# Trapping, reflection, and fragmentation in a classical model of atom-lattice collisions

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A classical one-dimensional model of the collision of an atom of mass $M$ with a cold, semi-infinite harmonic lattice comprised of identical atoms of mass $m$ is considered. In the model, the interactions between the incident atom (adatom) and the lattice are described in terms of a truncated parabolic potential by which the adatom is harmonically bound to the lattice at short distances but evolves freely when its distance is larger than a critical length $R_c$. The dynamics of the adatom colliding with an infinitely cold lattice is studied as a function of the initial velocity of the adatom. In order to determine whether the colliding atom is bound or reflected from the lattice in the asymptotic time limit, ''secondary'' collision events in which the incident atom leaves and reenters the interaction zone of the lattice are carefully considered. It is demonstrated that secondary collisions anticipated to be important for heavy adatoms ($\mu=m/M<1$) also occur in the case of light adatoms ($\mu\geqslant 1$). It is shown that the neglect of secondary collisions leads to an underestimation of the lower energy bound for adatom reflection of roughly 10% for $\mu$ close to 1. By generalizing the model to allow for the breaking of lattice bonds, the phenomenon of collision-induced lattice fragmentation is investigated.

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## I. INTRODUCTION

The collision of an atom with polyatomic complexes or solid surfaces is an important and complicated process, which generally must be described within a quantum-mechanical framework. Nevertheless, valuable insight into the mechanism of energy transfer in such processes can be gained from simplified classical models [1]. About forty years ago Cabrera [2] and Zwanzig [3] investigated the possibility of the trapping of an incident atom by a cold harmonic lattice using a simple one-dimensional model. The Cabrera-Zwanzig model, hereafter referred to as the CZ model, consists of a semi-infinite one-dimensional chain of classical particles (atoms) labeled $i=1,2,3,\ldots$, beginning from the terminal atom at the free end of the chain (see Fig. 1). In the CZ model, the atoms $i=2,3,\ldots$ representing the lattice have mass $m$ and are initially frozen in the equilibrium positions, $x_i(0)=x_i^0=a(i-1)$, where $a>0$ is the equilibrium bond length in the lattice. The corresponding initial velocities $v_i(0)$ and displacements $q_i(0)=x_i(0)-x_i^0$ of the lattice atoms are taken to be zero. The terminal atom $i=1$ represents the incident particle (adatom) colliding with the cold lattice. At $t=0$, the adatom is assumed to be moving towards the rest of the chain with positive initial velocity $v_1(0)$ from a position $x_1(0)<0$ displaced from its equilibrium position at the origin by $q_1(0)=x_1(0)$. The relative displacements of the atoms $u_i=q_{i+1}-q_i$ are all zero at $t=0$ except for that of the first link of the chain, which is initially stretched, $u_1(0)=-q_1(0)>0$. The adatom interacts with the terminal atom of the lattice ($i=2$) via a truncated potential $U_1$ given by

$$U_1=\begin{cases}\frac{1}{2}k(x_2-x_1-a)^2 & \text{if } x_2-x_1<R_c\\ \frac{1}{2}k(R_c-a)^2 & \text{otherwise,}\end{cases} \tag{1}$$

where $k$ is the force constant and $R_c$ defines a cutoff length for the truncation of the harmonic potential. In the CZ model, $R_c$ is defined to be the initial length of the first link $R_c=a+u_1(0)$, so that the adatom is just entering the interaction zone at $t=0$. The interaction potential for the adatom with the lattice can, therefore, be written in terms of the relative displacements of the two atoms as

$$U_1=\begin{cases}\frac{1}{2}ku_1^2 & \text{if } u_1<u_1(0)\\ \frac{1}{2}ku_1(0)^2 & \text{otherwise.}\end{cases} \tag{2}$$

All other pairs of nearest neighbors in the chain interact via harmonic potentials with force constant $k$. For this potential, the evolution of the system occurs in such a way that if the relative displacement $u_1(t_e)$ between the adatom (atom 1) and the terminal atom of the chain (atom 2) exceeds its initial value $u_1(0)$ at a time $t_e>0$, the lattice exerts no force on the adatom that may then escape. On the other hand, if the initial ratio of kinetic and potential energies for the adatom

$$\alpha=\frac{Mv_1^2(0)}{ku_1^2(0)} \tag{3}$$

is less than a certain threshold value $\alpha_c$, one finds that $u_1(t)<u_1(0)$ for all times $t>0$, which implies that the adatom remains bound to the lattice. In the Cabrera-Zwanzig solution of the CZ model, it was assumed that the condition

$$u_1(t_e)=u_1(0), \quad t_e>0 \tag{4}$$

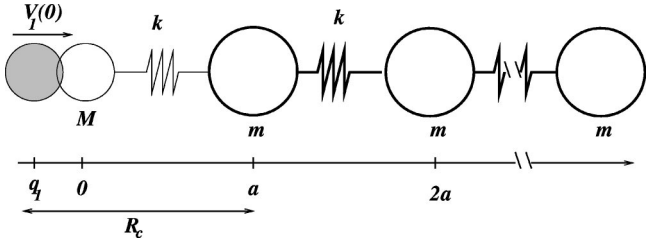


FIG. 1. A schematic of the Cabrera-Zwanzig model.

