

Adiabatic molecular-dynamics-simulation-method studies of kinetic friction

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(Received 11 February 2005; published 28 June 2005)

An adiabatic molecular-dynamics method is developed and used to study the Muser-Robbins model for dry friction (i.e., nonzero kinetic friction in the slow sliding speed limit). In this model, dry friction between two crystalline surfaces rotated with respect to each other is due to mobile molecules (i.e., dirt particles) adsorbed at the interface. Our adiabatic method allows us to quickly locate interface potential-well minima, which become unstable during sliding of the surfaces. Since dissipation due to friction in the slow sliding speed limit results from mobile molecules dropping out of such unstable wells, our method provides a way to calculate dry friction, which agrees extremely well with results found by conventional molecular dynamics for the same system, but our method is more than a factor of 10 faster.

DOI: 10.1103/PhysRevE.71.066125

PACS number(s): 81.40.Pq, 78.20.Ci, 42.70.Qs, 42.30.Wb

I. INTRODUCTION

Static friction is the force needed to initiate motion between bodies. Dry friction is the kinetic friction in the slow sliding speed limit. Muser *et al.* argued that for clean incommensurate crystalline surfaces in contact there should be no static friction, unless there are mobile molecules present at the interface [1]. A dilute concentration of molecules, which is initially randomly distributed over surfaces, will, in time, move to the deepest interface potential wells. The deepest interface potential wells occur when potential minima from each of the two surfaces nearly coincide. When the two surfaces slide relative to each other, the locations of the potential minima no longer coincide and at some point an interface potential minimum can become unstable. At that point, a molecule in that well jumps into a deeper minimum. The occurrence of such instabilities is likely to be the source of energy dissipation due to kinetic friction in the slow sliding speed limit. When an instability occurs, the molecule moves a relatively large distance to the nearest stable well very rapidly and stays there. When a well remains stable, a molecule residing in it stays at almost the same place during the sliding of the two surfaces, if the surfaces are slid by equal amounts in opposite directions.

For a dilute concentration of mobile molecules, an iterative method, for treating the slow sliding speed limit for noninteracting molecules, was developed by Daly *et al.* [2], which is much faster than molecular dynamics. For interacting particles, however, this method is difficult to apply, and hence it is still necessary to use molecular dynamics. In the usual molecular-dynamics simulations (which we will refer to as conventional molecular dynamics or CMDS), we integrate Newton's laws numerically. Thus, in principle, we are able to study the precise motion of all the particles in a many-body system. In the problem that we are considering in the slow sliding speed limit, in which we are only interested in calculating the energy dissipation and the kinetic friction that produces it, we do not need the detailed information that we can obtain from CMDS. This is because in the slow sliding speed limit, each molecule always remains at a minimum of the interface potential, unless the potential well in

which a molecule resides becomes unstable (an unstable well is illustrated in Fig. 1). When this occurs, the molecule will drop down into a lower-energy potential well. The kinetic energy generated in this process is assumed to be rapidly converted to various excitations of the solids. We believe that this process is the main source of kinetic friction in the slow sliding speed limit. Therefore, in order to obtain the friction in the slow sliding speed limit, it is only necessary to study the evolution of the interface potential wells and to determine when a well becomes unstable, as the molecules that occupy such wells are the only ones that contribute significantly to the friction in the slow sliding speed limit. Therefore, we have developed an adiabatic molecular-dynamics simulation (AMDS) method, which saves a considerable amount of computer time by locating the unstable wells and then calculating the force of friction from the energy losses that occur as molecules drop out of unstable wells.

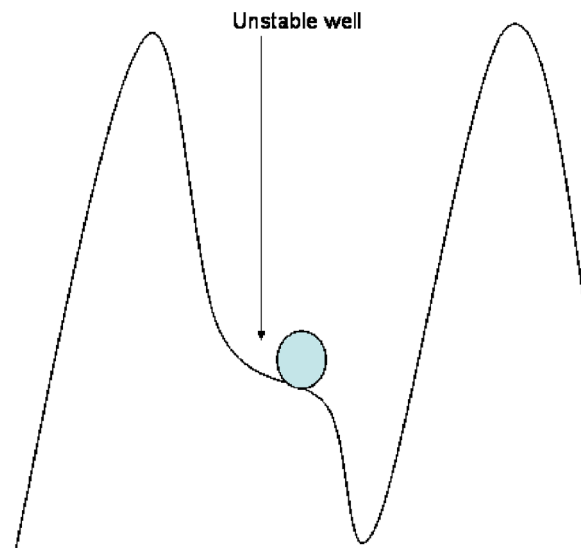


FIG. 1. An unstable potential well is illustrated.

