Effects of ballistic atom movements on ordering transitions of binary alloys

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We studied chemical order-disorder transitions in equiatomic alloys on a square lattice in the presence of both thermal and ballistic atom movements. Using Monte Carlo simulations with a vacancy mechanism, we determined the steady states of the alloys for various combinations of $f$ (fraction of ballistic atom movements) and $T$ (temperature), and located the order-disorder phase boundary on a diagram of $T$ vs $f$. For symmetric interatomic potentials, the dynamical critical temperature decreased with $f$ as $(1 - 1.58f)$ when $f \leq 0.36$, and decreased rapidly with $f$ when $0.36 < f \leq 0.43$. No ordered phase was stable at any temperature when $f$ was greater than a critical value of $f_c^o > 0.43$. An Onsager-type kinetic rate equation was modified to include ballistic atom movements, and was used to identify two reasons why the ballistic atom movements dilute the enthalpy driving force for ordering, and (2) at low temperatures the ratio of thermal mobility coefficient to ballistic mobility coefficient becomes small.

I. INTRODUCTION

High-energy ball milling$^1$ and high-energy ion bombardment$^2$ are popular methods for synthesizing alloys in states far from thermodynamic equilibrium. In these energetic processes, some atom movements occur athermally in response to defects generated by the milling process or by nuclear collisions. Atoms in these “driven” alloys are forced out of local environments characteristic of their thermodynamic distribution. Acting in parallel are the usual thermal movements, which tend to restore these thermodynamic environments. Because both kinetic processes are Markovian, a steady state will be achieved eventually. This steady state is termed a “dynamical steady state” to distinguish it from the steady state of thermodynamic equilibrium.

To model these dynamical phenomena, Martin and co-workers proposed a model of driven systems that is amenable to study by analytical methods and computer simulations.$^4$ In this model, the ballistic atom movements are assumed to occur at random, while the thermal atom movements follow conventional activated state rate theory. Much work was devoted to constructing and elucidating the properties of a “stochastic potential,” which is the analogy for a driven alloy of the free energy for a thermodynamic alloy.$^4$ This stochastic potential is sensitive to features of the kinetic mechanism; a dependence of the dynamical critical temperature on the details of replacement collision sequences was found previously.$^5,9$ The stochastic potential is also sensitive to the nature of the approximations (point or pair, for example) used in the analytical theory, however.

In the present study, we used Monte Carlo simulations with a vacancy mechanism for both the thermal and ballistic atom movements. The vacancy mechanism provides a richness of kinetic features that are not available with the pair interchange mechanism, and offers new ways by which the mechanism of atom movements can affect the dynamical steady state of the alloy.$^9$ Especially at low temperature, however, the vacancy mechanism exhibits subleties of behavior that cannot be included in analytical theories based on approximations with small cluster variables. The present work examined how the strong diffusional correlation factors unique to the vacancy mechanism$^{12-17}$ affect the phase boundary between ordered and disordered phases at various temperatures, $T$, and fraction of ballistic atom movements, $f$. Our results suggest a simple but general picture of how the shape of a dynamical phase boundary can be affected by a combination of thermodynamic and kinetic effects.

II. MONTE CARLO SIMULATIONS

Monte Carlo simulations were performed with equiatomic alloys on a square lattice with periodic boundaries. The typical lattice had $N = 256 \times 256 = 65,536$ sites, but larger lattices of 262,144 sites were also used. We included only first-nearest-neighbor (1nn) pairwise interactions between the two species of atoms, $A$ and $B$. The 1nn $M$-$N$ ($M,N = A$ or $B$) pair potential is denoted by $V_{MN}$ (its units are $kT$). The $1nn$ pairwise exchange potential $V$ is defined as

$$V = (V_{AA} + V_{BB} - 2V_{AB})/2.$$  \hspace{1cm} (1)

For all results reported here, we fixed $V_{AB} = 0$. We also used $V_{AA} = V_{BB} > 0$ (so $V = V_{AA} = V_{BB}$), unless otherwise specified. The pairwise exchange potential, $V$, sets the thermodynamic critical temperature $T_c^o$. For thermodynamic alloys without ballistic atom movements ($f = 0$), it is known that$^{18}$

$$T_c^o = \frac{V}{0.88}$$ \hspace{1cm} (2)

exactly, or

$$T_c^o = \frac{V}{0.5}$$ \hspace{1cm} (3)
in the mean-field Bragg-Williams approximation. It is the
goal of this study to investigate how the critical tem-
perature is altered by ballistic atom movements when
\( f \neq 0 \).