 

guarantees the adatom will escape from the lattice and hence be reflected in the asymptotic time limit. Under this assumption, Eq. (4) can be used to find the critical ratio of kinetic and potential energies $\alpha_c$ for reflection. The dynamics of the adatom displacements $u_1(t)$ depends on the ratio of the lattice and adatom masses $\mu=m/M$. For two special cases, corresponding to $\mu=1$ and $\mu=2$, it is possible to obtain an analytical closed-form solution for $u_1(t)$ in terms of tabulated functions. Using Eq. (4) as the condition to determine the threshold for reflection $\alpha_c$, Zwanzig obtained [3] $\alpha_c \approx 24.54$ for the mass ratio $\mu=1$, and a value about ten times smaller for the mass ratio $\mu=2$.

While the CZ model is clearly too simplified for a realistic description of the collision of an atom with a surface, the model demonstrates the importance of multiphonon excitations for gas-surface processes. Besides providing a qualitatively correct description of the adatom trapping, the model also predicts [3,4] a much higher transfer of energy from the light adatom to the lattice than what one would expect from the interaction of the adatom with a single surface atom. Although the energy transfer is overestimated in the one-dimensional CZ model, the enhanced energy transfer is in agreement with both experiment and more sophisticated three-dimensional models [1]. For a finite chain and $M \to \infty$, the model is relevant to scattering of molecular clusters from a hard surface, which is the topic of the extensive current research [5]. In this context, the model has been considered recently in Ref. [6].

Since the early work of Cabrera and Zwanzig, the CZ model has been revisited many times and generalized in a multitude of ways to describe three-dimensional [1], anharmonic [4], finite [7], and noncold lattices [8]. In addition, more realistic potentials [1] for the adatom-lattice interactions have been considered, and mass ratios $\mu \geqslant 1$ have been investigated by McCarroll and Ehrlich using an infinite series expansion of Bessel functions [4]. The behavior of the system for other mass ratios has also been discussed qualitatively by Zwanzig who noted that if the adatom is heavier than the chain atoms ($\mu<1$), the criterion for trapping obtained using Eq. (4) may not be appropriate since the lattice vibrations induced by the adatom collision may lead to recollision and recapture events [3].

The main goal of this paper is to show that actually Eq. (4) cannot be used alone to determine the conditions for adatom reflection even when the mass of the adatom is equal to or less than the mass of lattice atoms, $\mu \geqslant 1$. The inapplicability of Eq. (4) to unambiguously define an escape condition can readily be seen from the fact that it does not involve the adatom velocity $v_1$. In the Zwanzig solution of the model, it is implicitly assumed that the adatom velocity is directed away (i.e., it has negative velocity) from the lattice at the moment of the break of the first link. One may anticipate that generally this assumption breaks down when the rupture of the link occurs by a mechanism in which the velocities of the adatom (atom 1) and the terminal atom of the lattice (atom 2) are both positive and $v_2 > v_1$ just before the break. We will show that such a mechanism is important for large $\mu$. Since the velocity of the adatom after leaving the interaction zone remains constant, such a break will be virtual in a sense that it does not lead to the escape of the adatom since it later reenters the interaction region of the lattice and is trapped. Moreover, even when supplemented with the additional requirement that $v_1(t_e)<0$ at the moment of rupture, the dynamics described Eq. (4) may still correspond to a virtual break of the adatom-lattice bond since the adatom may move too slowly after the bond is ruptured to escape the lattice. It will be shown that such an eventuality arises, in particular, for the cases $\mu=1$ and $\mu=2$ considered by Zwanzig. For $\mu=1$, we demonstrate that the actual value $\alpha_c$ is approximately 27.33, which is about 10% larger than the value $\alpha_c^* \approx 24.54$ obtained by Zwanzig. For $\alpha_c^* < \alpha < \alpha_c$, the adatom moves out of the interaction zone after the first collision with the lattice for a period of time until the vibrating lattice recaptures the adatom. There is only one such secondary collision, after which the distance between the adatom and the outermost lattice atom never reaches the critical value $R_c$.

In the following section we consider the case $\mu=1$ in detail, while in Sec. III, the extension of the analysis of the reflection dynamics is extended to arbitrary values of $\mu$. In Sec. IV, we discuss the behavior of the chain in which not only the first, but all pairs of nearest neighbors interact via truncated parabolic potential. This model leads to the more complicated scenario of atom-lattice collisions than in the original CZ model and can be used to study collision-induced fragmentation.

## II. THE CASE $\mu=1$

The solution of the equations of motion for a harmonic chain can be written as linear combinations of initial displacements and velocities with time-dependent coefficients expressed in terms of the Bessel functions $J_n(t)$. For a semi-infinite chain of identical atoms, the displacements and velocities are given by

$$q_i(t)=\sum_{k=1}^{\infty}\left\{q_k(0)W_{ik}(t)+v_k(0)\int_0^t dt' W_{ik}(t')\right\}, \quad (5)$$

$$v_i(t)=\sum_{k=1}^{\infty}\left\{v_k(0)W_{ik}(t)+q_k(0)\frac{d}{dt}W_{ik}(t)\right\}. \quad (6)$$

where

$$W_{ik}(t)=J_{2|i-k|}(2\omega t)+J_{2(i+k-1)}(2\omega t), \quad (7)$$

and $\omega^2=k/m$. As this solution is less familiar than that for the infinite chain or for the chain with both ends fixed, we outline its derivation in the Appendix. Note that these equations hold for atoms located a finite distance from the free end of the chain.