II. ADIABATIC AND CONVENTIONAL MOLECULAR-DYNAMICS-SIMULATION METHODS

When we use the CMDS method to calculate kinetic friction in the slow sliding speed limit, we calculate all particles' positions by solving the equations of motion for all particles. In contrast, in the AMDS method, we divide the potential wells into two types—stable and unstable. We deal with the stable and unstable wells in different ways. For unstable wells, we still use CMDS. For stable wells, we use an adiabatic method. For stable potential wells during sliding from position s to $s \pm \Delta s$ (where the plus sign is for the upper and the minus sign is for the lower surface), we choose $\Delta s = 0.005a$ (a is a lattice constant of a surface), which is 50 times larger than the Δs value used in our CMDS calculations (done for comparison), for a surface-sliding speed of $0.001a/t_0$, where $t_0 = (ma^2/V_0)^{1/2}$ is the time scale in the CMDS method. Here V_0 is the strength of the surface potential and m is the mass of a molecule. For this small a value of Δs the location of the stable potential wells' minima do not change by much. In our slow sliding speed limit, the stable potential wells change smoothly, thus, the particles occupying these wells change equilibrium positions smoothly. The stable particles reach the new equilibrium positions in a relatively short time (compared to the time needed for the stable well changes) and hence the new equilibrium positions are very close to the old ones (see more details in the Appendix). Therefore, for stable particles we have found that we require only 100 iterations of the equation of motion to locate the new equilibrium positions for each sliding step Δs . If during the sliding from s to $s \pm \Delta s$, those stable wells occupied by particles become unstable, we must switch to the conventional method for a short time to deal with the unstable wells. When these particles finally jump into the nearest stable wells, we switch back to the adiabatic method. Since AMDS can use a relatively large sliding step and can locate the stable particles' new equilibrium positions much faster than the conventional method, the computer time needed for AMDS is much shorter than for conventional MDS, for the same problem. Let us now determine how much faster AMDS is than CMDS. Let us consider N particles. We will choose the surfaces sliding step $\Delta s = 0.005a$, and the time step $= 0.001t_0$ for one iteration. For each surface's sliding step Δs , we can count the average iteration number, defined as the number of iterations needed for the surfaces to slide by $\Delta s = 0.005a$, for AMDS and CMDS. For CMDS since the surfaces' sliding speed is chosen to be $0.001a/t_0$, the sliding distance for one iteration is $0.001 \times 0.001a$. So the iteration number of N particles for each Δs for CMDS is $0.005aN/(0.001 \times 0.001a) = 5000N$. To estimate the iteration number for the adiabatic method we have made use of the fact that it is only necessary to make 100 iterations for each Δs for a stable well; when we switch to the conventional method we have found that we only require about 500 iterations for each Δs for an unstable molecule to settle into a neighboring stable well. At each Δs if the average ratio of the number of stable particles to total number of particles is b , then the average number of stable particles is bN , and the average number of unstable particles is $(1-b)N$. Hence, the average iteration number for AMDS for a given Δs is

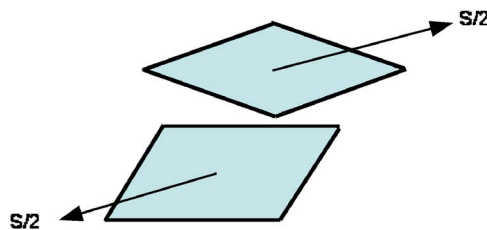


FIG. 2. Illustration of two parallel surfaces rotated with respect to each other and then slid symmetrically with respect to each other.

$100bN + 500(1-b)N$. Then at each Δs the ratio of the average iteration number for CMDS over AMDS is $5000N/[100bN + 500(1-b)N] = 50/(5-4b)$. So the AMDS is $50/(5-4b)$ times faster than CMDS. When b is large, the AMDS is much faster. That means when more potential wells are stable at each Δs , the AMDS is faster. Therefore, in our case, the AMDS must be at least more than 10 times faster than the CMDS.

During runs involving many interacting molecules, when one molecule becomes unstable, several of its neighbors become unstable as well. As a result, in such a situation it is necessary to integrate coupled equations for these particles using CMDS for about 500 iterations. For the positions of stable particles that appear in these equations of motion, we can use the old positions (i.e., before the Δs step that we initially do) to an excellent approximation, since, as mentioned earlier, the stable particle molecule positions change very little in a single Δs step.

III. MODELS USED IN OUR STUDY

We studied the model of two parallel crystalline surfaces rotated with respect to each other with mobile molecules trapped between them, and slid symmetrically with respect to each other (i.e., in opposite directions by the same amount) in the slow sliding speed limit, as illustrated in Fig. 2.

There are two parts to the interaction between a mobile molecule and each surface. The conservative part is the potential acting on a mobile molecule, for which we use the Steele potential [3], whose lowest-order Fourier series at a given distance from a surface has the form

$$v_1(\mathbf{r}) = V_0 \sum_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}, \quad (1)$$

where the vectors \mathbf{G} denote the smallest reciprocal lattice vectors of a surface and V_0 is the Fourier coefficient for the smallest reciprocal lattice vectors for each surface plus the interaction potential between two mobile molecules for which we use the Lennard-Jones potential

$$V_{LJ}(r) = -4\epsilon[(\sigma/r)^6 - (\sigma/r)^{12}], \quad (2)$$

where r is the distance between two particles, ϵ is the energy parameter in the Lennard-Jones potential, and σ is the surface's length parameter.

For the nonconservative part we use the damping force

$$F_{\ell,i}^{nc} = -\gamma m_i (v_i - v_\ell), \quad (3)$$

where $F_{\ell,i}^{nc}$ is a nonconservative force acting on the i th particle from the ℓ th surface ($\ell=t$ for the top and b for the bottom surface), γ is the damping constant, m_i is the mass of i th particle, v_i is the velocity of i th particle, and v_ℓ is the sliding velocity of the ℓ th surface.

We have studied two two-dimensional triangular lattice surfaces, which are rotated with respect to each other by an arbitrary angle (as this is what normally occurs for two crystalline surfaces in contact). Because of this rotation, the resultant potential is incommensurate. For one triangular lattice surface model system, we chose the lowest-order term in the Fourier series for Steele potential, which is given by

$$v_1(x,y) = V_0 \{ 2 \cos[(2\pi/a)x] \cos[(2\pi/3^{1/2}a)y] + \cos[(4\pi/3^{1/2}a)y] \}, \quad (4)$$

where a is lattice constant.

When we rotate one surface with respect to other by an angle ϕ and then we slide two surfaces symmetrically with respect to each other (i.e., by equal movements in opposite directions) with displacement $(\Delta x, \Delta y)$ and sliding direction angle Θ with respect to the x axis, for the top surface we get

$$v_t(x,y) = v(x_t, y_t), \quad (5)$$

where

$$x_t = (x + \Delta x/2) \cos(\phi) + (y + \Delta y/2) \sin(\phi), \quad (6)$$

$$y_t = -(x + \Delta x/2) \sin(\phi) + (y + \Delta y/2) \cos(\phi), \quad (7)$$

and for the bottom surface we get

$$v_b(x,y) = v(x_b, y_b), \quad (8)$$

where

$$x_b = (x - \Delta x/2) \cos(\phi) - (y - \Delta y/2) \sin(\phi), \quad (9)$$

$$y_b = (x - \Delta x/2) \sin(\phi) + (y - \Delta y/2) \cos(\phi), \quad (10)$$

where the displacement $\Delta x = s_0 \cos(\Theta) + b \sin(\Theta)$, $\Delta y = s_0 \sin(\Theta) - b \cos(\Theta)$, where $s_0 = vt$. Here v is the sliding speed of the top surface relative to the bottom surface along sliding direction angle Θ and b is the perpendicular distance (in x - y plane) of the path taken by the origin of the top surface from the origin of the bottom surface.

