Diffusion of particles interacting by long-range and oscillating forces.

Filip Krzyżewski, Magdalena A. Zaluska-Kotulski
Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02–668 Warsaw, Poland

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Collective diffusion coefficient in a one dimensional lattice gas adsorbate is calculated using variational approach. Particles interact via either a long-range, or a long range electron-gas-mediated (for a metallic substrate), or a 12 – 6 Lennard-Jones interaction. Diffusion coefficient as a function of the adsorbate density depends on the relationship between the substrate lattice constant and the characteristic length of the inter–particle interaction potential (which determines positions of the potential energy minima). The diffusion coefficient at fixed density as a function of the interaction characteristic length has an oscillating character due to the interplay between the inter–particle distances allowed by the substrate lattice structure and the average inter–particle distances which minimize the total interaction energy.

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I. INTRODUCTION

Manipulation of single atoms and self-assembly techniques are very useful methods in quantum engineering. Self-assembly is determined by inter–atomic interactions, which at the crystal surfaces can be direct or indirect (i.e. induced by the substrate). Recent studies on adatom arrangement and their dynamics on metallic surfaces show that they experience an indirect electron-gas-mediated interactions. Electronic surface states are a source of a long range interactions, which decay with the inter–particle distance as 1/r and often have an oscillatory character. Such interactions between adatoms lead to their self-alignment. This ordering mechanism is a good candidate to be used for constructing and manipulating nanostructure systems. Linear arrangements have unique magnetic and/or electronic properties. The ordering dynamics and a stability of an ordered structure depend on diffusion of adatoms on the surface while diffusion in a system of adatoms is controlled by interactions between them.

The collective or chemical diffusion coefficient of adsorbed species characterizes a relaxation of the local density fluctuations in a many particle system. It involves jumps of individual atoms (adsorbed particles) from one binding site to another. Theoretical description of the collective diffusion process is a complicated many–body problem and various approaches have been applied to it, ranging from analytic ones based on master, Fokker–Planck, or Kramers equations to numerical Monte Carlo or molecular dynamics simulations. An important background is provided in the works of Reed and Ehrlich, an early summary by Gomez, and in reviews by Danani et al. and Ala-Nissila et al. The variational approach to the collective diffusion problem, used here, was developed in a series of works, and was shown to be a very efficient tool to analyze collective diffusion problems for various types of inter–particle interactions for homogeneous or inhomogeneous substrates either in one or two dimensions.

We have shown in Ref. that the long range repulsive interactions can be responsible for rapid macroscopic rearrangements of adatoms upon minuscule adsorbate density changes. We have shown that the adsorbate density dependent diffusion coefficient has peaks at densities corresponding to any ordered phase in a devil staircase phase diagram. It is well known that the devil staircase structure emerges when the inter–particle interaction potential is repulsive and decays faster than 1/r. It has been shown, one the other hand, that adatoms on metallic surfaces often interact via forces with oscillating in r potential energies. They exhibit a 1/r decay modified by Friedel oscillations of the electron gas correlation function meaning that particles attract each other at some distances and repel at others. Such a distance dependence of the inter–particle interactions should, in principle, result in a diffusion character similar to that already investigated for pure 1/r repulsion. On the other hand, the oscillating interaction potential has local minima. Similarly, a minimum is present also for the interaction of the Lennard–Jones type. The question arises how the presence of such a minimum (or minima) affects the diffusion kinetics in a many particle system. In particular, it is an interesting question how does the oscillating character of the interactions decaying like 1/r modify diffusion in comparison with the interactions decaying like 1/r^2 monotonically.

It is well known that the shape of interaction potential, in particular, existence of its attractive parts is very important for the static behavior of the system. Systems with attractive interactions form stable clusters of ordered phases, whereas ordering via repulsion is always global — it affects the entire system. Consequently, an ordered phase due to attractive interactions occurs for a wider range of adatom densities so it is easier to observe experimentally. Such difference in static properties has to affect the dynamic behavior too, so it should affect also the diffusion process. For example, a fast collective diffusion in ordered structures leads to a fast reorganization of the adsorbed layer.

