We investigate crystal-growth kinetics in the presence of strong shear flow in the liquid, using molecular-dynamics simulations of a binary-alloy model. Close to the equilibrium melting point, shear flow always suppresses the growth of the crystal–liquid interface. For lower temperatures, we find that the growth velocity of the crystal depends non-monotonically on the shear rate. Slow enough flow enhances the crystal growth, due to an increased particle mobility in the liquid. Stronger flow causes a growth regime that is nearly temperature-independent, in striking contrast to what one expects from the thermodynamic and equilibrium kinetic properties of the system, which both depend strongly on temperature. We rationalize these effects of flow on crystal growth as resulting from the nonlinear response of the fluid to strong shearing forces.

Crystal growth on the other hand needs to be discussed as a non-equilibrium process that is strongly influenced by external driving forces \[16\]. Once an initial crystal has formed, in a sheared liquid crystal growth and flow-induced erosion compete and lead to a non-equilibrium coexistence that depends on temperature and flow rate \[17\]. It has already been emphasized that a near-equilibrium thermodynamic description of flow-modified growth kinetics is not viable \[17\]. It is therefore much less clear, how crystal growth changes under strong fluid flow, and which are the governing microscopic processes.

Here we present molecular-dynamics (MD) simulations of crystal growth in a homogeneously sheared fluid, over a wide range of temperatures and shear rates. We argue that the nonlinear response of the fluid to the shearing force is a relevant microscopic dynamical process that determines a set of qualitatively different growth regimes. Strikingly, we find that the growth velocity of the crystal in a deeply undercooled fluid is a non-monotonic function of the shear rate. After an initial strongly temperature-dependent increase, a regime of intermediate shear rates appears where the crystal grows with a velocity that is nearly temperature independent. It is rationalized as the result of strong shear thinning of the undercooled fluid. This nonlinear-response effect has so far, to our knowledge, been neglected in the modeling of solidification processes. It is achieved once shear-induced “surface erosion” and structural relaxation of the viscoelastic melt compete. This regime of flow rates is of particular relevance for soft materials, but can in principle also be reached for sufficiently undercooled metallic melts.

We performed molecular-dynamics (MD) simulations of a binary mixture that crystallizes into a \(B\)\(_2\) structure (CsCl lattice). To provide a specific reference point, we use an embedded-atom model of the intermetallic compound \(\text{Al}_{50}\text{Ni}_{50}\) \[20\], a material that is used in many applications, e.g., for turbines in aeroplanes or power stations. \(\text{Al}_{50}\text{Ni}_{50}\) melts congruently, so that crystal growth can be studied without any constitutional effects. The model has also been extensively studied in previous MD simulations, investigating its liquid dynamics \[21\], glass-forming ability \[22\], quiescent crystal growth \[22\], \[24\], and disorder trapping \[25\]. Using \(N = 27040\) particles in a box of average dimensions \(L_x : L_y : L_z = 1 : 1 : 6.4\) and \(L_x \approx 38\) \(\text{Å}\) (employing periodic boundary conditions in all Cartesian directions), seeded with an initial crystal that is surrounded by liquid regions, we study crystal growth along the normal of the (100) face (along the z-direction). The system is first prepared in its \(B\)\(_2\) state and relaxed to the target temperature. Next, particles in the central third of the box (\(L_z/3 \approx 81\) \(\text{Å}\)) are fixed, and the surrounding system is molten at \(T = 3000\) \(\text{K}\) before
it is brought to the desired temperature again.

Simple shear flow parallel to the interface is imposed by assigning a fixed center-of-mass velocity to small fluid layers (width 12 Å) at the z-boundaries of the simulation box, while keeping a layer of 10 Å fixed in the crystalline center. After an initial transient (of about 100 ps), a homogeneous linear velocity profile develops in the liquid, as shown in Fig. 1. The shear rate, \(\dot{\gamma}\), is extracted from the averaged velocity, \(\dot{\gamma} = \partial_z v_y\). Data are analyzed in small time windows during which the shear rate does not change appreciably. To release latent heat as the crystallization process.

The temperature- and shear-rate dependent growth velocity \(v_I(T; \dot{\gamma})\) of the crystal is shown in Fig. 2 as a function of shear rate \(\dot{\gamma}\). Here and in the following, we use the time scale of atomic vibrations, \(\tau_0 \approx 0.2 \text{ ps} \) to define a dimensionless shear rate, the (bare) Péclet number \(Pe_0 = \gamma \tau_0\). We briefly remark on the behavior close to the equilibrium melting temperature \((T_m \approx 1540 \text{ K in our model})\). Here, shear flow always suppresses crystal growth, and the growth velocities \(v_I\) closely follow a quadratic dependence on \(\dot{\gamma}\). The zeroes of the \(v_I\)-versus-\(\dot{\gamma}\) curves identify a non-equilibrium crystal–fluid coexistence (at a shear rate \(\dot{\gamma}_{coex}(T)\)) that has been discussed earlier \([17, 19]\). Crystal growth velocities close to \(T_m\) are usually expressed in terms of thermodynamic free-energy barriers, and it is tempting to relate the quadratic decrease of \(v_I\) to a shifted effective chemical-potential difference between the liquid and the crystal (and hence to a process-dependent effective undercooling \([29]\)). However, the shear-induced change in the strained crystal’s free energy is much too small to quantitatively explain the simulation data \([18]\).