IV. MOLECULE INSTABILITIES AND EQUILIBRIUM POSITIONS

We study many molecules' instabilities with intermolecular interaction in the slow sliding speed limit. In a stable potential well, which is occupied by the molecule, the molecule will try to reach its new equilibrium position as the surface is sliding. When the potential well that is occupied by the molecule becomes unstable, the molecule will quickly jump into the nearest stable well. When this occurs, the molecule's kinetic energy increases from close to zero (when it is in the minimum of a stable potential well) to a value equal to

the drop in the molecule's potential energy that occurs when the well becomes unstable. In the slow sliding speed limit, it is reasonable to assume that this molecule remains in its new potential minimum long enough for all of its kinetic energy to get absorbed by the various energy excitations of the system which is simulated by the damping force given in Eq. (3). This is expected to be the main source of dissipation in the slow sliding speed limit. Thus, it is reasonable to assume that dissipation due to kinetic friction is due to instabilities. From the energy dissipation we can calculate kinetic friction. In CMDS, the time-averaged energy dissipation due to the damping force is given by [4]

$$\begin{aligned} & (1/\tau) \int_0^\tau \gamma m_i [(v_i - v_0)^2 + (v_i + v_0)^2] dt \\ & = (1/\tau) \int_0^\tau 2\gamma m_i [v_i^2 + v_0^2] dt, \end{aligned} \quad (11)$$

where τ is the duration of the simulation, γ is damping constant, m_i is mass of i th unstable particle, and v_i is the velocity of i th unstable particle. v_0 is the velocity of surface sliding.

Then we can calculate the time-averaged kinetic friction force, F_k , from this average energy dissipation given by Eq. (11).

$$F_k = (1/\tau v_0) \sum_i 2\gamma \int_0^\tau m_i [v_i^2 + v_0^2] dt. \quad (12)$$

In AMDS, the force of friction is calculated in the same way, but only the contribution from the dissipation that occurs for particles that become unstable is included.

V. COMPARISON OF THE RESULTS OF ADIABATIC AND CONVENTIONAL MDS FOR A 2- AND A 20-MOLECULE SYSTEM WITH INTERMOLECULAR INTERACTIONS

For our simulations, using conventional MDS, we chose the velocity of surface sliding as $0.001a/t_0$ and time step of sliding as $0.001t_i$. At each sliding step, we solve the equations of motion for all particles in order to get all particles' positions.

In adiabatic MDS, for stable wells, we chose the sliding step of surfaces $\Delta s = 0.005a$, and at each sliding step we iterate the Langevin equation 100 times to get the particles' new equilibrium positions. For unstable wells, the iteration number is ≈ 500 at each Δs .

We first use conventional and adiabatic MDS methods separately to deal with a two-interacting-molecule system, followed by a 20-interacting-molecules system, and then a 100-interacting-molecules system. We chose an initial density such that the distance between two neighboring atoms is $0.9a$. For 20 atoms, we initially place the molecules at the interface in a triangular lattice configuration of lattice constant $0.9a$. We rotated the two parallel surfaces at angle 0.1485 rad and then slid the two surfaces symmetrically with respect to each other from origin at a given sliding direction angle 0.1309 rad. We calculate the total minimum potential and time-averaged kinetic friction.

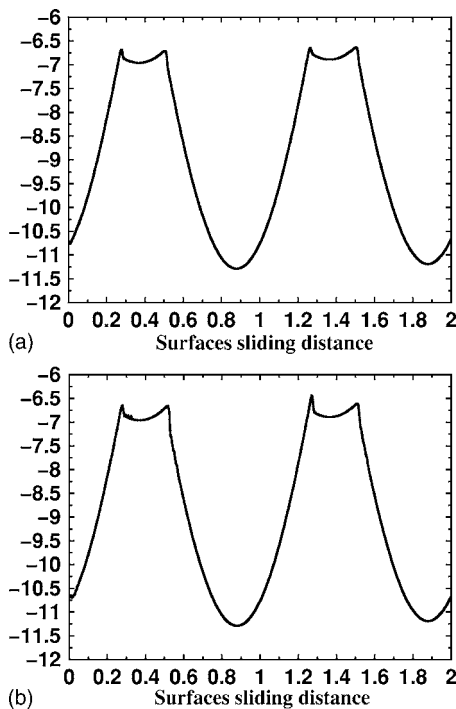


FIG. 3. Two particles' total minimum potential value vs surfaces sliding distance. The unit of minimum potential value is energy unit v_0 (strength of Steele potential), and the unit of surfaces sliding distance is length unit a (surface lattice constant). Top figure presents CMDS results; bottom figure, AMDS results.

The following are results for a two-interacting-particle-system simulation by CMDS and AMDS. We chose the two particles' initial positions as follows: particle 1's initial position (x,y) is $(0.0, 0.0)$, particle 2's initial position (x,y) is $(0.450\ 000a, 0.779\ 423a)$. Two surfaces symmetrically slide with respect to each other from origin up to 2 lattice constants. We chose the energy parameter ϵ to be $0.5V_0$ and chose length parameter σ to be $0.618\ 034a$ in the Lennard-Jones potential. The damping constant γ is $1.35(V_0/ma^2)^{1/2}$.

In AMDS in stable wells when the ratio of change of a particle's position in 100 iterations divided by 0.0003 is larger than 1, we assume that particle to be unstable and then switch to the conventional method to deal the particle. In unstable wells when the ratio of change of a particle's position in one iteration divided by 0.00001 is less than 1, we assume that particle to be stable and then switch back to the adiabatic method to treat the particle. The results obtained using both methods are very close, as can be seen in Figs. 3-7. We calculate the time factor, defined previously as $50/(5-4b)$. Here b is almost 1; therefore, the time factor is 50. Thus, the AMDS is almost 50 times faster than CMDS.