Each kinetic step occurred with a vacancy mechanism
algorithm,\textsuperscript{14–16} modified to include ballistic atom
movements. All sites of the lattice were occupied by \( A \) and \( B \)
atoms, except for one site left unoccupied as a vacancy.
An atom could move by exchanging its position with a
neighboring vacancy. To include ballistic atom move-
ments, a random number \( R \) was first chosen, where
\( 0 \leq R < 1 \). If \( R < f \) (\( f \) is the fraction of ballistic atom
movements), the atom movement was determined to be
ballistic. If so, the vacancy had an equal probability of
exchanging sites with any of its Inn atoms, and one of the
Inn atoms was chosen at random. Otherwise the
movement was a thermal movement, and every neighboring
atom had its own thermal movement frequency \( \omega_j \). The
thermal movement probabilities \( \{ P_j \} \) were set by the
competition among all \( z \) Inn atoms (\( z \) is the Inn coordi-
nation number, equal to 4 for the square lattice):
\[
P_j = \frac{\omega_j}{\sum_{j'} \omega_{j'}} . \tag{4}
\]
Using these thermal atom movement probabilities \( \{ P_j \} \) as
weights, the Monte Carlo algorithm then selected at ran-
don one of the neighboring atoms to exchange sites with
the vacancy. The thermal movement frequencies \( \{ \omega_j \} \)
were calculated with activated state rate theory:
\[
\omega_j \propto \exp \left( \frac{E_j}{kT} \right) . \tag{5}
\]
Here \( E_j \) is the initial bond energy for the \( j \)th neighboring
atom:
\[
E_j = N_{AA} V_{AA} + N_{BB} V_{BB} + N_{AB} V_{AB} , \tag{6}
\]
with \( N_{MN} \) defined as the number of \( M-N \) bonds
\((M,N = A \text{ or } B)\) to the \( j \)th atom. Note that \( E_j \) [Eq. \((6)\)],
and therefore \( \omega_j \) [Eq. \((5)\)] and \( P_j \) [Eq. \((4)\)], are dependent
on the particular local environment of each atom.

All simulations started from an initially random
arrangement of atoms (characteristic of a quench from
\( T = \infty \) unless otherwise specified. The simulated lattice
was examined periodically to obtain Warren-Cowley
short-range order (SRO) parameters \( \{ \alpha(r) \} \),\textsuperscript{19} an average
domain length scale \( \langle r \rangle \) and the long-range order (LRO)
parameter \( L \). The SRO parameter \( \alpha(1) \) was computed by
counting the number of all \( A-B \) pairs \( N_{AB} \), and \( \alpha(2) \) was
obtained by counting the \( 2 \times 2 \) \( A-B \) pairs, \( N_{AB2} \):
\[
\alpha(1) = 1 - \frac{N_{AB}}{N} , \tag{7a}
\]
\[
\alpha(2) = 1 - \frac{N_{AB2}}{N} , \tag{7b}
\]
where \( \alpha(1) = \alpha(2) = 0 \) for the disordered state, and
\( \alpha(1) = -\alpha(2) = -1 \) for perfect order. The LRO pa-
rameter, \( L \), was obtained by a simulated x-ray-diffraction pro-

The autocorrelation function, \( A \otimes A(R) \), was calculated
for various magnitudes \( |R| \) (where \( |R| = \sqrt{R_x^2 + R_y^2} \)),
and then averaged over the \( x \) and \( y \) directions. We de-
termined the zero crossing on graphs of the averaged
\( A \otimes A \) versus \( |R| \). This value of \( |R| \) at the zero crossing
was defined as the characteristic length for the ordered alloy
\( \langle r \rangle \).