Throughout this paper, we use dimensionless displacements $\xi_i$ and velocities $\zeta_i$, which are normalized by the initial coordinates of the adatom

$$\xi_i(t)=q_i(t)/|q_1(0)|, \quad \zeta_i(t)=v_i(t)/v_1(0). \quad (8)$$

As functions of reduced time $\tau=2\omega t$, $\xi_i(\tau)$ and $\zeta_i(\tau)$ are related by the equation $\dot{\xi}_i(\tau)=\beta\zeta_i(\tau)$, where $\dot{\xi}_i(\tau)$ denotes

the time derivative of $\xi_i(\tau)$ and the parameter $\beta$ is related to the initial ratio $\alpha$ of the kinetic and the potential energies for the adatom defined in Eq. (3), by

$$\beta = \frac{1}{2\omega}\frac{v_1(0)}{|q_1(0)|} = \tfrac{1}{2}\sqrt{\mu\alpha}. \tag{9}$$

It follows from Eqs. (5) and (6) that

$$\xi_i(\tau) = \sum_{k=1}^{\infty}\left\{\xi_k(0)W_{ik}(\tau) + \beta\zeta_k(0)\int_0^{\tau} d\tau' W_{ik}(\tau')\right\}, \tag{10}$$

$$\zeta_i(\tau) = \sum_{k=1}^{\infty}\left\{\zeta_k(0)W_{ik}(\tau) + \beta^{-1}\xi_k(0)\frac{d}{d\tau}W_{ik}(\tau)\right\}. \tag{11}$$

The derivative and the integral of the function $W_{ik}(\tau)$ appearing in the above equations can be expressed in terms of sums of Bessel functions noting that

$$\int_0^{\tau} d\tau' W_{ik}(\tau') = 2\sum_{l=0}^{\infty} J_{2|i-k|+2l+1}(\tau) + 2\sum_{l=0}^{\infty} J_{2(i+k+l)-1}(\tau), \tag{12}$$

$$\frac{dW_{ik}}{d\tau} = \tfrac{1}{2}\{J_{2|i-k|-1}(\tau) - J_{2|i-k|-1}(\tau)\} + \tfrac{1}{2}\{J_{2(i+k)-3}(\tau) - J_{2(i+k)-1}(\tau)\}. \tag{13}$$

In practical calculations, since the Bessel functions of large index make increasingly small contributions to the sum in Eq. (12), the sum may be truncated at an index $N_w$ determined by the desired level of numerical accuracy.

The initial conditions for the CZ model described in the Introduction are

$$q_i(0) = q_1(0)\delta_{i1}, \quad v_i(0) = v_1(0)\delta_{i1}, \tag{14}$$

with $q_1(0) < 0$ and $v_1(0) > 0$. The lattice with which the adatom (atom 1) collides is assumed to lie on the right half of the $x$ axis, and the initial conditions correspond to a situation in which the adatom collides with the lattice from the left. In the dimensionless coordinates, the initial conditions assume the form

$$\xi_k(0) = -\delta_{1k}, \quad \zeta_k(0) = \delta_{1k}, \tag{15}$$

and hence from Eqs. (10) and (11), one obtains

$$\xi_i(\tau) = -J_{2(i-1)}(\tau) - J_{2i}(\tau) + \beta\int_0^{\tau} d\tau[J_{2(i-1)}(\tau') + J_{2i}(\tau')], \tag{16}$$

$$\zeta_i(\tau) = J_{2(i-1)}(\tau) + J_{2i}(\tau) - \frac{1}{2\beta}[J_{2i-3}(\tau) - J_{2i+1}(\tau)]. \tag{17}$$

This solution of the dynamics of the system remains valid until the relative displacement

$$\varphi_1(\tau) = \xi_2(\tau) - \xi_1(\tau) \tag{18}$$

for the first link of the chain is greater than its initial value of 1 at which point the link breaks.

Using Eq. (16), one finds that the first link breaks at a time $\tau_1 > 0$ [that is, $\varphi_1(\tau_1) = 1$] provided the parameter $\beta$ exceeds its critical value $\beta_c^* \approx 2.4768$. According to Eq. (9), this value corresponds to $\alpha_c^* \approx 24.54$, in agreement with Zwanzig's result [3]. For reduced times $\tau > \tau_1$ after the break of the first link, the adatom no longer interacts with the lattice and evolves freely according to

$$\zeta_1(\tau) = \zeta_1(\tau_1) = \text{const} \tag{19}$$

$$\xi_1(\tau) = \xi_1(\tau_1) + \beta\zeta_1(\tau_1)(\tau - \tau_1). \tag{20}$$

The evolution of the lattice atoms after the rupture, on the other hand, is given by

$$\zeta_{i+1}(\tau) = \sum_{k=1}^{\infty}\left(\zeta_{k+1}(\tau_1)W_{ik}(\Delta_1) + \beta^{-1}\xi_{k+1}(\tau_1)\frac{d}{d\Delta_1}W_{ik}(\Delta_1)\right), \tag{21}$$

$$\xi_{i+1}(\tau) = \sum_{k=1}^{\infty}\left(\xi_{k+1}(\tau_1)W_{ik}(\Delta_1) + \beta\zeta_{k+1}(\tau_1)\int_0^{\Delta_1} d\Delta W_{ik}(\Delta)\right), \tag{22}$$