Now we present results for a 20-interactive-particle-system simulation by CMDS and AMDS. We chose the energy parameter ϵ to be $0.5V_0$ and the length parameter σ to be $0.618\ 034a$ in the Lennard-Jones potential. As before, the damping constant γ is $1.35(V_0/ma^2)^{1/2}$. We began our plots after a sliding distance equal to $1.5a$ and continue the plot up to $20.0a$. We calculated time-averaged kinetic friction force

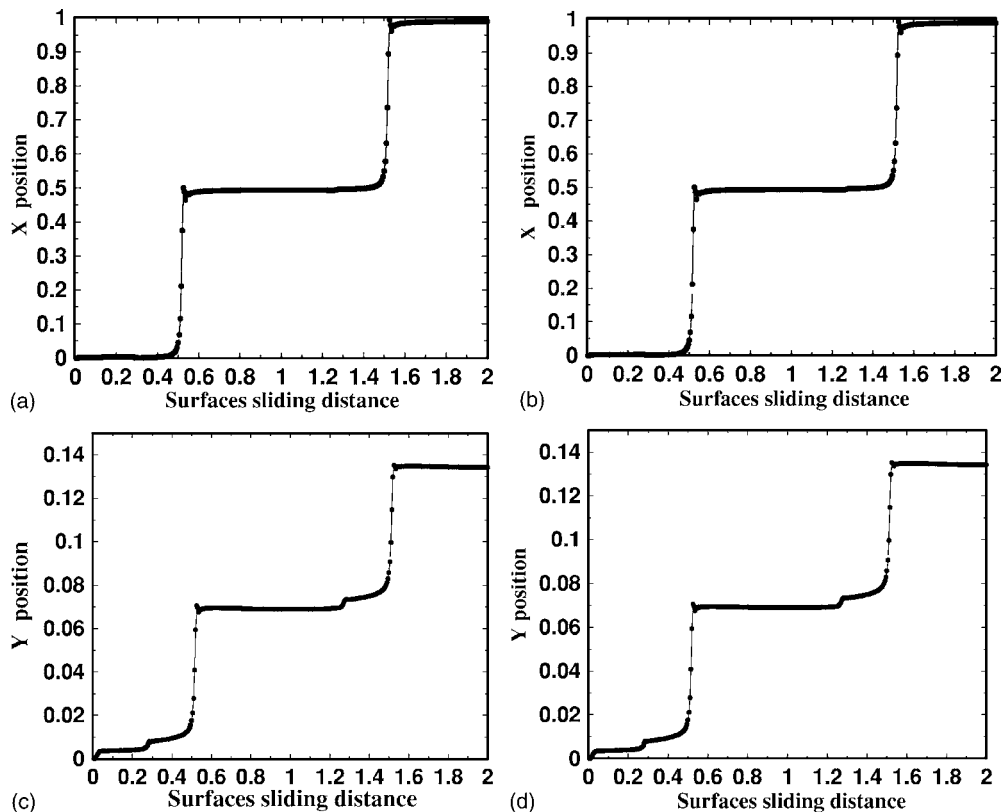


FIG. 4. Particle 1's (x,y) coordinates vs surfaces sliding distance. The units for both the x and y axes are length unit a (surface lattice constant). Left is for CMDS, and right is for AMDS. From these figures, we can find two instabilities for particle 1; one is around the surfaces sliding distance $0.5a$, and another one is around the surfaces sliding distance $1.5a$.

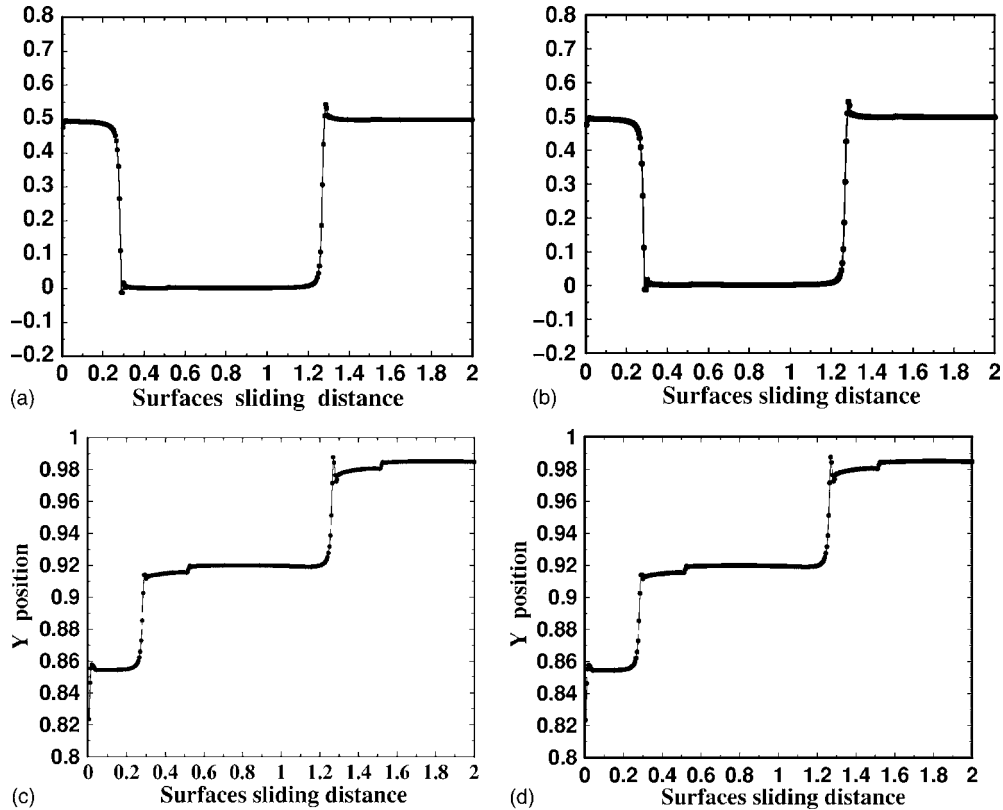


FIG. 5. Particle 2's (x, y) coordinates vs surfaces sliding distance. The units for both the x and y axes are length unit a (surface lattice constant). Left is for CMDS, and right is for AMDS. From these figures, we can find two instabilities for particle 2; one is around the surfaces sliding distance $0.3a$, and another one is around the surfaces sliding distance $1.3a$.

for the 20-particle system. In AMDS, the criterion used for classifying a well as unstable, and hence switching briefly to CMDS, was described in the previous paragraph. There is very good agreement between the results found using CMDS and those found using AMDS. We now calculate the time factor, defined previously as $50/(5-4b)$. In this case b is 0.55, therefore, the time factor is 17.86. The value of this time factor, determined by taking the ratio of the time to do our 20-particle simulations using CMDS and AMDS, agrees quite well with these estimates. Thus the AMDS is almost 18 times faster than CMDS for the 20-particles case. Results for the force of friction, determined from Eq. (12), are given in Fig. 7.