Our interest was in determining the steady states of
the alloys, not their kinetic behavior. This required moni-
toring the state of order in the alloy during the simulation
to ensure that \( L \) did not change if the simulation proceeded
further, except for expected fluctuations. To ensure that
the steady state was attained, we typically waited for
times that were a factor of 10 longer than the time for
which the steady-state value of \( L \) was first detected. In
several cases we confirmed that the steady states were
indeed correct by starting the simulations with the alloys
having perfect ordered structures, and verifying that the

\[
I(k) = \left| \sum_{\text{all sites}} f_{\text{at}}(r) \exp(-i \mathbf{k} \cdot \mathbf{r}) \right|^2 . \tag{8}
\]
Here \( f_{\text{at}}(r) \) is the atomic form factor for the atom at site
\( r \), and \( f_{\text{at}} = 1 \) for \( A \) atoms and \( f_{\text{at}} = 0 \) for \( B \) atoms. The
lowest order superlattice diffraction peak corresponding
to the checkerboard ordered structure on a square lattice
is \( (\frac{1}{2}, \frac{1}{2}) \), while the lowest order fundamental peak is \((1,0)\).
The intensities of these peaks, \( I_{10} \frac{1}{2} \frac{1}{2} \), and \( I_{10} \), were ob-
tained by integrating \( I(k) \) over a square around their centers
in \( k \) space of edge length \( 2\pi/(16a) \) (\( a \) is the lattice
constant of the square lattice). The LRO parameter
\( L \) was then obtained from the intensities in the usual way:
\[
L = \left( \frac{I_{10} \frac{1}{2} \frac{1}{2}}{I_{10}} \right)^{1/2} , \tag{9}
\]
where \( 0 \leq L \leq 1 \), with 1 corresponding to perfect order.

To determine a characteristic length of the ordered
domains, \( \langle r \rangle \), we calculated a real-space autocorrelation
function after the alloy was transformed as follows.

The autocorrelation function of the transformed alloy,
\( A \otimes A \), was then calculated by

The autocorrelation function, \( A \otimes A(R) \), was calculated
for various magnitudes \( |R| \) (where \( |R| = \sqrt{R_x^2 + R_y^2} \)),
and then averaged over the \( x \) and \( y \) directions. We de-
termined the zero crossing on graphs of the averaged
\( A \otimes A \) versus \( |R| \). This value of \( |R| \) at the zero crossing
was defined as the characteristic length for the ordered alloy
\( \langle r \rangle \).
same order parameters were eventually attained as for the
cases of initially disordered alloys. Finally, we note that
our approach of fixing the fraction, $f$, may seem different
from previous work that used a constant rate of ballistic
jumps. For example, the thermal jump rate depends
on the state of order in the alloy, so a constant ballistic
jump rate may be more appropriate for determining the
kinetics of the alloy. For determining the steady states of
a given alloy, however, both methods must provide the
same result, since both $L$ and $f$ are constant in steady
state, and are set by temperature and the ballistic jump rate.
In particular, we expect the steady-state critical
temperature to be the same with either approach.

### III. MONTE CARLO RESULTS

We performed a series of Monte Carlo simulations
with variable $V$ and fixed $f$. Typical results are presented
in Fig. 1. For the thermodynamic case with $f=0$, the
critical temperature, $T^c_0$, was identified with the inflection
point of the curve to be near $V/kT=0.88$, consistent with
Eq. (2). There are many similarities between the $L$ vs $V$
curves for $f=0$ and for some cases of $f>0$, although the
ballistic atom movements tend to disorder the alloy and
suppress the critical temperature. The critical temperatures,$T^c_f$, were determined for $f>0$ either by identifying
the inflection points of the $L$ vs $V$ curves, or by locating the
points where $L$ had the same value as at $T^c_0$ when
$f=0$. Numbers obtained from both methods agreed well,
and we do not distinguish them hereafter. On the other
hand, the $L$ vs $V$ curve for $f=0.55$ has an almost flat and
featureless shape, and is quite different from the curves
for $f=0$, 0.2, and 0.35. When $f=0.55$, the largest value
of $L$ was no more than 0.2, even for temperatures as low
as $V/kT=100$. Direct observations showed that the
lattice had only small ordered domains and no long-range
ordering. Evidently there is no ordering transition at any
temperature when $f=0.55$.