where $i = 1,2,\ldots$, $\Delta_1 = \tau - \tau_1$, and $\xi_i(\tau_1), \zeta_i(\tau_1)$ are given by the functions (16) and (17) at $\tau = \tau_1$. However, if one tracks the evolution of $\varphi_1(\tau)$, one observes that $\varphi_1(\tau)$ first increases then *decreases* to its initial value $\varphi_1(\tau_2)$ at a reduced time $\tau_2$ (see curves 1–3 in Fig. 2) provided the $\beta$ parameter, determined by the initial kinetic energy of the adatom, falls in the interval $\beta_c^* < \beta < \beta_c$, with $\beta_c \approx 2.617$. At time $\tau_2$, the adatom reenters the region of interaction with the lattice and is once again bound by the chain. The dynamics of the chain after the adatom reenters the region of interaction with the lattice ($\tau > \tau_2$), is described by

$$\zeta_i(\tau) = \sum_{k=1}^{\infty}\left(\zeta_k(\tau_2) + \beta^{-1}\xi_k(\tau_2)\frac{d}{d\Delta_2}\right)W_{ik}(\Delta_2), \tag{23}$$

$$\xi_i(\tau) = \sum_{k=1}^{\infty}\left(\xi_k(\tau_2)W_{ik}(\Delta_2) + \beta\zeta_k(\tau_2)\int_0^{\Delta_2} d\Delta W_{ik}(\Delta)\right), \tag{24}$$

where $\Delta_2 = \tau - \tau_2$, and $\zeta_i(\tau_2), \xi_i(\tau_2)$ are the functions (21) and (22) at $\tau = \tau_2$. Equations (23) and (24) give a relative displacement $\varphi_1(\tau) < 1$ for all $\tau > \tau_2$, which implies the adatom leaves the interaction zone only once. Rupture events of the adatom-lattice bond leading to the reflection of the adatom in the asymptotic time limit occur for $\beta > \beta_c$, where the

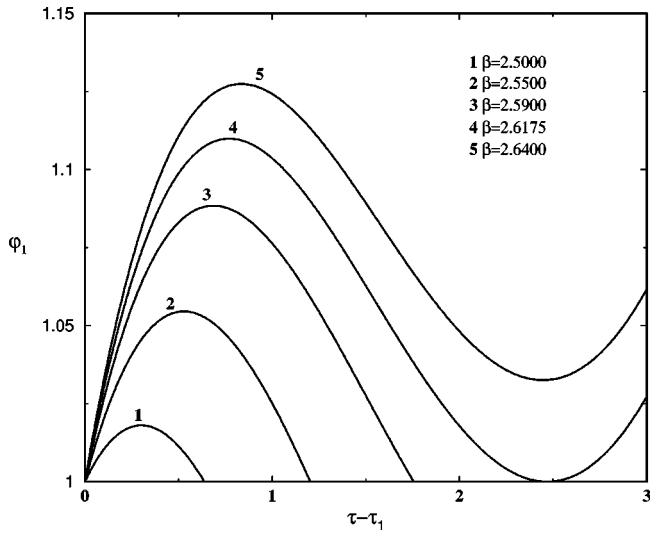


FIG. 2. Relative displacement $\varphi_1=\xi_2-\xi_1$ between the adatom and the outermost lattice atom after the adatom leaves the interaction zone $\varphi_1<1$. Curves 1, 2, and 3 correspond to situations where the adatom is recaptured, while curves 4 and 5 correspond to adatom reflection.

kinetic energy of the adatom is still large enough after one oscillation of the chain that the lattice is unable to recapture the adatom (see curves 4 and 5 in Fig. 2). Thus, one can conclude that the adatom is reflected by the lattice only for $\beta>\beta_c$, which gives a critical value $\alpha_c\approx 27.395$, roughly 10% larger than the value $\alpha_c^*\approx 24.54$ predicted by Zwanzig [3].

If $\beta>\beta_c$ and the adatom has left the scene of interaction, the outermost lattice atom ($i=2$) becomes the terminal atom for the rest of the chain. If one now assumes that at this stage atom 2 begins to interact with atom 3 via a truncated parabolic potential, the new terminal atom can escape the lattice provided it gains enough energy from the collision of the adatom with the lattice. For this model, we find that the first link of the remaining chain, between atoms 2 and 3, experiences a ''virtual'' break for a critical value of $\beta\approx 3.94$, while bond-breaking events leading to the final escape of atom 2 occurs when $\beta\approx 4.35$. This process can be continued to examine how energetic adatom-lattice collisions lead to sequential fragmentation of the lattice. In Sec. IV, we examine a slightly different model of surface fragmentation in which all lattice atoms interact via a truncated parabolic potential, thus allowing bond-breaking events to occur between any two lattice atoms at all times.

### III. ARBITRARY MASS RATIOS

To generalize the previous discussion of adatom-lattice collision dynamics to an arbitrary mass ratio $\mu=m/M$, it is instructive to consider the set of integral-differential equations for atom positions, which have the form of a generalized Langevin equation [9,10]. For the adatom, the equation has the form

$$\ddot{q}_1(t)=-\omega_1^2 q_1(t)+\omega_1^2\int_0^t dt' K(t-t')q_1(t')+F_1(t),$$

where $\omega_1^2=k/M$, the memory function $K(\tau)$ is given by $K(\tau)=2J_2(2\omega t)/t$, and the ''stochastic'' force $F_1(t)$ is a linear function of initial coordinates and momenta of the lattice atoms ($i=2,3,\ldots$). The equations for the lattice atoms are given by

