

Driven Alloys in the Athermal Limit

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Static molecular simulations of binary alloys under extrinsic forcing show that complex ordered or segregated structures may evolve even in the absence of thermally activated diffusion. This result is in opposition to the standard theoretical framework for so-called “driven alloys,” which assumes that extrinsic driving is an ideally randomizing process, and therefore predicts only random atomic configurations in the athermal limit. We propose a qualitative modification to the theory that introduces a new control parameter and use additional Monte Carlo simulations to demonstrate the physical plausibility of this modification. New research directions in nonequilibrium dynamic systems are also suggested by this analysis.

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A wide variety of theoretical methods have been used to study so-called “driven alloys,” evolved under dynamic forcing as by, e.g., irradiation-induced mixing or mechanical alloying through severe plastic deformation [1]. The existing theoretical framework for these systems has addressed a wide variety of interesting phenomena observed in experiments, including kinetic ordering and disordering [2–5], kinetic roughening, faceting, and smoothing of interfaces [6–9], compositional patterning [10,11], and novel rheologies in “jammed” particulate systems [12,13]. Driven alloy theory is largely centered around the competition between thermally activated diffusion, which tends to drive the system towards equilibrium, and the extrinsic ballistic mixing, which is regarded as completely randomizing. A general rule of thumb used to interpret the relative contributions of these processes was provided in the pioneering work of Martin [14]. For the problem of mixing and demixing in the presence of external driving, he derived the “law of corresponding states” for a system at temperature T :

$$T_{\text{eff}} = T(1 + \Delta), \quad (1)$$

where T_{eff} is the effective temperature of the system and Δ is a kinetic enhancement factor due to ballistic mixing given by

$$\Delta = \frac{D_b}{D_t}, \quad (2)$$

where D_b is the ballistic diffusion coefficient driving the system towards a random state and D_t is the thermally activated interdiffusivity promoting equilibrium. Equation (1) indicates that the steady-state configuration of a driven alloy at temperature T with driving force Δ is equivalent to the configuration of an undriven alloy at temperature T_{eff} ; the external driving force acts simply as an excess temperature. Despite some isolated discrepancies with respect to experimental work on driven alloys, Eq. (1) stands as the benchmark model for these problems [15]. Furthermore, although Eq. (1) was derived only for

the configuration of a solid-solution alloy, similar results have been suggested for various more complex situations [1,6–9,16], although in all cases the possibility of athermal relaxations due to, e.g., local stresses, have been neglected.

In Eq. (1), D_t has the usual Arrhenius temperature dependence, so T_{eff} diverges to infinity at both infinite and zero temperature; this is illustrated schematically in Fig. 1. The divergence at 0 K implies that in the limit where ballistic effects are dominant only completely random configurations are dynamically stable. In fact, it is the fundamental assumption of many works in this area

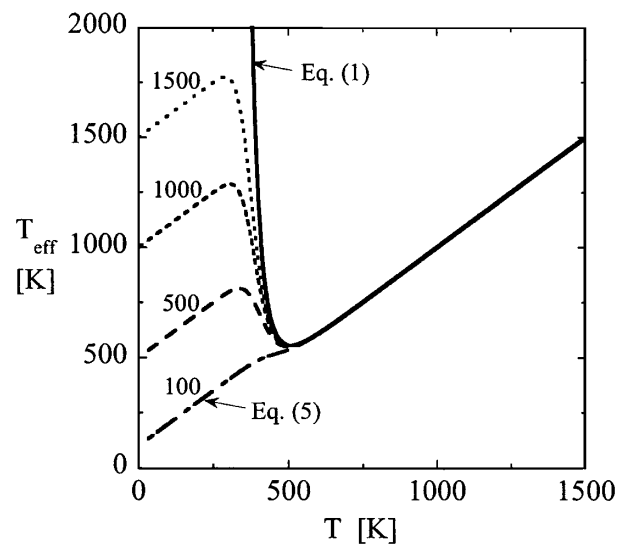


FIG. 1. Schematic representation of how extrinsic driving forces result in effective system temperatures T_{eff} with non-monotonic temperature dependencies. The standard theoretical framework for driven systems [Eq. (1), solid line] sees T_{eff} diverging to infinity as $T \rightarrow 0$, while the proposed model [Eq. (5), broken lines] produces more complex behavior in this limit. The labels on the broken lines give the value of T_0 from Eq. (5) in kelvins.

that ballistic atom exchanges are purely randomizing and have no bias whatever towards equilibrium [1,9,14,17–20]. In this Letter, we explore driven alloy systems at this athermal limit through molecular statics simulations; contrary to Eq. (1) and the generally accepted framework for driven alloys, we find that binary alloys can mix, demix, and even order under an external driving force at $T = 0$ K.