In this work we compare three types of interactions:
monotonically decaying like $1/r^2$, the oscillating ones decaying like $1/r^6$ with electron-gas-mediated oscillations, and the 12 − 6 Lennard–Jones interactions. We analyze the influence of the shape of the interaction potential on the diffusion coefficient at different adsorbate densities. Magnitude of the diffusion coefficient depends on several parameters, most of them related to the character and strength of the inter–particle interaction. In what follows we analyze how periodic in $r$ variation of the potential superimposed on the $1/r^6$ decay influences diffusion. We show that for systems of particles interacting via oscillating electron-gas-mediated forces or via forces corresponding to the 12 − 6 Lennard–Jones potentials the diffusion process depends sensitively on the ratio between the distance $r$ at which the potential has a minimum and the substrate lattice constant. This ratio allows to distinguish between the commensurate and incommensurate type of diffusion kinetics. We show that the diffusion coefficient depends periodically on the characteristic length of the potentials under investigation.

The paper is organized as follows. In Section II the approach to the diffusion coefficient calculation is shortly described. Section III contains description of results for electron-gas mediated, oscillation potential, and then for 12 − 6 Lennard–Jones potential. Section IV summarizes main results of the work.

II. MODEL

System of $N$ particles interacting via long range forces is distributed homogeneously over a one-dimensional substrate of length $L$ with a lattice constant $a$. The interaction of two particles at the lattice positions $l_i$ and $l_j$ contributes the potential energy $\varepsilon(l_i - al_j)$ to the total energy of the system. Following Ref. [28,29] we consider systems with the pair potential energy $\varepsilon(r)$ decreasing rapidly with $r$. This justifies to neglecting the next-nearest-particle interactions and accounting only for pair interactions between neighbors no matter how large the intra-pair separation $al$ is. The total interaction energy of the system is $\sum n_i \varepsilon(al_i)$ where $n_i$ is the number of nearest neighbors pairs of length $l$ (in units of $a$) and only $l$’s satisfying the condition $\sum l_nu = L$ are admitted in the sum. In a grand canonical ensemble approach we let $l$ to vary from 0 to $\infty$ and keep, instead, the system under fixed external pressure $P$ (in 1D it is just an external force) which is determined by the condition that the mean nearest neighbor pair length $\langle l \rangle$ is equal to the inverse of the actual coverage $\theta = N/L$. In such case a probability of a pair of a length $l$ is [28,29]

$$p_l(P,T) = Z_l^{-1}(P,T)e^{-\beta\varepsilon(l,P)},$$

where

$$\varepsilon(l,P) = \varepsilon(al) + aPl$$

and

$$Z_1(P,T) = \sum_{l=1}^{\infty} e^{-\beta\varepsilon(l,P)}$$

is a single nearest neighbor-pair isothermal–isobaric partition function.

Eqs. (1) through (3) allow to determine the thermodynamic properties of the system. In particular, the equation of state, relation between the coverage, pressure and temperature is obtained by evaluating the mean nearest neighbor pair length

$$\langle l \rangle = \frac{1}{Z_1^{-1}(P,T)} \sum_{l=1}^{\infty} le^{-\beta\varepsilon(l,P)} = -\frac{1}{\beta a} \left( \frac{\partial \ln Z_1}{\partial P} \right)_T,$$

and identifying it with $1/\theta$. In the low temperature limit the main contributions to this sum come from one or at most two terms only.

Collective diffusion of the system is modeled by a kinetic lattice gas with the particle hopping rates depending on the actual potential energy of the particle. The potential energy landscape is build by the static potential due to the substrate, as experienced by a single particle, and by interactions of the particle with its neighbors. Time evolution of the system is controlled by a set of master rate equations for the probabilities $P\{c\}, t$ that a microstate $\{c\}$ of a lattice gas occurs at time $t$