$$\ddot{q}_i(t)=-\omega^2 q_i(t)-\omega^2(q_i-q_{i-1})+\omega^2\int_0^t dt' K(t-t')q_i(t')+F_i(t),$$

where the force $F_i(t)$ is a linear function of initial coordinates and momenta of atoms $i+1, i+2, \ldots$ For the initial conditions of the CZ model [see Eq. (14)], the fluctuating forces $F_i$ vanish. Then introducing the reduced time $\tau=2\omega t$, the above equations can be written as

$$\ddot{q}_1(\tau)=-\frac{\mu}{4}q_1(\tau)+\frac{\mu}{4}\int_0^\tau d\tau' M(\tau-\tau')q_1(\tau'), \quad (25)$$

for the adatom, and

$$\ddot{q}_i(\tau)=-\frac{1}{2}q_i(\tau)+\frac{1}{4}q_{i-1}+\frac{1}{4}\int_0^\tau d\tau' M(\tau-\tau')q_i(\tau'), \quad (26)$$

for the lattice atoms, $i=2,3,\ldots$ Here and below, the notation $\dot{B}(\tau)$ and $\ddot{B}(\tau)$ denote the first and second derivatives of an arbitrary variable $B(\tau)$ with respect to $\tau$. The memory function $M(\tau)$ in these equations takes the form

$$M(\tau)=\frac{2}{\tau}J_2(\tau)=\tfrac{1}{2}[J_1(\tau)+J_3(\tau)], \quad (27)$$

which has the Laplace transform, $\tilde{M}(s)=s^2-s\sqrt{s^2+1}+1/2$.

Using the method of Laplace transformation, one can obtain the solution of Eqs. (25) and (26) in the convenient iterative form

$$q_1(\tau)=A(\tau)q_1(0)+\left\{\int_0^\tau A(\tau')d\tau'\right\}\dot{q}_1(0), \quad (28)$$

$$q_i(\tau)=\int_0^\tau M(\tau-\tau')q_{i-1}(\tau')d\tau', \quad i\geqslant 2, \quad (29)$$

where the function $A(\tau)$ has the Laplace transform

$$\tilde{A}(s)=\frac{2}{(2-\mu)s+\mu\sqrt{s^2+1}}. \quad (30)$$

Equations (28) and (29) can be expressed in terms of the dimensionless displacements and velocities as

$$\xi_1(\tau)=-A(\tau)+\beta\int_0^\tau A(\tau')d\tau', \quad (31)$$

$$\zeta_1(\tau)=A(\tau)-\beta^{-1}\dot{A}(\tau), \quad (32)$$

for the adatom, and

$$\xi_i(\tau)=\int_0^\tau M(\tau-\tau')\xi_{i-1}(\tau')d\tau', \tag{33}$$

$$\zeta_i(\tau)=\int_0^\tau M(\tau-\tau')\zeta_{i-1}(\tau')d\tau'-\frac{1}{\beta}\delta_{i,2}M(\tau) \tag{34}$$

for the lattice atoms, $i\geqslant 2$.

There are two cases when the inverse transform of $\tilde{A}(s)$ in Eq. (30) has a closed form. For $\mu=1$, one finds that $A(\tau)=2J_1(\tau)/\tau=J_0(\tau)+J_2(\tau)$ and Eqs. (28) and (29) coincide with the general solution obtained previously in Eqs. (5) and (6) for the homogeneous chain. The second simple case is when $\mu=2$, which yields the concise result $A(\tau)=J_0(\tau)$.

To obtain $A(\tau)$ for mass ratios $\mu$ other than 1 and 2, one notes that $\tilde{A}(s)$ is a two-valued function with branch points at $s=\pm i$. The corresponding Riemann surface, consisting of two sheets, can be constructed making a cut along the imaginary axis between the branch points. To obtain the inverse Laplace transform of $\tilde{A}(s)$, one must choose the first sheet on which the function $\sqrt{s^2+1}$ is positive when $s$ is real and positive since integration on the second sheet leads to a function $A(\tau)$ that behaves unphysically either in the limit $\tau=0$, or when $\tau\to\infty$ (or in both limits). If $\mu<2$, the only singular points of the function $\tilde{A}(s)$ on the first sheet are at the branch points $\pm i$. The integration path of the inverse Laplace transform for this case can be transformed into a closed curve around the cut. For this path, one obtains the following integral representation for $A(\tau)$ for $\mu<2$,

$$A(\tau)=\frac{1}{\pi}\frac{\mu}{\mu-1}\int_0^1 dy\cos(y\tau)\frac{\sqrt{1-y^2}}{\gamma-y^2}, \tag{35}$$

where $\gamma=(\mu^2/4)/(\mu-1)$. If $\mu>2$, on the other hand, there are also contributions to $A(\tau)$ from two simple poles lying on the imaginary axis at $s=\pm i\sqrt{\gamma}$, and one gets

$$A(\tau)=\frac{1}{\pi}\frac{\mu}{\mu-1}\int_0^1 dy\cos(y\tau)\frac{\sqrt{1-y^2}}{\gamma-y^2}+\frac{\mu-2}{\mu-1}\cos(\sqrt{\gamma}\tau). \tag{36}$$