For deeper undercooling, in particular, the situation is far more complex: the growth rate displays a non-monotonic dependence on the shear rate at any fixed temperature, with a maximum at a non-zero intermediate rate, and an inflection point around \(\dot{\gamma}_{coex}\). Between the maximum and the coexistence point, the temperature dependence of the growth rate is remarkably weak, i.e., the interface velocity is described well by a temperature-independent master curve \(v_I(\dot{\gamma})\) in an intermediate shear-rate regime. This is unexpected from the point of view of thermodynamics (where Boltzmann factors imply a temperature dependence when keeping other parameters fixed), or from the strong slowing down of the transport
kinetics in the fluid that occurs upon cooling.

To understand the mechanisms responsible for the non-monotonic dependence of the growth velocity on the shear rate, let us divide the $v_I$-versus-$\gamma$ curves into four regimes, as labeled in Fig. 2 (i) for slow shear, the suppression of growth due to shear that is observed close to $T_m$, changes to an enhancement below some temperature ($T \approx 1000 \text{K}$ in the figure). (ii) At intermediate shear rates, $v_I$ decreases towards zero with increasing $\gamma$. The curves for $T \lesssim 1200 \text{K}$ approach a $T$-independent master curve for $0.03 \lesssim Pe_0 \lesssim 0.1$ ($0.15 \text{ps}^{-1} \lesssim \gamma \lesssim 0.5 \text{ps}^{-1}$). The interplay between (i) and (ii) causes the maximum in the growth velocity for a finite shear rate, visible at the lowest temperatures shown in Fig. 2(a). (iii) The coexistence regime around $v_I(\gamma_{\text{coex}}) = 0$ becomes broader in the sense that the dependence of the growth velocity on shear rate becomes weak, i.e., near-stationarity of the interface is achieved for a wider range of shear rates. (iv) At larger shear rates, the crystal shrinks again.

For the explanation of regime (i) of Fig. 2 recall that the undercooled liquid dynamics is characterized by slow structural relaxation: density fluctuations decay on a time scale $\tau \gg \tau_0$. With decreasing temperature, $\tau$ increases much more rapidly than expected from the high-temperature Arrhenius behavior. Hence, the mobility of atoms in the liquid drops sharply, and the crystal-growth mechanism in the quiescent liquid changes from thermodynamically limited around $T_m$ to kinetically limited at $T \ll T_m$. As shown in Fig. 3, the resulting growth velocity $v_I(T; \gamma = 0)$ exhibits a maximum as a function of temperature (around $T = 1200 \text{K}$ in our simulation) that gives rise to shear thinning – a pronounced decrease in the fluid’s shear viscosity with increasing shear rate, as shown in Fig. 4 for our system. All data shown in Fig. 4 for $T \lesssim 1100 \text{K}$ correspond to $Pe \gtrsim \gamma_c$. As a result, particle mobility in the fluid is enhanced by the flow, and the growth velocity $v_I$ increases with increasing $\gamma$ initially for those $T$ where the equilibrium growth is limited kinetically.

Regime (ii) is essentially $T$-independent; this is clearly seen in Fig. 4 where the curve for $Pe_0 = 0.05$ approaches a constant for low temperatures. As opposed to regime (i), $v_I(\gamma)$ now decreases with increasing shear rate, which indicates that a qualitatively different process limits the growth. Hydrodynamic momentum transport across the interface region is governed by the rate $r_+ \sim \eta/L^2\rho$, where $\rho$ is the fluid mass density and $L$ the interface width ($L \approx 10 \text{Å}$ in our simulations for all state points). Note that at $T_m$, one gets $r_+ \approx 1/\tau_0$, the natural scale for the rate of momentum transport in the crystal. Assuming that the rate $r_+$ limits the attachment of atoms to the interface and hence the growth, and that it balances the detachment rate at the non-equilibrium coexistence point, we get

$$v_I(\gamma) \sim v_0 \cdot (\eta(\gamma) - \eta(\gamma_{\text{coex}})) \tau_0/L^2\rho$$

where $v_0$ is a velocity scale set by the thermodynamic features of the system ($v_0 = O(1 \text{m/s})$ in our simulation). In Eq. (2) we have accounted for the fact that the viscosity $\eta(\gamma)$ depends sensitively on the shear rate in the shear-thinning regime (ii). At the same time, structural relaxation in the fluid becomes nearly $T$-independent, since it is dominated by shear and thus $1/\gamma$ is the only relevant time scale. The fluid then flows plastically, i.e., at the expense of a nearly constant yield stress $\sigma_y$. As a result, the shear viscosity $\eta(\gamma_I)$ entering Eq. (2) is nearly temperature-independent. Expression (2) is shown for the lowest three temperatures in Fig. 4 (dashed lines), evaluated using the viscosity of the bulk fluid (see below). It gives a reasonable qualitative account for $v_I(\gamma)$ in the range $0.04 \lesssim Pe_0 \lesssim 0.1$. For comparison, a thermodynamic argument based on an effective free-energy barrier would not account for the weak $T$-dependence we observe. Equation (2) naturally explains that in regime (ii), the growth velocity decreases with increasing shear rate: for true yield-stress flow, $\eta(\gamma) \sim \sigma_y/\gamma$, and thus $v_I \sim 1/\gamma$ up to a constant and weakly dependent on temperature.