In contrast to the simulations that we have discussed in this section and in Sec. VI, in which the interparticle interactions are relatively weak, for strongly interacting systems, most particles become unstable at almost every value of the sliding distance. When we use AMDS for such a system, we must calculate the change of the unstable particle positions very accurately because the change of one particle's position depends strongly on other unstable particles' positions. Thus, when we deal with unstable particles in strongly interacting particle systems, we must use many more iterations to calculate the positions of the unstable particles, which means we must use as many iterations as we use in CMDS. This, of course, is not surprising because, when most of the particles become unstable, it is necessary to use CMDS for almost all the particles. This will greatly decrease the speed of the cal-

culational when we use AMDS, when most particles are unstable. In fact, we found in our simulations that when the average fraction of particles which are stable, b , is less than 0.5, we need to use many more iterations to calculate the unstable particle positions.

VI. STUDY OF 100 MOLECULES TRAPPED BETWEEN TWO SURFACES USING AMDS

The following are results for a 100-interacting-particle-system simulation by AMDS. We use the same values for ϵ and σ for the 100 as we used for the 20-atom system.

The value for the force of friction per adsorbed molecule that we obtain in our work is $\sim 1.0V_0/a$, which is comparable to what we found in Ref. [2] (which neglects interactions), which implies that the intermolecule interaction does not have a large effect on the friction, even for the relatively high concentrations of molecules (i.e., a large fraction of a monolayer) considered in our 100-molecule runs, as can be seen from the left panel of Fig. 8. As the run progresses, however, the molecules spread out considerably, as can be seen in the right panel. This probably accounts for the fact that the friction decreases slowly during the run, as can be seen in Fig. 9. These results imply that for submonolayer concentrations of adsorbed molecules, the friction appears to increase with increasing concentration, which is in qualitative agreement with Ref. [4], which reports results of CMDS for the Muser-Robbins model. We also find that for the high

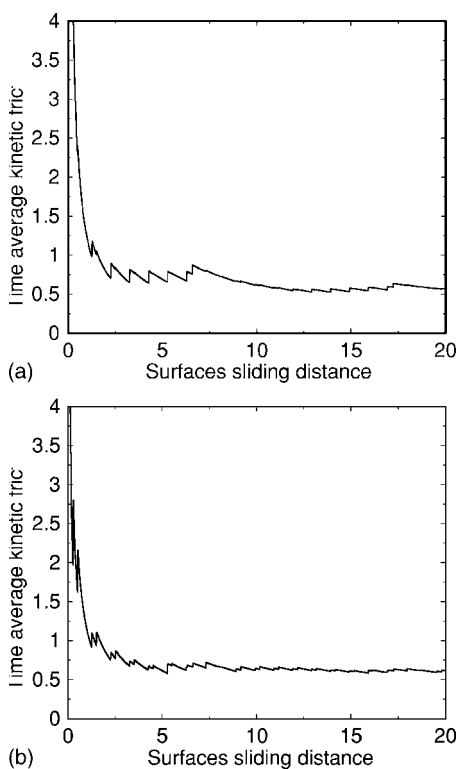


FIG. 6. Time-averaged kinetic friction for the two-particle system vs surface sliding distance are plotted. The unit of kinetic friction force is the force unit v_0/a (V_0 is energy unit, a is the length unit), and the unit of surfaces sliding distance is length unit a . Top figure presents the results for CMDS; bottom figure, results for AMD.

concentrations that we consider, there are multiparticle instabilities, as was found in Ref. [4]. In our AMDS calculations, they manifest themselves due to the fact that we generally find that when our criterion for a molecule becoming unstable is satisfied, the criterion is also satisfied for several neighboring molecules as well.

VII. STUDY OF A FIVE-MOLECULES SYSTEM WITH STRONG INTERMOLECULAR INTERACTION BY CMDS

For the 100-atom system with relatively weak interatomic interaction (in comparison to V_0), we found that the adsorbed atoms tended to separate as the surfaces slid relative to each other. We believe that for stronger interactions, the atoms will not separate. In order to confirm this, we studied a system with five strongly interacting atoms by CMDS. For these calculations, we chose the interaction ϵ to be $3V_0$ and chose length parameter σ to be the value chosen in the previous section in the Lennard-Jones potential, and the same value of γ as before. In Fig. 10, we plot the five atoms' positions at surfaces sliding distance equal to $10a$ and $200a$. From Figs. 10(a) and 10(b), we observe that the particles do not spread out in this case, presumably due to the stronger interactions between particles. We did not attempt to use the AMDS in these calculations because, as noted above, for the strong interaction system, the AMDS is not as fast for a strongly

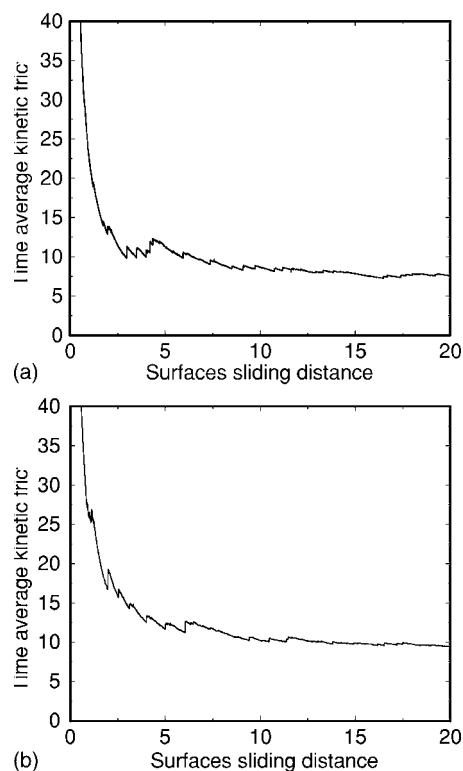


FIG. 7. Time-averaged kinetic friction for the 20-particle system vs surface sliding distance are plotted. The unit of kinetic friction force is the force unit V_0/a (v_0 is energy unit, a is the length unit), and the unit of surfaces sliding distance is length unit a (top: CMDS; bottom: AMD).

interacting system as it is for a weakly interacting one. The reason for this is that the atoms tend to move together, and hence when one atom becomes unstable, they all do.