Equations (31)–(36) give a complete description of the system dynamics until the break of the first link of the chain at time $\tau_1$. After the chain breaks, the dynamics is described by Eqs. (19)–(22) that, in turn, hold until the adatom is recaptured by the lattice. As in the special case $\mu=1$, one finds that $\beta_c^*\neq\beta_c$ for any mass ratio $\mu$, where $\beta_c^*$ and $\beta_c$ denote the critical values of the parameter $\beta$ at which the first link breaks and the adatom is asymptotically reflected, respectively. For a light adatom with $\mu>5$ at $\beta=\beta_c^*$, the adatom velocity at the moment of bond rupture is positive and hence directed toward the lattice, implying that the adatom is recaptured by the lattice. Such recapture events persist for $\mu$ values as large as 40, and presumably occur for larger $\mu$. However, since the difference between $\beta_c^*$ and $\beta_c$ becomes increasingly small with large $\mu$, it is numerically difficult to detect recapture events for very light adatoms. For very light adatoms, $\beta_c^*\approx\beta_c$, and hence the original CZ criterion to solve for the critical value of $\beta$ for adatom reflection is approximately correct. On the other hand, for a relatively heavy adatom ($\mu<5$), the situation is qualitatively similar to that described in the preceding section for $\mu=1$: At the moment of rupture, the adatom is moving away from the lattice for $\beta=\beta_c^*$ with a small velocity and is subsequently recaptured by the vibrating lattice.

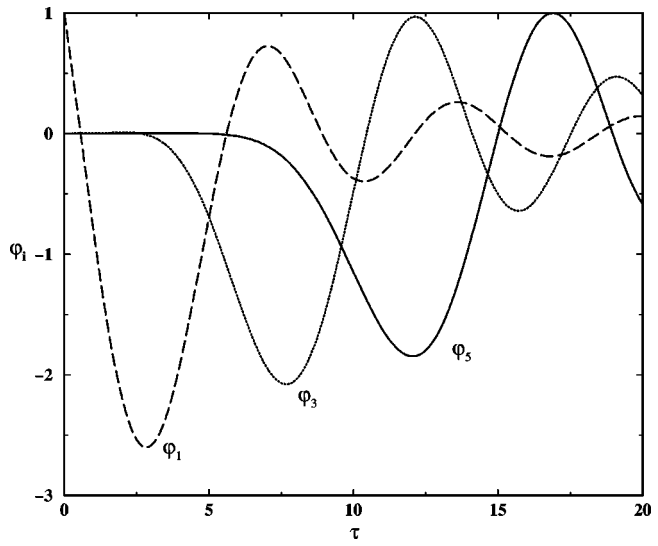


FIG. 3. Relative displacements $\varphi_i=\xi_{i+1}-\xi_i$ of the first ($\varphi_1$), third ($\varphi_3$), and fifth ($\varphi_5$) links of the chain for $\beta=1.6941$. Positive and negative values of $\varphi_i$ correspond to stretching and compressing of the link, respectively.

## IV. GENERALIZED MODEL

One rather unexpected feature of the semi-infinite, homogeneous chain dynamics after the adatom collision is that the maximal stretching of the first link of the chain may be less than that for the subsequent links (see Fig. 3). Due to this surprising observation, first noted in Ref. [4], it is interesting to consider a generalization of the CZ model in which *all* nearest neighbor atoms in the lattice interact via the same truncated potential. Since the maximal bond stretching induced by the adatom collision with the lattice does not occur at the first link, one may anticipate that the result of an adatom collision in the generalized CZ (GCZ) model will not be a reflection but rather a fragmentation of the chain. Restricting ourself to the case $M=m$, we demonstrate in this section that the rupture events in the inner chain are virtual for low-energy adatom collisions, yielding short-lived chain fragments that are recaptured by the lattice. As a result of the recapture events, low-energy adatom-lattice collisions result in either trapping or reflection of the adatom without fragmentation of the chain. However, as the adatom energy increases, clusters of atoms may escape the lattice in addition to the reflected adatom.

To explore the possibility of the lattice fragmentation in the GCZ model, one also needs the general solution of equa-

tions of motion for a free cluster in addition to the solutions (5) and (6) for the semi-infinite chain. In the Appendix, it is shown that the displacements of an atom in a free cluster obey

$$q_i(t)=q_c(0)+v_c(0)t + \sum_{k=1}^{N}\left( q_k(0)V_{ik}(t)+v_k(0)\int_0^t dt' V_{ik}(t')\right), \tag{37}$$

where $N$ is the number of atom in a cluster, $q_c(0)=N^{-1}\Sigma_i q_i(0)$ and $v_c(0)=\dot{q}_c(0)$ are the initial coordinate and the velocity of the center of mass of the cluster. The function $V_{ik}(\tau)$ in Eq. (37) is given by

$$V_{ik}(\tau)=\frac{1}{N}\sum_{j=1}^{N-1}[\cos\{2(i-k)y_j\}\cos(\tau\sin y_j) - \cos\{2(i+k-1)y_j\}\cos(\tau\sin y_j)],$$

where $\tau=2\omega\tau$, and $y_j=\pi j/(2N)$. In the limit of large clusters, $V_{ik}(t)$ reduces to the corresponding function $W_{ik}(t)$ for the semi-infinite chain given in Eq. (7). The dimensionless displacements $\xi_i$ and velocities $\zeta_i$ for atoms in the cluster obey

$$\zeta_i(\tau)=\sum_{k=1}^{N}\left(\zeta_k(0)+\beta^{-1}\xi_k(0)\frac{d}{d\tau}\right)V_{ik}(\tau)+\zeta_c(0), \tag{38}$$

$$\xi_i(\tau)=\sum_{k=1}^{N}\left(\xi_k(0)+\beta\zeta_k(0)\int_0^\tau d\tau\right)V_{ik}(\tau)+\xi_c(0) + \beta\tau\zeta_c(0), \tag{39}$$

where $\zeta_c(0)=N^{-1}\Sigma_i\zeta_i(0)$ and $\xi_c(0)=N^{-1}\Sigma_i\xi_i(0)$.

