a recent publication [27].

An Arrhenius plot of the different diffusion coefficients is shown in fig. 5. As in a recent simulation study of Al\(_{50}\)Ni\(_{50}\) [27], the interdiffusion coefficient is about a factor 4 to 6 higher than the self-diffusion constants. This is due to the thermodynamic factor (note that the Onsager coefficient lies below the self-diffusion constants). The origin of this behavior is a large resistance to macroscopic concentration fluctuations in dense liquids (a similar property of dense liquids is their very low compressibility). With respect to crystal growth kinetics in a binary alloy such as Al\(_{50}\)Ni\(_{50}\), it is not clear whether one has to consider self- or interdiffusive transport as the limiting growth mechanism.

Also shown in fig. 5 are fits with Arrhenius laws (4). From these fits, we obtain the activation energies \(Q = 0.49\) eV for \(D_{Al}\), \(Q = 0.48\) eV for \(D_{Ni}\), and \(Q = 0.51\) eV for \(L\). The prefactors \(D_0\) are \(1.05 \times 10^{-7}\) m\(^2\)/s, \(1.15 \times 10^{-7}\) m\(^2\)/s, and \(0.91 \times 10^{-7}\) m\(^2\)/s for \(D_{Al}\), \(D_{Ni}\), and \(L\), respectively. These values for the prefactors can be compared to those proposed by eq. (4). With the reasonable choices \(\lambda = 3\) Å and \(\nu = 6\) THz, similar values for \(D_0\) as in the fits are obtained, i.e. \(D_0 \approx 10^{-7}\).

Moreover, the expression (3) for the kinetic coefficient \(k_{WF}\) does not predict the order of magnitude correctly. To see this, we can compute the value of \(k_{WF}\) at \(T_m \approx 1520\) K using the results from the simulation. With \(l = 0.23\) eV, \(D_\alpha \approx 2 \times 10^{-9}\) m\(^2\)/s, \(\Lambda^2/6 \approx 1.5\) Å\(^2\), \(d = 3\) Å and \(f = 1\), the value \(k_{WF} \approx 0.05\) m/s/K is yielded which is about one order of magnitude higher than the value for \(k\), as obtained in our simulation. The result for \(k_{WF}\) is even worse if we replace the self-diffusion constant by the interdiffusion constant in our estimate. In this case, we find \(k_{WF} \approx 0.25\) m/s/K.

But why does the Wilson-Frenkel theory overestimate the speed of crystal growth? To address this question we propose the following scenario: We assume that the speed of crystal growth is limited by the atoms in the liquid-crystal interface region and not by the atoms in the liquid region where the liquid behaves like a bulk liquid. If this is true, one has to study the diffusion dynamics in the interface region: if diffusion in the interface region is much slower than in the bulk liquid, a failure of the Wilson-Frenkel model would be plausible since this model only takes into account diffusive transport of the bulk liquid. To check this scenario, we have simulated inhomogeneous systems with two crystal-liquid interfaces at the melting temperature \(T_m = 1520\) K. From these runs, we determined the diffusion profiles \(D_{z,\alpha}(z)\) (\(\alpha = Ni, Al\)) along the \(z\)-direction that are shown in fig. 6 together with the number density profile. \(D_{z,\alpha}(z)\) was computed from the long-time limit of the mean-squared displacement in \(z\)-direction,

\[
D_{z,\alpha}(z) = \lim_{t \to +\infty} \frac{1}{N_s} \sum_{i_s = 1}^{N_s} \frac{(z_i(t) - z_i(0))^2}{2t}, \tag{5}
\]
where $z_i$ is the $z$ coordinate of a tagged particle that was at time $t=0$ in one of 30 slabs that we introduced along the $z$-direction, each slab having a thickness of about 2.4 Å. $N_s$ is the number of particles in slab $s$ ($s = \{1, \ldots, 30\}$). As can be seen in fig. 6, the interface region extends over 5–6 atomic layers. Within this region the self-diffusion constants decrease roughly by about one order of magnitude. When one considers crystal growth, this slowing–down of diffusion has to be taken into account, since the formation of new crystalline layers occurs in the interface region. This can be the reason why the Wilson–Frenkel model overestimates the speed of crystal growth.

**Conclusions.** – Extensive MD simulations have been used to investigate the crystallization kinetics as well as the diffusion dynamics of Al$_{50}$Ni$_{50}$. Although crystal growth is relatively slow in this system, the simulation yields accurate estimates of the melting temperature and the kinetic growth coefficient (for the (100) orientation of the intermetallic B2 phase). The small value of the latter quantity, $k = 0.0025 \text{ m/s/K}$, reveals that the growth kinetics of the intermetallic B2 phase is controlled by diffusive mass transport. However, the classical model for diffusion-limited growth due to Wilson and Frenkel does not give an accurate description. We argue that this is due to the neglect of diffusive transport in the crystal-liquid interface region. Microscopic theories of crystal growth shall take into account the latter diffusive processes.

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