We also performed a series of Monte Carlo simulations
with variable $f$ and fixed $V$. Figure 2 shows typical $L$ vs $f$
curves for different $V$. Qualitatively, the shapes of
these curves are reminiscent of curves of $L$ vs $T$. Again,
by examining the inflection points of the curves, or by
matching values of $L$ to those on the curve for $f=0$, critical
values of $f$ for the ordering transition, denoted $f_c$, were
determined. For example, for $V/kT=1.5$ and 2,
$f_c=0.275$ and 0.355, respectively. Figure 2 shows that
with reduced temperature, the curves of $L$ vs $f$ shift to-
wards the right on Fig. 2, and converge toward the curve
for $V/kT=100$. Accordingly, the critical fraction of
ballistic atom movements $f_c$ increases and approaches an
ultimate limit $f^c$, as discussed below.

For ordered alloys at low values of $T$ and $f$, there still
remains the question of whether the ordered domains
tend towards infinite length. This question cannot be
answered rigorously with Monte Carlo simulations on
finite systems, but we did perform some tests by extrap-
olation. The characteristic length of ordered domains,
$\langle r \rangle$, was calculated as described in Sec. II, and Fig. 3(a)
shows typical data on $\langle r \rangle$, in units of the lattice con-
stant, as a function of $f$ at temperatures above $T^c_f$ (or
equivalently, for $f>f_c$). The two curves of $\langle r \rangle$ vs $f$
were obtained at fixed temperature, and so are labeled
with their individual value of $V/kT$. As $f$ approaches $f_c$,

**FIG. 1.** The steady-state LRO parameter, $L$, as a function of
$V$ (i.e., inverse temperature) with $f=0$ (triangles), $f=0.2$ (cir-
cles), $f=0.35$ (squares), and $f=0.55$ (diamonds). The data
point labeled with "$V/kT=100$" was for $f=0.55$ and $V=100$.

**FIG. 2.** The steady-state LRO parameter $L$ as a function of $f$
at various temperatures. Each curve is marked with its value of
$V/kT$.

**FIG. 3.** (a) The steady-state average domain length scale $\langle r \rangle$,
and (b) its reciprocal $1/\langle r \rangle$ as functions of $f$ at $V=1.5$
(squares) and $V=2$ (circles), respectively.
from above, \( \langle r \rangle \) increases rapidly and approaches a size comparable to the size of the lattice in the simulation. With analogy to a thermodynamic alloy, we might expect \( 1/\langle r \rangle \) to decrease linearly with \( -f \) as \( f \) approaches \( f_c \). Figure 3(b) presents curves of \( 1/\langle r \rangle \) vs \( f \) corresponding to the curves in Fig. 3(a). The plateaus at \( 1/\langle r \rangle = 0.33 \) and 0.25 correspond to integral changes in \( \langle r \rangle \) from 3 to 4, and are not significant. For larger \( \langle r \rangle \), however, there seems to be a linear decrease of \( 1/\langle r \rangle \) as \( f \) approaches \( f_c \). Extrapolating the linear parts of both curves to \( 1/\langle r \rangle = 0 \) gives \( f_c = 0.261 \) and 0.338 for \( V/kT = 1.5 \) and 2, respectively. These values are reasonably close to those obtained from the curves of \( L \) vs \( f \) in Fig. 2.

We compared the dynamical critical temperatures, \( T_c' \), that were determined from the data of \( L \) vs \( V \) and from the data of \( T \) vs \( V \). The values of \( T_c' \) from all curves in Fig. 2 are presented as solid circles in Fig. 4. The left axis of Fig. 4 is temperature, normalized by the thermodynamic critical temperature \( T_c^0 \) of Eq. (2). Also presented in Fig. 4 as open squares are some results from data of \( L \) vs \( V \). These two sets of data are in excellent agreement. Figure 4 is the \( T \)-\( f \) phase diagram for the steady states of our driven alloy. The solid curve separates the regions of ordered and disordered phases. At \( f = 0 \), the dynamical phase diagram provides the thermodynamic critical temperature of Eq. (2). The ordered phase is stable for small values of \( T \) and \( f \), whereas the disordered phase is stable for large values of \( T \) and \( f \). Slightly below the phase boundary, the LRO is imperfect. Slightly above the phase boundary, there is significant SRO. This is typical of a second-order phase transition, and the continuous curves of Figs. 1 and 2 do imply that the transition is of second order for all \( f \).