We have performed static molecular simulations of binary $A_{50}B_{50}$ alloy systems, in fully periodic two-dimensional simulation cells. The atomic species interacted according to 6–12 Lennard-Jones potentials, with minima for each interaction assigned as $\epsilon_{AA} = -0.038$ eV and $\epsilon_{BB} = -0.073$ eV, while ϵ_{AB} was assigned to produce a given value of the system heat of mixing. The potentials were further adjusted to give a radius ratio $r_{BB}/r_{AA} = 1.2$, with $r_{AB} = \frac{1}{2}(r_{AA} + r_{BB})$, and the minimum energy configuration of the system (typically containing 800–1800 atoms) was found using the standard method of conjugate gradients. Starting from segregated or randomly mixed close-packed configurations, two types of external driving force were considered: (i) Irradiation-induced randomization: From the initial configuration, random nearest-neighbor pairs were selected, and their positions switched; this process has been previously used in Monte Carlo simulations [21] to the same end. The minimum energy configuration was recalculated after each such switch. (ii) Mechanical alloying: From the initial configuration, shear deformation was applied by explicitly repositioning the atoms through self-affine transformations. After each of these small strain increments, the minimum energy configuration of the system was recalculated. To maintain reasonable system aspect ratios (≤ 4), the structures were periodically halved and stacked back upon themselves as in Ref. [22].

It is important to emphasize that in all of these simulations thermally activated motion of any kind is strictly prohibited; all results discussed below occur only as a consequence of the external forcing.

To quantify the system evolution, we employ a short-range order parameter Ω :

$$\Omega = \frac{\frac{c}{1-c} N_A^B + \frac{1-c}{c} N_B^A}{N_A^A + N_B^B} - 1, \quad (3)$$

where $c = 0.5$ is the number fraction of A atoms, and N_i^j are the average number of nearest neighbors of type j around atoms of type i ($i, j = A$ or B). This definition conveniently separates segregated ($\Omega = -1$), randomly mixed ($\Omega = 0$), and short-range ordered ($\Omega = 1$) systems, as well as the full spectrum of intermediate states. With this parameter, the structural configuration is readily tracked as a function of simulated time, as shown in Fig. 2. Regardless of the initial state of the system, extrinsic forcing drives it through a transient period to a stationary state that depends on the system heat of

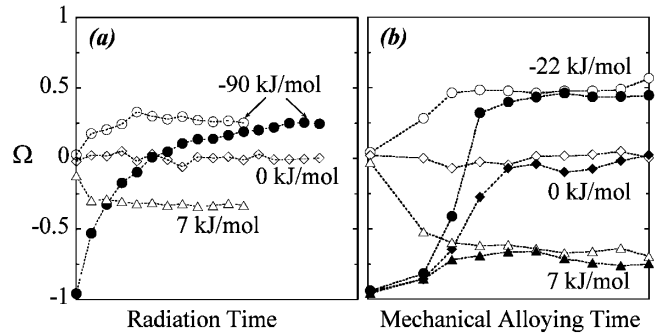


FIG. 2. Evolution of chemical order in driven systems at 0 K, starting from random solid solutions (open points) or segregated bilayers (solid points). For both irradiation (a) and mechanical alloying (b), structures obtain a steady-state configuration independent of the starting conditions, but dependent on the system heat of mixing (shown next to each data set). The x axis has been arbitrarily scaled for clarity of presentation.

mixing. It is of particular importance that the steady-state order parameters for these systems are unequivocally different from zero for nonzero heats of mixing; the structures have nonrandom chemical mixity, as also observed qualitatively in Fig. 3. Systems with negative heats of mixing [Figs. 3(a) and 3(b)] show a noticeable tendency towards chemical ordering; those with zero heat of mixing [Fig. 3(c)] exhibit no such preference; and in those with a positive heat of mixing [Fig. 3(d)] there is clear visual evidence for chemical demixing. It is interesting to