Equation (2) implies that the fluid viscosity determines the non-equilibrium coexistence between the sheared liquid and the crystal, region (iii). To corroborate this argument, we show in Fig. 4(d) the shear-rate dependent viscosity of the bulk liquid, as determined from separate MD simulations (in a system of $N = 5000$ particles following the SLLOD equations of motion [26]). Despite the fact that the bulk-liquid viscosity drops by more than an
In agreement with earlier simulations\textsuperscript{17} and a recent model\textsuperscript{33}, a non-equilibrium phase diagram is obtained in the $T$-$\dot{\gamma}$-plane, shown in Fig. 5. A quadratic fit (red line in Fig. 5), gives a good description of $T_{\text{coex}}(\dot{\gamma}_c^2)$, extrapolating to $T_{\text{coex}}(0) \approx 1531$ K in reasonable agreement with the value of $T_m$ reported for the model before\textsuperscript{24}. The surface-erosion picture is consistent with a weak $\dot{\gamma}$-dependence of $\dot{\gamma}_l$ close to $\dot{\gamma}_{\text{coex}}$. As long as shear-induced changes in the thermodynamic forces are negligible, any fast enough shear rate will be sufficient to erode fluctuations in the interface.

Only in regime (iv), effective thermodynamic forces again dominate the crystallization process; they always lead to shear-induced melting of the crystal. To the strongly sheared liquid, an increased effective temperature $T_{\text{eff}}(\dot{\gamma}) \geq T$ can be assigned\textsuperscript{34}, leading to a reduced effective undercooling that controls the growth velocity. Indeed, our data in regime (iv) closely follows a single $\eta$-dependent curve, where the viscosity is a proxy for the fluid’s effective temperature.

In conclusion, the growth velocity of a crystal is a non-monotonic function of the shear rate at fixed temperature. Flow initially enhances crystal growth at sufficiently strong undercooling, due to the enhanced particle mobility in the fluid. In the presence of stronger flow, the hydrodynamics of surface erosion causes a decrease in the growth velocity as a function of shear rate that is insensitive to temperature. This non-monotonic dependence is rationalized as the result of the pronounced nonlinear-response behavior of the non-Newtonian undercooled fluid.

The strain supported by nearest-neighbor cages marks the cross-over from the regime of small shear rates to the nonlinear-response dominated regime. This cross-over is reached once the dressed Péclet number (formed with the structural-relaxation time rather than the timescale of atomic vibrations) reaches $\text{Pe} \approx 0.1$. The line corresponding to $\text{Pe} = 0.1$ is shown in Fig. 5 (dashed line).

The mechanism we propose is very generic since it rests solely on the fact that the liquid becomes shear thinning. This is the case for most undercooled (viscoelastic) fluids, including colloidal suspensions, soft materials, as well as metallic melts. Our results point out that nonlinear-response effects in the undercooled fluid likely should be taken into account in effective coarse-grained models of rapid solidification\textsuperscript{35–37}. It is difficult to assess the actual shear rates in experiments on metallic melts. Still, an enhancement of crystal growth by (convective) flow has been reported in experiments combining high-speed imaging, electromagnetic levitation and microgravity conditions\textsuperscript{29,38,39} to determine crystal growth velocities of alloys in the presence of convective flow on a mesoscopic scale. For the change in microscopic growth kinetics that occurs at $\text{Pe} \approx 0.1$, the relevant shear rate is a local velocity gradient in front of the interface, extending over about 5 to 10 atomic layers in our
model. Local fluid flow velocities can be in excess of tens of m/s, indicating that the nonlinear regime to right of the cross-over curve in Fig. 4 might be reached in melts that can be undercooled sufficiently far.

The temperature-independent growth regime in particular is a signature of plastic yield-stress flow. It suggests the use of controlled-flow conditions in applications where the speed of crystallization needs to be adjusted separately from thermal control. We expect this mechanism to apply also to more complex systems and geometries, for example in the presence of concentration gradients [10]. In fact, Al$_{50}$Ni$_{50}$ is already an example where the quiescent growth mechanism is an intricate combination of attachment and intra-layer delayed reorganization [24]. Although we observe disorder trapping where the quiescent growth mechanism is an intricate organization [24]. Although we observe disorder trapping at the highest growth velocities, similar to the quiescent case at strong undercooling [25, 41], such details appear to leave the qualitative appearance of the different growth regimes as a function of shear rate unchanged. Our findings will be essential to further explore unusual growth kinetics observed in metallic materials, e.g., in Al-rich Al-Ni alloys where the growth velocity decreases with increasing driving force and in the presence of forced convection [42].

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