The nearly linear part of the phase boundary in Fig. 4, between \( f = 0 \) and \( f = 0.36 \), was fit to a straight line with a slope of \(-1.58 \pm 0.01\):

\[
T_c' = -(1 - 1.58f) T_c^0 .
\]

(11)

As \( f \) increased beyond this nearly linear region, \( T_c' \) decreased dramatically. At \( f = 0.43 \), \( T_c' = 0.01 \) \( T_c^0 \). A logarithmic extrapolation to zero temperature of the dashed curve in Fig. 4 provides an ultimate fraction of ballistic atom movements, \( f_c^0 = 0.43 \), beyond which ordering does not occur at any temperature.

IV. STEADY STATES WITH BALLISTIC AND THERMAL MOVEMENTS

Here we develop a simple but general analytical theory for the steady state of an ordering alloy in the presence of both ballistic and thermal atom movements. The approach is similar to that of Martin.21 We use Onsager-type kinetic rate equations, suitably modified to include ballistic atom movements. Onsager-type kinetic rate equations allow us to neglect the details of atom movement mechanisms, thereby simplifying the problem. Nevertheless, this approach should be valid near the steady state of the alloy when \( dL/dt \) is zero or nearly zero, which is our present interest for interpreting phase boundaries. We write the time dependence of the LRO parameter for the thermodynamic alloy (\( f = 0 \)) as

\[
\frac{dL}{dt} = -\frac{1}{kT} \frac{\partial F}{\partial L} ,
\]

(12)
or equivalently,

\[
\frac{dL}{dt} = -\frac{1}{kT} \frac{\partial E}{\partial L} + \frac{1}{k} \frac{\partial S}{\partial L} ,
\]

(13)

where \( l \) is the mobility coefficient. \( F \) and \( E \) denote the Helmholtz free energy and enthalpy, respectively. At steady states, \( L \) does not change with time. Therefore,

\[
T \frac{\partial S}{\partial L} = \frac{\partial E}{\partial L} .
\]

(14)

In a mean-field thermodynamic calculation (\( f = 0 \)), the contributions to \( \partial F/\partial L \) are

\[
\frac{\partial E}{\partial L} = \frac{N}{2} zLV ,
\]

(15)

and

\[
T \frac{\partial S}{\partial L} = T \ln \left( \frac{1-L}{1+L} \right) ,
\]

(16)

It is straightforward to take the mean-field thermodynamic expressions of Eqs. (15) and (16), substitute them into Eq. (14), and recover the mean-field critical temperature \( T_c^0 \) of Eq. (3).

For a driven alloy having a fraction of ballistic atom movements, \( f \), the fraction of thermal atom movements is \( 1-f \). For the thermal atom movements alone, Eq. (13) becomes

\[
\frac{dL}{dt}_{\text{thermal}} = -\frac{1}{k} (1-f) \left[ \frac{1}{T} \frac{\partial E}{\partial L} - \frac{\partial S}{\partial L} \right] .
\]

(17)

Because the random ballistic atom movements are assumed to occur at infinite temperature, we have

\[
\frac{dL}{dt}_{\text{ballistic}} = -\frac{l}{k} f \left[ \frac{1}{\infty} \frac{\partial E}{\partial L} - \frac{\partial S}{\partial L} \right] ,
\]

(18)
or
\[
\frac{dL}{dt_{\text{ballistic}}} = \frac{l'}{t} \int^\frac{\Delta S}{\partial L}
\]
for the ballistic atom movements. Equation (19) is an entropy contribution. The enthalpy contribution is zero because the ballistic atom movements are independent of temperature and local environment.