VIII. SUMMARY

We have developed an adiabatic molecular-dynamics method (AMDS) for the Muser-Robbins model for dry friction. In AMDS, if we slide the two surfaces symmetrically with respect to each other, when the wells are stable, the particles' equilibrium positions do not significantly change. This allows us to quickly locate the stable particles' new equilibrium positions. We do not need to track the motion of each stable particle as in conventional MDS.

In adiabatic MDS, when the wells are stable, we use the adiabatic method to deal with them. When the wells are unstable, we switch to the conventional method to deal with those unstable wells. Conventional MDS deals with stable wells and unstable wells in the same way. Adiabatic MDS can save much computer time when it treats stable wells because it determines changes in the locations of stable wells, which occur as a result of surface sliding, much more rapidly. The simulation results from these two methods are almost identical, but the adiabatic MDS is more than a factor of 10 faster.

We hope in the future to explore the possibility of applying similar adiabatic simulation methods to other systems in

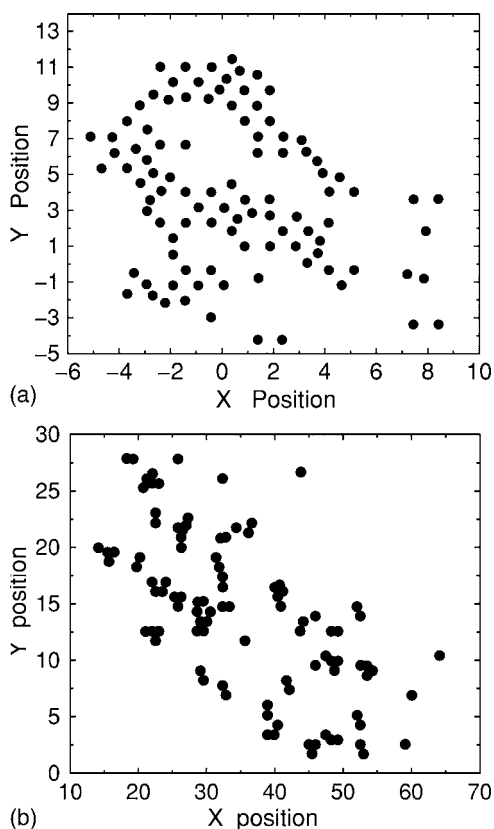


FIG. 8. The x vs y coordinates of the 100 particles' positions. The top figure shows the 100 particles' positions at surfaces sliding distance equal to $15a$. The bottom figure is for 100 particles' positions at surfaces sliding distance equal to $200a$. The units for both x and y axes are length unit a (surface lattice constant).

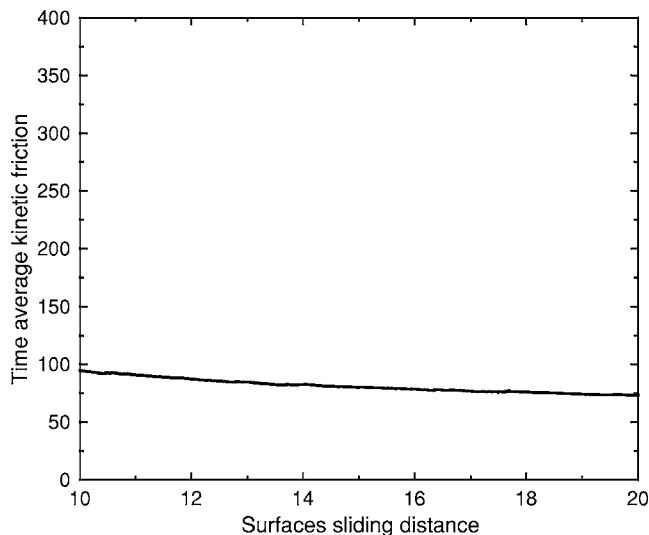


FIG. 9. Time-averaged kinetic friction for the 100 particles system vs surfaces sliding distance are plotted. The unit of kinetic friction force is force unit V_0/a (V_0 is energy unit, a is length unit), and the unit of surfaces sliding distance is length unit a .

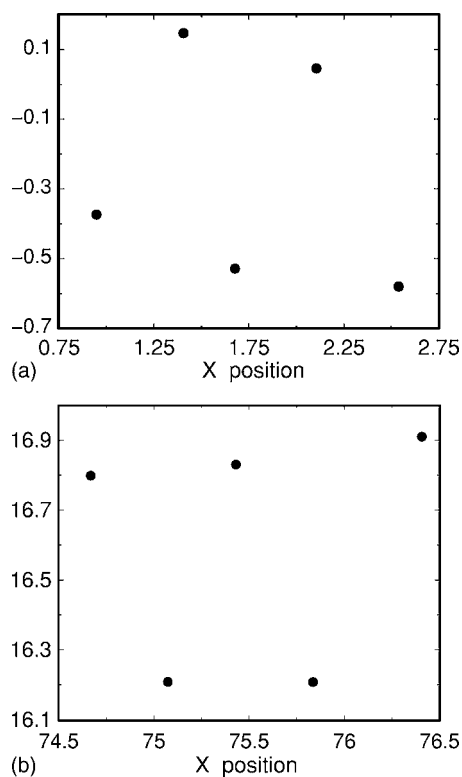


FIG. 10. The x vs y coordinates of the five particles' positions. The top panel shows the five-particles' positions at surfaces sliding distance equal to $10a$. The bottom one is for the five-particles' positions at surfaces sliding distance equal to $200a$. The units for both x and y axes are length unit a (surface lattice constant).

which the response of the system to a slowly varying parameter is dominated by microscopic instabilities (as we found to be the case in the present problem).