$$\frac{d}{dt} P\{c\}, t$$

$$= \sum_{\{c'\}} [W\{c\}, \{c'\}]P\{c', c\} - W\{c', c\}P\{c\}, t].$$

The microstate $\{c\}$ is understood as a set of variables specifying which particular sites in the lattice are occupied and which are not. $W\{c', c\}$ is a transition probability per unit time (transition rate) that the microstate $\{c\}$ changes into $\{c'\}$ due to a jump of a particle from an occupied site to an unoccupied neighboring site. Microstates $\{c\}$ and $\{c'\}$ differ here only by the position of a single particle, the one which jumped. For thermally activated jumps, the hopping rate depends on the difference between the energy of the system when the hopping particle is at an intermediate position between the sites engaged in the jump and the energy of the system when the particle is in its initial position. The only contributions that do not cancel out in the difference is the energy of the hopping particle in its initial position and its energy in the activated state at the top of the potential barrier which it jumps over. For the particle hopping from the adsorption site specified by a pair of integers $(l, s)$ (i.e. with the nearest neighbors of adsorbed particles being at a distance $al$ and $as$, respectively, to its left and right) to a neighboring site $(l', s') = (l \pm 1, s \mp 1)$ the potential energy at the initial adsorption site is

$$E_A = E_A^{al} + \varepsilon(al) + \varepsilon(as),$$
where \( E_A^0 \) is static potential energy at given site due to the interactions with the substrate. The hopping rate can be written as

\[
W(\{c\}, \{c’\}) = W_{l,s}^{l’,s’} = W^0 e^{-\beta \left[ \Delta_{l,s}^{l’,s’} \right]},
\]

where \( W^0 = \nu \exp[-\beta (E_B^0 - E_A^0)] \) is a hopping rate for an isolated (i.e. non–interacting) particle and \( \nu \) is an intrinsic attempt frequency. \( \Delta_{l,s}^{l’,s’} \) is the amount by which the potential energy \( E_B^0 \) of the hopping particle at a bridge site between its initial and the final position is modified by interactions with the neighbors at each its side. We parametrize a microstate \( \{c\} \) as \( \{c\} = \{X, \{m\}\} \) by selecting one particle as a reference particle, denoting its lattice position as \( X \) and specifying positions \( \{m\} = \{m_1, m_2, \ldots, m_{N-1}\} \) of all remaining \( N-1 \) particles with respect to it. \( \{m\} \) is referred to as a configuration. Master equations (5) are linear in set of probabilities \( P(X, \{m\}, t) \) and so their lattice Fourier transform with respect to \( X \) can be easily done. The result is that \( k \)-components of the probabilities, \( P_{\{m\}}(k, t) \), evolve in time independently of each other. The rate equations for \( P_{\{m\}}(k, t) \) can be expressed in terms of a \( k \)-space microscopic rate matrix \( \mathcal{M}(k) \) (with rows and columns labelled by \( \{m\}\) containing the individual hopping rates and phase factors like \( e^{\pm ik \alpha} \). Details can be found in Refs. 25,28. The collective diffusion coefficient is related to that eigenvalue \( \lambda_D(k) > 0 \) (termed the diffusive eigenvalue) of \( \mathcal{M}(k) \) which vanishes like \( k^2 \) in the limit \( k \to 0 \). This eigenvalue is then estimated from above in a spirit of a variational principle \( 25 \) as

\[
\lambda_D(k) = \frac{\phi \cdot [-\mathcal{M}(k)] \cdot \phi}{\phi \cdot \phi} \to -D k^2,
\]

where the \( \to \) stands for the \( k \to 0 \) limit and \( \phi \) and \( \phi \) are variational trial left and right, respectively, eigenvectors of \( \mathcal{M}(k) \) corresponding to the diffusive eigenvalue. It has been shown \( 25,28 \) that for a homogeneous substrate the \( \{m\}-th \) component of the trial left eigenvector has the form

\[
\tilde{\phi}_{\{m\}}(k) = 1 + \sum_{j=1}^{N-1} e^{ik \alpha m_j},
\]

and that \( \phi_{\{m\}}(k) = P_{\{m\}}^{eq} \tilde{\phi}_{\{m\}}(k) \), where \( P_{\{m\}}^{eq} \) is the probability of the configuration \( \{m\} \) in equilibrium.