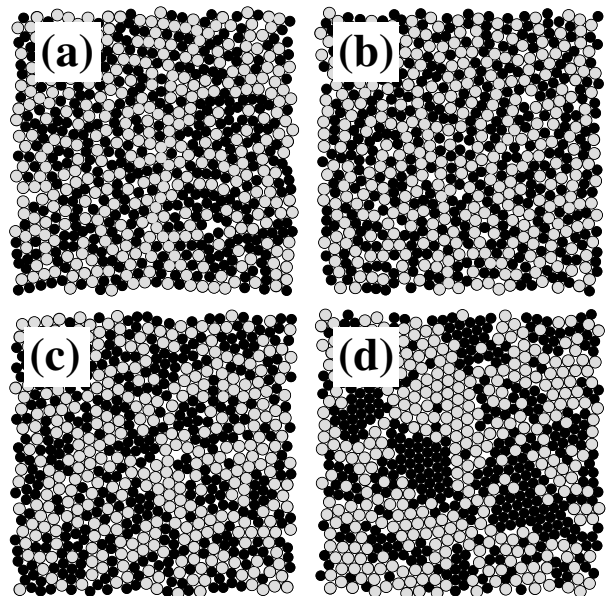


FIG. 3. Steady-state atomic configurations for irradiated [(a),(d)] and mechanically alloyed [(b),(c)] systems. The development of ordered or segregated steady-state structures is determined by the system heat of mixing, (a) -90 , (b) -22 , (c) 0 , and (d) 7 kJ/mol.

note that these systems were not constrained to a single coherent lattice, and atomic-level stresses and the attendant athermal relaxation of them led to the formation of defects, including incoherent grain and phase boundaries, and even amorphous structures; the issue of atomic coherency will be discussed at more length later.

The qualitative illustrations in Fig. 3 together with the quantitative values of Ω in Fig. 2 demonstrate that the structural transformations observed in driven alloys at 0 K are conspicuous. This result is in clear opposition to the generally accepted expectations of driven alloy theory [e.g., Eq. (1)], which predicts only random structures ($\Omega = 0$) to be kinetically stable in the athermal limit. We believe that the disagreement between our simulations and the established theory is due to the assumption that random extrinsic forcing necessarily gives rise to perfectly random atomic mixing. We propose that in incoherent systems (i.e., systems with local stresses due to either an atomic size mismatch or a high density of crystalline defects) atoms have a microscopic degree of freedom to select their preferred nearest neighbors whenever there is a force enabling their motion. Since there is no fixed lattice site for a given atom, subatomic translations enable the formation of preferred bonds; the trajectory of a randomly forced atom is influenced by its neighborhood because off-lattice trajectories are possible.

Our results suggest a driven system can move towards static equilibrium due not only to thermally activated diffusion, but also intrinsically as a result of nonrandom motions during the ballistic mixing process. As a simple illustration of this effect we propose that Δ could be modified as

$$\Delta' = \frac{D_b}{D_t + d_b}, \quad (4)$$

in which d_b is introduced as an intrinsic diffusivity quantifying the tendency towards equilibrium in the absence of thermal diffusion. This term is introduced in the denominator because it acts similarly to thermally activated diffusion, and as a first-order linear kinetics approximation we take its contribution to be additive. For the present simulation results to have meaning within this model, T_{eff} must have a finite value at $T = 0$ K. Examining Eqs. (1) and (4), we find that if d_b has a temperature dependence greater than $O(T)$, then T_{eff} will still diverge to infinity at $T = 0$ K. In the converse case where d_b has a temperature dependence smaller than $O(T)$ or is temperature independent, then $T_{\text{eff}} \rightarrow 0$ in the athermal limit; this would imply that the extrinsic driving has no impact on the steady-state configuration, which is clearly not the case for any driven alloy. We suggest that the simplest reasonable form for d_b is therefore a linear proportionality to temperature. Considering the limit of Eq. (1) as $T \rightarrow 0$ then yields

$$T_{\text{eff}} = T \left[1 + \frac{D_b}{D_t + D_b(T/T_0)} \right], \quad (5)$$

where T_0 is derived as the finite limit of T_{eff} as $T \rightarrow 0$. This form is identical to Eq. (1) with the substitution of $\Delta' = T_0\Delta/(T\Delta + T_0)$ for Δ . Here T_0 is a new control parameter that quantifies the relative strengths of the randomizing and equilibrating tendencies of ballistic diffusion. The form of Eq. (5) is plotted in Fig. 1 with various values of T_0 . High values of T_0 correspond to more intensely randomizing processes, and in the limit $T_0 \rightarrow \infty$ the process is fully randomizing and Eq. (1) is recovered. Low values of T_0 describe gentler mixing processes that need not result in random structures at any temperature. We note that the introduction of a process-dependent T_0 for mixing problems is consistent with recent work identifying an effective temperature for athermal shear flow of jammed particulate systems [12], suggesting a broad generality of these concepts for driven systems. However, the usual approach of using a single kinetic control parameter (i.e., D_b) is clearly insufficient in general.