In the future, we plan to explore whether the use of other methods for minimizing the potential energy (such as the conjugate gradient method [5]) might improve the speed of our adiabatic method.

ACKNOWLEDGMENT

We wish to thank the Department of Energy (Grant No. DE-FG02-96ER45585). We also would like to thank C. Daly for useful ideas and insights.

APPENDIX A: ADIABATIC APPROXIMATION FOR SLIDING SURFACES

In the extreme adiabatic approximation, the surfaces are assumed to slide so slowly that the molecule remains at a potential minimum at all times. Let us consider the case of a single molecule at the interface. Using the fact that the potential acting on a molecule at an interface is given by

$$V(\mathbf{r}) = V_1(\mathbf{r} + (1/2)\mathbf{s}) + V_2(\mathbf{r} - (1/2)\mathbf{s}), \quad (A1)$$

where V_1 is the potential due to surface 1 acting on the molecule, V_2 is V_1 rotated around the origin, and \mathbf{s} is the displacement vector of surface 1 with respect to surface 2. Then

a potential minimum position at time t , denoted by $\mathbf{r}_{\min}(t)$ is the solution to

$$\frac{\partial V(\mathbf{r}_{\min})}{\partial x_\alpha} = 0, \quad (\text{A2})$$

where $x_\alpha = x, y, z$ for $\alpha = 1, 2, 3$, respectively. If \mathbf{s} changes by a small amount $\Delta \mathbf{s}$ during sliding, \mathbf{r}_{\min} should change by a small amount $\delta \mathbf{r}_{\min}$, given by

$$\frac{\partial V(\mathbf{r}_{\min})}{\partial x_\alpha} = \left. \frac{\partial V(\mathbf{r}_{\min}^0)}{\partial x_\alpha} \right|_{\delta \mathbf{s}=0} + \sum_{\beta} [D_{\alpha,\beta} \delta x_{\min}^\beta + M_{\alpha,\beta} \delta s_\beta] = 0, \quad (\text{A3})$$

where \mathbf{r}_{\min}^0 is the equilibrium position of the molecule for $\delta \mathbf{s} = 0$ and

$$M_{\alpha,\beta} = (1/2) \left[\frac{\partial^2 V_1(\mathbf{r} + (1/2)\mathbf{s})}{\partial x_\alpha \partial x_\beta} - \frac{\partial^2 V_2(\mathbf{r} - (1/2)\mathbf{s})}{\partial x_\alpha \partial x_\beta} \right] \Bigg|_{\mathbf{r}_{\min}^0} \quad (\text{A4})$$

and

$$D_{\alpha,\beta} = \left[\frac{\partial^2 V_1(\mathbf{r} + (1/2)\mathbf{s})}{\partial x_\alpha \partial x_\beta} + \frac{\partial^2 V_2(\mathbf{r} - (1/2)\mathbf{s})}{\partial x_\alpha \partial x_\beta} \right] \Bigg|_{\mathbf{r}_{\min}^0}. \quad (\text{A5})$$

By the definition of \mathbf{r}_{\min}^0 , the first term on the right-hand side of Eq. (3A) is zero. Thus, as long as the minimum in question is not unstable (which means that the matrix \mathbf{D} can be inverted), we can find the components of $\delta \mathbf{r}_{\min}$ by solving Eq. (3A), giving

$$\delta x_{\min}^\alpha = - \sum_{\beta,\beta'} D_{\alpha,\beta}^{-1} M_{\beta,\beta'} \delta s_{\beta'}. \quad (\text{A6})$$

Since in molecular dynamics it is impossible to slide the surfaces at infinitesimal speed, there is always a correction to the adiabatic approximation, meaning that the actual position of the molecule is $\mathbf{r}_{\min} + \delta \mathbf{r}$, where $\delta \mathbf{r}$ is the correction to the adiabatic approximation, which in the slow speed limit should be small. Then the equation of motion is

$$m\ddot{x}_\alpha + m\gamma\dot{x}_\alpha = - \frac{\partial V}{\partial x_\alpha} \approx - \sum_{\beta} \frac{\partial^2 V}{\partial x_\alpha \partial x_\beta} \delta x_\beta. \quad (\text{A7})$$

In the slow sliding speed limit, we can neglect the inertial term (the first term on the left-hand side) compared to the damping term. The solution to Eq. (A7) is

$$\delta x_\alpha = - \sum_{\beta} G_{\alpha,\beta} \gamma \dot{x}_{\min}^\alpha \quad (\text{A8})$$

where G is the phonon Green's function,

$$\int d\omega e^{-i\omega t} \left[im\gamma\omega\delta_{\alpha,\beta} - m^{-1} \frac{\partial^2 V}{\partial x_\alpha \partial x_\beta} \right]^{-1}. \quad (\text{A9})$$

For slow speed motion (at which only small values of ω contribute to G , $G \approx \omega_0^{-2}$, where ω_0 is a harmonic approximation frequency for a typical potential well. Then from Eq. (A8) to a good approximation

$$\delta x_\alpha \approx (\gamma/\omega_0^2) \dot{x}_{\min}^\alpha. \quad (\text{A10})$$

Thus, the criterion for the validity of the adiabatic approximation (namely, that the amount that the molecule's position differs from the location of the well minimum must be much smaller than a lattice spacing) is given by $|\delta x_\alpha| \ll a$, which from Eq. (A10) becomes

$$\omega_0^2 \gg \gamma \dot{x}_{\min}^\alpha / a. \quad (\text{A11})$$

Dividing Eq. (A5) by the time that it takes to slide the surfaces by Δs_α , we find that away from instabilities, $\dot{x}_{\min}^\alpha \approx \dot{s}_\alpha$ and hence the criterion in Eq. (A11) becomes

$$\omega_0^2 \gg \gamma \dot{s}_\alpha / a. \quad (\text{A12})$$

In adiabatic molecular dynamics, we change \mathbf{s} by an amount $\Delta \mathbf{s}$ and integrate the equations of motion to get the particle to settle into its new potential minimum. Since the new equilibrium position of the particle is very close to the old one, we can use the harmonic approximation for the equations. Then we must solve the equation of motion