We calculate the diffusion coefficient \( D \) as a ratio (the \( k \to 0 \) limit is implied)

\[
D = -\frac{\lambda_D}{k^2} = \frac{\mathcal{M}(k)}{\mathcal{N}(k)k^2}.
\]

to the “normalization” denominator

\[
\mathcal{N}(k) = \sum_{\{m\}} P_{\{m\}}^{eq} \left| \tilde{\phi}_{\{m\}}(k) \right|^2.
\]

Detailed balance condition was used to derive Eq. (11) so each \( \langle \{m\}, \{m'\}\rangle \) term in it accounts for transitions between \( \{m\} \) and \( \{m'\} \) in either direction. Therefore, each configuration pair \( \langle \{m\}, \{m'\}\rangle \) appears in the sum in Eq. (11) only once [as indicated by the comment “no rep” above the sum] in order to avoid double counting. In the grand canonical ensemble approach, mentioned earlier, both \( \mathcal{N} \) and \( \mathcal{M} \) are functions of \( P, T, \) and \( N \). We note in passing that \( \mathcal{N} \) and \( \mathcal{M} \) are directly related to the diffusion coefficient static (or thermodynamic) and kinetic factor, respectively, which the diffusion coefficient is customarily factorized into. \( 17,18 \). The former is controlled only by the static interactions, determining the equilibrium properties of the system, while the latter is also sensitive to the dynamic interactions within the adsorbate and the dynamic interactions with the substrate, both controlling the rate of an approach to the thermodynamic equilibrium. Certain characteristic features of the density dependence of the static factor, often being signatures of an onset of an organization within the system, may or may not be compensated by the features present in the kinetic factor, resulting in the density dependent diffusion coefficient from which such features may be absent. This issue for long range repulsive inter–particle interaction was examined in detail in Ref. 28.

It was shown \( 28 \) that, for the one dimensional system with long range interactions, the denominator \( 12 \) can be expressed as \( 28 \)

\[
\mathcal{N}(k = 0; P, T, N) = \frac{\mathcal{N}(l^2 - \langle l^2 \rangle )}{\langle l^2 \rangle},
\]

while the numerator can be written as

\[
\mathcal{M}(k; P, T, N) = \langle k^2 \rangle \sum_{i=s}^{\infty} W_{l+1,s-1}^{l,s} P_{l}(P, T) P_{s}(P, T).
\]

The “no rep” restriction in Eq. (11) results in only the rates of jumps from the left to right to be explicitly present in Eq. (13) [alternatively, expression mathematically equivalent to (14) with only the right–to–left jump rates explicitly appearing in it can be used].

To evaluate \( \mathcal{M}(k) \) using Eq. (14) the potential energy correction due to interactions of the activated particle is needed. One of the simplest models accounting for the activated particle interactions is obtained by realizing that the particle hopping from the adsorption site \( (l, s) \) to \( (l + 1, s - 1) \) surmounts a potential energy barrier at a bridge site situated, approximately, at a distance \( l + \frac{1}{2} \) and \( s - \frac{1}{2} \) from its nearest left and right adsorbed particle neighbor, respectively, and by evaluating the interaction
potential energy at the bridge by using $\xi(ad)$ generalized to half-integer arguments. Consequently, the potential energy correction due to interactions of a particle at the bridge site between $(l, s)$ and $(l + 1, s - 1)$ site is

$$\Delta l^s_{l+1, s-1} = \xi(al + a\frac{1}{2}) + \xi(as - a\frac{1}{2}),$$

(15)

which, used in Eq. (14), leads to the following hopping rate for the left–to–right jumps

$$W^l_{l+1, s-1} = W^0 e^{-\beta [\xi(al + a\frac{1}{2}) + \xi(as - a\frac{1}{2}) - \xi(al) - \xi(as)]}. $$

(16)

Using (16) in (14) yields the kinetic factor

$$\mathcal{M}(k; P, T, N) = (ka)^2 \frac{NW^0}{Z_1(P, T)} \left[ \sum_{l=1}^{\infty} e^{-\beta l(l+1)} \right]^2$$

(17)

in which the definition of $\xi$ in Eq. (2) is used. Similarly, like in $Z_1(P, T)$ in Eq. (3) the main contribution to the sum over $l$ in Eq. (17) comes from one or at most two terms for low enough temperatures but, for a given value of $P$, these terms may correspond to different $l$’s than those most significant in $Z_1$. In general, the sum has to be evaluated numerically.