One major consequence of the above developments is that even in the athermal limit the structure of a driven alloy can be predicted with a law of corresponding states. At $T = 0$ K a driven alloy has the equilibrium structure of a nondriven alloy at $T = T_0$. To further validate that ballistic mixing behaves as an effective temperature, we have performed Monte Carlo simulations using the same atomic interaction potentials described above. In these simulations there is no external driving, and the equilibrium configuration of the system is determined as a function of temperature only. To best compare with the static molecular simulations described above, we model a two-dimensional close-packed grid with periodic boundary conditions and equiatomic composition. The results of these Monte Carlo simulations are presented in Fig. 4, where the chemical ordering (Ω) is plotted as a function of system heat of mixing for multiple temperatures ranging from $T = 0.1$ – 10^6 K. Also shown for comparison are the results of the mechanical alloying simulations, which were performed at $T = 0$ K. As expected on the basis of Eq. (5), the mechanical alloying data agree well with the Monte Carlo simulations at a finite temperature ($T_0 \approx 2000$ K). This confirms that a law of corresponding states is valid, but must converge to a finite effective temperature in the athermal limit.

The conclusion drawn above, that extrinsic forcing acts essentially in the same way as temperature, is consistent with competing Kawasaki spin exchange dynamics [23,24] used in kinetic Ising-type models [9]. In driven systems using these dynamics the extrinsic driving force is literally taken as equivalent to kT_0 as we define it here, and the probability of a ballistic atomic exchange is based upon the change in system energy. This approach has been explicitly discarded by some authors for driven systems

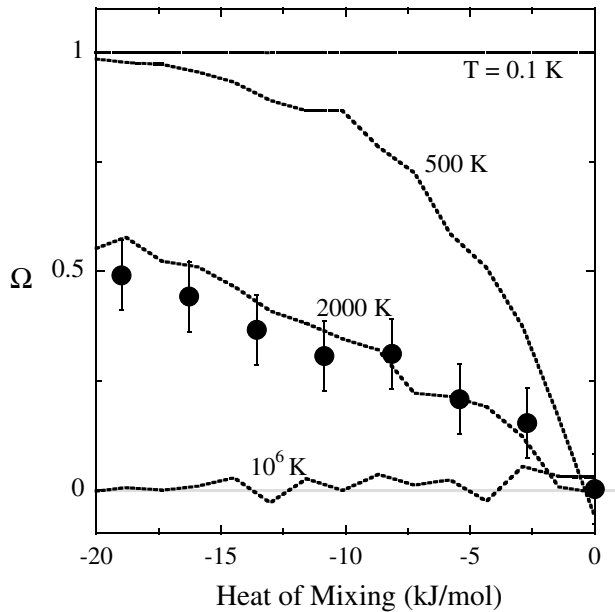


FIG. 4. Demonstration of the equivalence between a driven alloy at 0 K and a thermally equilibrated alloy at a finite temperature. The dashed lines are from Monte Carlo simulations of nondriven alloys, while the data points are from molecular simulations of mechanical alloying in the absence of temperature.

[1], on the grounds that atoms have no prescience as to their ultimate energy change after a ballistic jump. Similarly, other authors [9] have stipulated that the extrinsic driving energy (i.e., kT_0) is infinite, in line with the standard assumption that driving processes are inherently randomizing. Again, the present results demonstrate that even under random forcing atoms prefer some exchanges to others; we propose that competing Kawasaki dynamics, or some variation thereof, may provide a simple means of capturing these effects in Monte Carlo simulations.

Unlike the above results from mechanical alloying (giving $T_0 \sim 10^3$ K), we have found that a very high value of $T_0 > 10^4$ K characterizes the data from our irradiation simulations, suggestive of a considerably more randomizing process. This shows that T_0 is a process-dependent variable that may be experimentally tailorable, and by extension the steady-state alloy configuration should be as well. Although it is beyond the scope of this Letter, we mention in passing that T_0 also has a clear dependence on radius mismatch, suggesting that incoherency and atomic-level stresses play a strong part in an alloy's

intrinsic ability to order or segregate under external forcing. This indicates that lattice Monte Carlo simulations may be fundamentally limited in their ability to model the full range of driven alloy behavior, since they implicitly assume full coherency. As a final note, we emphasize that the mathematical developments above are meant only as a qualitative first approximation for what is clearly a complex problem. Although our findings require that some correction must be made to the current theoretical framework, we expect that future research will refine the mathematical description of these systems.

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