Comment on "Calculation and Simulation of Chemical-Diffusion Coefficients: The Inadequacy of the Mean-Field Theory"

In a recent Letter [1], Atzmon has shown that mean-field (MF) theories cannot accurately describe diffusion under large driving enthalpies $|\eta| = |\Delta H_{mix}/k_B T| \gtrsim 1$. The particular model used in his calculations and simulations is atom-exchange dynamics with a heat-bath transition probability $\exp(-\Delta\epsilon/k_B T)[1+\exp(-\Delta\epsilon/k_B T)]^{-1}$, where $\Delta\epsilon$ is the energy change on exchanging atoms. While the breakdown of MF theory demonstrated in Ref. [1] is quite general, we show here that the detailed nature of the diffusivity outside the linear-response regime depends quite sensitively on the particular dynamics of the system of interest. In particular, a simple atomistic model incorporating the exponential activation of diffusive hopping leads to an exponential growth of $|D|$ with increasing $|\eta|$ rather than the saturated kinetics of heat-bath Monte Carlo simulations observed in Ref. [1].

In the absence of a thermodynamic driving force, the jump rate of atoms over an intervening energy barrier $\Delta E \gg k_B T$ and into nearest-neighbor sites is conveniently written [2] as $\nu = \nu_0 \exp(-\Delta E/k_B T)$, where ν_0 is an attempt frequency. In a simple model of a nonideal solution, the energy barrier to diffusive jumping is raised or lowered by half the atomic energy change on hopping so that the rate of jumping becomes $\nu\exp(-\Delta\epsilon/2k_B T)$. Unlike the heat-bath dynamics, this does not saturate with increasingly negative $\Delta\epsilon$ (in most physical systems $\Delta\epsilon \ll \Delta E$). The behavior suggests a Monte Carlo dynamics in which all atom pairs exchange at an *exponential rate* proportional to $\exp(-\Delta\epsilon/2k_B T)$ (in inverse Monte Carlo steps). This dynamics is not limited by the rate at which atoms are picked. Using an appropriate modification of Eq. (7) in Ref. [1], we have calculated the atomic fluxes, which are proportional to ∇c for small gradients, and the resulting diffusion coefficients as a function of η. These are compared in Fig. 1 with the results of Ref. [1]. The new dynamics show an exponential change of D with $|\eta|$, instead of the saturation observed with the heat-bath Monte Carlo dynamics. In metallic alloys, the detailed non-mean-field behavior of the diffusion coefficient at high driving forces will likely depend on effects such as vacancy generation and trapping. However, there is no physical mechanism in the atomic jump process which gives saturation when the enthalpy of mixing is comparable to $k_B T$. At high thermodynamic driving forces, the behavior of heat-bath Monte Carlo simulations with atom exchange is fundamentally different than the behavior of systems with diffusive hopping over a large energy barrier.

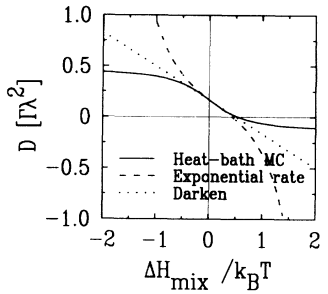

FIG. 1. Diffusion coefficients of heat-bath Monte Carlo and exponential-rate dynamics compared to Darken prediction.

Finally, as an aside, we note that Tu's nonlinear mean-field theory [3] discussed in Ref. [1] employs $\nabla\mu$ as a thermodynamic driving force which combines contributions from the configurational entropy with those from enthalpy and vibrational entropy. However, the role of configurational entropy is fundamentally distinct from that of the other two and can be separately incorporated into diffusion equations which go beyond linear-response theory [2].

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