The initial dynamics of the chain (before a break in the chain) in the GCZ model is described by the same expressions (16) and (17) as for the original CZ model. Using these equations, one finds that the minimal $\beta$ for the chain rupture is $\beta_1=1.6941...$, which corresponds to the break of the *fifth* link at the reduced time $\tau=\tau_1=16.89,...$, at which time

$$\varphi_5(\tau_1)=\xi_6(\tau_1)-\xi_5(\tau_1)=1, \tag{40}$$

$$\varphi_i(\tau)<1, \quad i\neq 5, \tau\leqslant\tau_1. \tag{41}$$

At time $\tau_1$, the original chain decomposes into a cluster of five atoms and a semi-infinite lattice. For $\tau>\tau_1$, the cluster evolves according to Eqs. (38) and (39) from the coordinates and velocities values $\xi_i(\tau_1)$ and $\zeta_i(\tau_1)$,

$$\xi_i(\tau)=\xi_c(\tau_1)+\beta\Delta_1\zeta_c(\tau_1)+\sum_{k=1}^{5}\left(\xi_k(\tau_1)V_{ik}(\Delta_1) + \beta\zeta_k(\tau_1)\int_0^{\Delta_1}d\Delta V_{ik}(\Delta)\right), \tag{42}$$

$$\zeta_i(\tau)=\sum_{k=1}^{5}\left(\zeta_k(\tau_1)+\beta^{-1}\xi_k(\tau_1)\frac{d}{d\Delta_1}\right)V_{ik}(\Delta_1)+\zeta_c(\tau_1), \tag{43}$$

where $\Delta_1=\tau-\tau_1$, and the time dependence of the atoms of the remaining lattice is given by

$$\xi_{i+5}(\tau)=\sum_{k=1}^{\infty}\left(\xi_{k+5}(\tau_1)W_{ik}(\Delta_1) + \beta\zeta_{k+5}(\tau_1)\int_0^{\Delta_1}d\Delta W_{ik}(\Delta)\right), \tag{44}$$

$$\zeta_{i+5}(\tau)=\sum_{k=1}^{\infty}\left(\zeta_{k+5}(\tau_1)W_{ik}(\Delta_1) + \beta^{-1}\xi_{k+5}(\tau_1)\frac{d}{d\Delta_1}W_{ik}(\Delta_1)\right), \tag{45}$$

where $i=1,2,\ldots$

Equipped with these results, it is straightforward to show that the bond rupture occurring at the fifth link for $\beta_1<\beta<\beta_2$ (where $\beta_2=1.71...$) are virtual in the sense that the cluster leaves the interaction region of the lattice for a short time and is then captured by the lattice at time $\tau_2$. For $\tau>\tau_2$, the evolution of the chain is once again described by Eqs. (23) and (24), and the lattice is stable.

Similar analysis shows that neither the reflection of the adatom nor the fragmentation of the lattice occurs for $\beta$ less than the threshold value $\beta_c=1.86\ldots$. If $\beta$ is slightly larger than $\beta_c$, the chain first experiences a virtual break at the third link, leading to a three-atom cluster, which is later recaptured by the lattice. At subsequent times, the chain is unstable and quickly ruptures at the first link. This break is not virtual and leads to the final reflection of the adatom. The remaining lattice is then stable for all time and does not fragment. This behavior is reminiscent of that observed in the tunneling mechanism of chain breaking [11] according to which bond rupture results from two subsequent processes with different time scales, the fast vitual disappearance of one bond followed by the slow collective motion of the chain.

As $\beta$ increases further, the evolution of the system becomes more complicated and fragmentation of the lattice is possible. To illustrate this point, consider the chronology of the chain decay for $\beta=2.47$ for which the chain first breaks at the second link. For this value of $\beta$, the two-atom cluster is not recaptured by the lattice. The remainder of the lattice vibrates after the cluster breaks free for a reduced time interval $\delta t\approx 15$, after which the chain experiences a virtual rupture at the sixth-link on the remaining chain, forming a six-atom cluster, which is quickly recaptured. After the cluster is recaptured, the lattice is still unstable and finally fragments at the fifth link, leading to the ''evaporation'' of a five-atom cluster from the lattice, which is henceforth stable.

## V. CONCLUDING REMARKS

In this paper, it has been demonstrated that the Cabrera-Zwanzig model of the collision of an atom with a cold lattice has much richer behavior than previously reported. In particular, we have shown that secondary collisions in which the adatom reenters the interaction zone of the lattice after a virtual break are important over a wide range of mass ratios $\mu$. Due to the presence of secondary adatom-lattice collsions, the adatom reflection threshold energy cannot be computed based on a single bond-breaking event. It was demonstrated that threshold energies calculated in this fashion provide only a lower bound for the adatom to leave the interaction zone and do not guarantee that the adatom will be reflected by the lattice in the asymptotic time limit.