It is important to note that the Onsager mobility constants in Eqs. (13) and (19) are different. As discussed in Sec. V, we expect the thermal atom movements to be increasingly correlated at low temperatures, whereas the ballistic atom movements are not. We define \(\zeta\) as the ratio of mobility coefficients for the ballistic and thermal atom movements:
\[
\zeta \equiv \frac{l'}{l}.
\]

It was found in a previous study with the vacancy mechanism that the mobility of the vacancy was enhanced by ballistic atom movements,\(^1\) so we expect \(l' > l\) and \(\zeta > 1\).

Combining Eqs. (17), (19), and (20), we write a complete kinetic equation for the driven alloy:
\[
\frac{dL}{dt} = -\frac{l}{kT(1-f)} \frac{\Delta E}{\Delta L} + \frac{l}{k} \left[1 + (\zeta-1)f\right] \frac{\Delta S}{\partial L}.
\]

To obtain the steady-state value of \(L\) as a function of \(T\) and \(f\), we set Eq. (21) equal to zero and obtain:
\[
T \frac{1+(\zeta-1)f}{1-f} \frac{\Delta S}{\Delta L} = \frac{\Delta E}{\Delta L}.
\]

Consider first the case when \(\zeta = 1\), that is, the ballistic atom movements have the same mobility as the thermal atom movements. In this case Eq. (22) becomes
\[
T \frac{\Delta S}{\Delta L} = \frac{\Delta E}{\Delta L}.
\]

Upon comparison to Eq. (14), we see that the effective temperature, \(T_{\text{eff}}\), of the driven alloy is rescaled with respect to the thermal temperature, \(T\):
\[
T_{\text{eff}} = T \frac{1+(\zeta-1)f}{1-f}.
\]

Equation (24) true, the dynamical critical temperature of ordering, \(T_c'\), would decrease linearly with the fraction of ballistic atom movements by simple dilution, becoming zero when \(f'=1\):
\[
T_c' = (1-f)T_c^0.
\]

This rescaling of temperature is a consequence of the ballistic atom movements being insensitive to the enthalpy driving force [Eq. (19)]. This reduction of \(T_c'\) by a factor of \(1-f\) can be regarded as a dilution of the enthalpy driving force in the presence of the fraction, \(f\), of ballistic atom movements.

In general, however, mobility differences must be considered, and this provides a second means for the ballistic jumps to affect \(T_c'\). We expect \(\zeta \neq 1\), and in fact \(\zeta\) may be a function of \(T, f\) and \(L\). From Eq. (22) we write
\[
T_{\text{eff}} = T \frac{1+(\zeta-1)f}{1-f},
\]
and
\[
T_c' = \frac{1-f}{1+(\zeta-1)f}T_c^0.
\]

There is no simple scaling of the critical temperature with \(f\) unless \(\zeta(T, f, L)\) has a simple form. A precise estimate of \(\zeta\) is not trivial, and we have not attempted to do so. On the other hand, we have used our Monte Carlo results for \(T_c^0\) (Fig. 4) to determine \(\zeta\).

V. DISCUSSION

The analysis of Sec. IV relies on a single order parameter \(L\) to characterize the microstructures of the driven alloy. It is appropriate to ask if a single LRO parameter is adequate to characterize the microstructures of the driven alloys, or if the steady-state microstructures of alloys having the same value of \(L\), but subjected to different combinations of \(T\) and \(f\) may have different order parameters on short length scales. To address this concern, we compared both the LRO and SRO parameters for the steady states of alloys with various combinations of \(T\) and \(f\). Figure 5 shows steady-state values of the SRO parameters \(\alpha(1)\) and \(\alpha(2)\) as functions of \(L\) for alloys with various combinations of \(T\) and \(f\). The curves are nearly identical. Direct observation of the alloys also confirmed that alloys with the same steady-state values of \(L\) were very similar in appearance. The LRO parameter \(L\) seems a reasonable single parameter for specifying the steady state of order in our driven alloys.