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = 0, \quad (\text{A13})$$

where $\omega_0 = (K/m)^{1/2}$ where K is the force constant of the potential well, for the initial conditions $x(t=0) = \delta x_{\min}$ and $\dot{x}(t=0) = 0$. The solution is

$$x = x_0 e^{-\gamma t/2} \left[\cos(\omega_1 t) + \frac{\gamma}{2\omega_1} \sin(\omega_1 t) \right], \quad (\text{A14})$$

where $\omega_1 = (\omega_0^2 - \gamma^2/4)^{1/2}$. When $\omega_0 > \gamma/2$ the time to settle into new well is about $2/\gamma$. For $\omega_0 = \gamma/2$, it is γ^{-1} , and for $\omega_0 \ll \gamma/2$, it is about γ/ω_0^2 , which is much longer than γ^{-1} . Thus we get optimum damping for ω_0 greater than or equal to γ^{-1} . For many particles, you get a similar harmonic approximation equation of motion for each of the phonon modes. This implies that it is necessary to wait at least a time as long as γ^{-1} for the oscillations to settle down completely. In practice, we have found that it is only necessary to wait one-tenth as long since the amplitudes of these oscillations x_0 quite small [i.e., of the order of $|\delta \mathbf{r}_{\min}|$ given by Eq. (A6)]. The reason for this might be due to the fact that initially x drops from x_0 to a much smaller value as part of its damped oscillations. Thus, since if ω_1 is significantly greater than γ , the cosine term in Eq. (A14) dominates, and hence if we wait for an amount of time comparable to about a quarter of the oscillation period, x will be quite close to zero. Although the velocity of the molecule will not be zero, this does not introduce an error in the friction. The reason for this is that in the adiabatic method the frictional dissipation, and hence the force of friction that is calculated from it, is assumed to be due only to the energy losses that occur as molecules drop out of unstable wells into stable ones of lower energy. Thus, the velocities attained by molecules in stable wells as they drop into their new equilibrium positions after the surfaces are slid by $\delta \mathbf{s}$ are not included in the calculation of the friction.

At the beginning of this Appendix, we considered the single-molecule case. We would now like to consider how the equilibrium position of a molecule changes as the sur-

faces are slid by a small amount for many interacting particles. Let us consider the equilibrium condition for the j th mobile molecule [i.e., the analog of Eq. (A3) for interacting molecules]

$$\begin{aligned} \frac{\partial V(\mathbf{r}_{j,\min})}{\partial x_{j,\alpha}} &= \left. \frac{\partial V(\mathbf{r}_{j,\min}^0)}{\partial x_{j,\alpha}} \right|_{\delta s=0} + \sum_{\ell \neq j} \frac{\partial v_i(\mathbf{r}_{j,\min}^0 - \mathbf{r}_{\ell,\min}^0)}{\partial x_{j,\alpha}} \\ &+ \sum_{\beta} [D_{\alpha,\beta} \delta x_{\min}^{\beta} + M_{\alpha,\beta} \delta s_{\beta}] \\ &- \sum_{\beta, \ell \neq j} \frac{\partial^2 v_i(\mathbf{r}_{j,\min}^0 - \mathbf{r}_{\ell,\min}^0)}{\partial x_{j,\alpha} \partial x_{\ell,\beta}} \\ &\times (\delta x_{j,\min,\beta} \delta_{j,\ell} - \delta x_{\ell,\min,\beta}) = 0, \end{aligned} \quad (\text{A15})$$

where the matrices are those defined in Eqs. (4) and (5) and where $\mathbf{r}_{j,\min}^0$ is the equilibrium position for the j th molecule

for $\delta s=0$. By the definition of $\mathbf{r}_{j,\min}^0$ the sum of the first two terms on the right-hand side of Eq. (A15) vanishes. Formally solving Eq. (A15) for $\delta x_{j,\min,\alpha}$ we obtain in place of Eq. (A6)

$$\begin{aligned} \delta x_{\min}^{\alpha} &= - \sum_{\beta, \beta'} D_{\alpha,\beta}^{-1} \left[M_{\beta,\beta'} \Delta s_{\beta'} \right. \\ &\left. - \sum_{\beta, \ell \neq j} \frac{\partial^2 v_i(\mathbf{r}_{j,\min}^0 - \mathbf{r}_{\ell,\min}^0)}{\partial x_{j,\beta} \partial x_{\ell,\theta}} (\delta x_{j,\min,\theta} \delta_{j,\ell} - \delta x_{\ell,\min,\theta}) \right]. \end{aligned} \quad (\text{A16})$$

In practice, we find in our simulations that for stable wells, the determinant of the matrix D is about 1000 times the matrix elements of the matrices \mathbf{D} and \mathbf{M} [2]. As a result, the components of $\delta \mathbf{r}_{\min}$, given by Eq. (A16) are of the order of one thousandth of $\delta \mathbf{s}$.

- [1] G. He, M. H. Muser, and M. O. Robbins, *Science* **284**, 1650 (1999); M. O. Muser, L. Wenning, and M. O. Robbins, *Phys. Rev. Lett.* **86**, 1295 (2001); M. H. Muser and M. O. Robbins, *Phys. Rev. B* **61**, 2335 (2000).
 [2] C. Daly, J. Zhang, and J. B. Sokoloff, *Phys. Rev. Lett.* **90**, 246101 (2003); *Phys. Rev. E* **68**, 066118 (2004).

- [3] W. Steele, *Surf. Sci.* **36**, 317 (1973).
 [4] M. Aichele and M. H. Muser, *Phys. Rev. E* **68**, 016125 (2003).
 [5] W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes in Fortran*, 2nd ed. (Cambridge University Press, Cambridge, England, 1992), pp. 77–81 and 413–416.