In addition, collision-induced fragmentation was considered by generalizing the CZ model to allow for the breaking of all lattice bonds. For the generalized CZ model (GCZ), it was shown that the collision of a low energy adatom with a cold lattice produces short-lived clusters, which are quickly recaptured by the vibrating lattice. It was demonstrated that the first fragmentation event surviving in the long time limit corresponds to the reflection of the adatom in spite of the production of virtual clusters at early times. Although the asymptotic phenomenology of the GCZ model is similar to that of the CZ model for low energy collisions, the energy threshold for adatom reflection for the GCZ model was found to be of approximately half its value in the simpler model, demonstrating the importance of the formation of virtual clusters in the energy transfer process. As the energy of the adatom collision with the lattice increases, the evolution of the system becomes complicated by the evaporation of clusters, resulting in real fragmentation of the lattice.

It should be emphasized that the present considerations are neither general nor complete. This study focused only on the situation in which the masses of the atoms composing the lattice are the same and the spring constants appearing in the (possibly truncated) parabolic potentials are all equal. In principle, it is possible to consider the collision of an adatom with nonhomogeneous lattices along the lines elaborated here, but the mathematical solution of the equations of motion of the nonhomogeneous system becomes cumbersome. Furthermore, one may anticipate that the phenomenology of the collisions of an atom with a nonhomogeneous lattice would be quite similar to that reported here. In particular, one expects the mechanism of secondary collisions to increase the minimum threshold energy for adatom reflection.

The present study demonstrates the importance of a careful consideration of the full dynamics of the adatom-lattice system after the initial bond-breaking event. The energy transfer from the adatom to the surviving lattice is strongly influenced by the formation of virtual clusters, which are recaptured by the ''surface'' in secondary collisions. Such behavior is likely to be important in more realistic models of the collision process of an atom with a surface, which are based on other potentials of interaction, other initial conditions, such as those appropriate for studying thermal desorption, or which involve multidimensional lattice structures for the surface.

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## APPENDIX

In this appendix, the solution of the equations of motions for a finite free harmonic chain and for a semi-infinite chain are presented. The Hamiltonian of the finite harmonic chain of $N$ atoms with both ends free

$$H=\sum_{i=1}^{N}\frac{p_i^2}{2m}+\sum_{i=1}^{N-1}\frac{k}{2}(q_i-q_{i+1})^2$$

can be reduced to the diagonal form

$$H=\frac{1}{2}\sum_{j=0}^{N-1}\{P_j^2+\omega_j^2Q_j^2\},$$

by means of the normal mode transformations

$$q_i=\frac{1}{\sqrt{m}}\sum_{j=0}^{N-1}A_{ij}Q_j,\quad p_i=\sqrt{m}\sum_{j=0}^{N-1}A_{ij}P_j,$$

with

$$A_{ij}=\left(\frac{\epsilon_j}{N}\right)^{1/2}\cos\left\{\pi j\,\frac{2(N-i)+1}{2N}\right\},$$

where $\epsilon_j$ takes the value of 1 if $j=0$ and 2 otherwise. The frequencies of the normal modes are given by

$$\omega_j=2\omega\sin\left(\frac{\pi j}{2N}\right),$$

where $\omega=\sqrt{k/m}$. The normal modes evolve as

$$P_j(t)=P_j(0)\cos(\omega_jt)-\omega_jQ_j(0)\sin(\omega_jt),$$

$$Q_j(t)=Q_j(0)\cos(\omega_jt)+\omega_j^{-1}P_j(0)\sin(\omega_jt),$$

for $j\neq0$, and

$$P_0(t)=P_0(0)=\text{const}$$

$$Q_0(t)=Q_0(0)+P_0(0)t$$

for the mode $j=0$. The momentum of the atom $i$ can then be written as

$$p_i(t)=\sqrt{m}\sum_{j=0}^{N-1}A_{ij}\{P_j(0)\cos(\omega_jt)-\omega_jQ_j(0)\sin(\omega_jt)\}+\sqrt{m}A_{i0}P_0.$$

Since the $A_{ij}$ satisfy orthogonality conditions with respect to both indices, one can express $P_j(0)$ and $Q_j(0)$ in the above equation in terms of $p_i(0)$ and $q_i(0)$. The resulting equation has the form

$$p_i(t)=\frac{1}{N}\sum_{k=1}^{N} p_k(0)+\sum_{k=1}^{N}\left(p_k(0)+mq_k(0)\frac{d}{dt}\right)V_{ik}(t),$$

where

$$V_{ik}(t)=\sum_{j=1}^{N-1} A_{ij}A_{kj}\cos(\omega_j t).$$

After simple trigonometric manipulations, the function $V_{ik}(t)$ can be written as

$$V_{ik}(t)=\frac{1}{N}\sum_{j=1}^{N-1}[\cos\{2(i-k)y_j\}\cos(2\omega t\sin y_j) - \cos\{2(i+k-1)y_j\}\cos(2\omega t\sin y_j)],$$

where $y_j=\pi j/(2N)$.

The case of the semi-infinite chain is recovered in the limit $N\to\infty$ by converting the sum to an integral

$$V_{ik}(t)=\frac{2}{\pi}\int_0^{\pi/2} dy[\cos(2y|i-k|)\cos(2\omega t\sin y) + \cos\{2y(i+k-1)\}\cos(2\omega t\sin y)],$$

which is just the integral representation for the sum of two Bessel functions

$$V_{ik}(t)=J_{2|i-k|}(2\omega t)+J_{2(i+k-1)}(2\omega t)$$

The solutions for displacements can be obtained in an analogous fashion.


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