We now use the analytical approach of Sec. IV with its Onsager-type kinetic rate equation for \(L\) to interpret the Monte Carlo results of Fig. 4. For \(f \leq 0.36\) or \(V/kT \leq 2\), Eq. (11) describes our data well. By comparing Eqs. (11) and (27), we obtain
\[
\zeta \equiv \frac{l'}{l} = 1.58 \frac{(1-f)}{1-1.58f}.
\]

According to Eq. (28), the mobility ratio \(\zeta\) increases

![FIG. 5. SRO parameters, \(\alpha(1)\) and \(\alpha(2)\), vs LRO parameter, \(L\), for steady states of several alloys. \(\alpha(1)\): open marks against the left axis; \(\alpha(2)\): solid marks against the right axis. Squares: thermodynamic alloys \((f=0)\) at various \(T\); diamonds: driven alloys at various \(T\) with fixed \(f=0.35\); circles: driven alloys with various \(f\) at fixed \(V/kT=2\).](image-url)
slightly as $f$ increases. A much more dramatic increase in $\xi$ occurs when $f > 0.36$ or $V/kT > 2$. These increases in $\xi$ are not surprising for ordered alloys, however. At low temperatures (corresponding to large $f$ on the phase boundary of Fig. 4) thermal diffusion in ordered alloys becomes highly correlated and inefficient, effectively suppressing $f$. For thermodynamic ordering transitions on a square lattice, there are dramatic changes in vacancy mobility when $V/kT > 2$. At these low temperatures, the vacancy becomes trapped in local regions from which it has insufficient thermal activation for escape. We found the same type of vacancy trapping in the present study. At the lowest temperatures, the vacancy moved cyclically between a set of sites until it was dislodged by a ballistic atom movement. This high degree of diffusional correlation suppresses strongly the effective thermal mobility coefficient $l$. On the other hand, we do not expect the mobility coefficient for ballistic atom movements $l$ to change with temperature. We therefore expect the mobility ratio $\xi$ to increase with decreasing temperature, suppressing $T_c$ dramatically when $V/kT > 2$.

To investigate further these effects of vacancy mobility, we performed some Monte Carlo simulations with asymmetrical chemical interaction potentials between $A$ and $B$ atoms ($V_{AA} \neq V_{BB}$), while maintaining the same thermodynamic pair exchange potential $V$. It was established previously that diffusion coefficients, and therefore the effective mobility constants, will change when $V_{AA} \neq V_{BB}$. Figure 6 shows typical $L$ vs $f$ curves for the same thermodynamic potential, $V=2$, but for two different cases, one with $V_{AA} = V_{BB}$, and the other with $V_{AA} \neq V_{BB}$. Although the shapes of the curves are similar, the critical values of $f$ are quite different: $f_c = 0.20$ for the asymmetrical case, while $f_c = 0.35$ for the symmetrical case. This cannot be a thermodynamic effect, since Eqs. (2) and (3) depend only on $V$. The symmetry of the interatomic potentials must affect $f_c$ through the mobility coefficients. Correlated thermal vacancy motion can explain this behavior. Vacancy trapping is controlled by the strongest interatomic potential, so in the approximately linear region of Fig. 4, we expect $f_c$ to decrease by the factor of $\frac{1}{3}$ as $V_{AA}$ increases from 2 to 3. This is approximately correct.

**VI. SUMMARY**

We performed a Monte Carlo study of steady states in alloys with thermal and ballistic atom movements. A vacancy mechanism was used for atom movements in equiatomic alloys on a square lattice. A $T$-$f$ phase diagram for the order-disorder transition was constructed for alloys with symmetrical interatomic potentials ($V_{AA} = V_{BB}$). When $f < 0.36$, the dynamical critical temperature decreased by the factor $1 - 1.58f$ in the presence of a fraction of ballistic atom movements $f$. For $f$ greater than 0.36, but less than 0.43, the reduction of the critical temperature with $f$ was much more rapid, and the critical temperature became zero at a critical value of $f$, $f_c = 0.43$. An Onsager-type analytical theory was used to explain this behavior. The decrease in critical temperature with $f$ occurred for two reasons. First, in the presence of ballistic atom movements, the enthalpy driving force for ordering, $-\partial E/\partial L$, is diluted by the factor $(1 - f)$. Second, the mobility coefficient for thermal atom movements becomes small at low temperatures, owing to a high degree of correlation in the vacancy diffusion mechanism. The ballistic atom movements are not subject to this correlation factor, and so are relatively more important at low temperatures, leading to a dramatic drop of $T_c$ to zero near $f = 0.43$.

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