### III. RESULTS

It has been shown that the potential energy of interactions of adatoms adsorbed on metallic surfaces like Cu/Cu(111), Co or Co on Cu(111), Fe or Co on Ag(111), Fe/Cu(111) and Ce/Ag(111) vary with the inter–atomic distance $r$ as

$$\xi(r) = -\xi_F \left( \frac{2 \sin(\delta_F)}{\pi} \right)^2 \frac{\sin(2q_F r + 2\delta_F)}{(qr)^2}$$

(18)

where $\xi_F$ and $q_F$ are, respectively, the Fermi energy and the Fermi wave vector of the surface electrons. Shape of the potential energy depends also on the Fermi–level phase shift $\delta_F$ which for many systems is equal to $-\pi/2$. This value will be used further in our calculations. The inter–particle distance dependence of the interaction energy (18) is plotted in Fig. 1 using a dashed line and compared with a long range purely repulsive potential energy $\xi(r) = \alpha/r^2$ used in Refs. [28,29]. The value of the parameter $\alpha$ used in Fig. [1] has been chosen in such a way that the repulsive potential energy curve forms an upper envelope of electron–gas–mediated potential energy (18). Strength of both types of interactions decays with the distance like $1/r^2$, however, whereas the forces corresponding to the $\alpha/r^2$ potential energy are repulsive at any inter atomic separation, the potential energy (18) oscillates, generating attractive forces at some inter–particle distances and the repulsive ones at others. Attractive forces in the system lead to the creation of stable structures at the surface and should affect the dynamic properties of the system. We compare here the diffusion kinetics in adsorbates with both types of inter–particle interactions and, in addition, in systems in which the interactions correspond to the $12 - 6$ Lennard–Jones potential energy

$$\xi_{LJ}(r) = 4\epsilon_{LJ} \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right),$$

(19)

typical for interactions between neutral atoms. The parameters $\epsilon_{LJ}$ and $\sigma$ decide about depth and position of the single potential minimum. The Lennard–Jones potential has a repulsive $\propto 1/r^{12}$ wall at short distances, much steeper than $1/r^2$, as it can be seen in the Fig. 1. At larger distances this potential is attractive and, decaying like $1/r^6$, it is weak in comparison with any of the other two. It will be shown, however, that the existence of this attractive part is sufficient for the diffusion kinetics in the system with the Lennard–Jones interactions to be qualitatively similar at some densities to that in systems with oscillating interactions.

#### A. Diffusion in systems with electron-gas-mediated interactions

It is known that a system of particles with long-range unscreened repulsive interactions orders at $T = 0$ at densities (coverages) given by a rational fraction (smaller than 1) when the interaction potential decays faster than $1/r$. The coverage plotted against external potential has a fractal form called a devil staircase. It is also known that systems with interactions decaying faster than $1/r$ but additionally screened to nearest neighbors no matter how far they are (as described in Sec. II) also form ordered phases at coverages equal to $1/n$ where $n$ is any natural number. The “phase diagram” (density vs. pressure or the chemical potential) in this case is not as complicated as that for the unscreened interactions — it has no fractal structure. For such a system it is possible to calculate all static properties as well as to investigate fully the collective diffusion kinetics for many models of microscopic kinetics. In general, the collective diffusion coefficient peaks at sufficiently low temperatures at densities at which the system orders (except when sharp drops in compressibility are compensated fully by kinetic friction). The collective diffusion coefficient peaks at sufficiently low temperatures at densities at which the system orders (except when sharp drops in compressibility are compensated fully by kinetic friction). The collective diffusion kinetics is of the second order, and formation of ordered domains surrounded by disordered regions with lower or higher densities is not possible. Such possibility opens for systems with interactions like in Eq. (18) which, depending on inter–particle distances alternate between repulsion and attraction. When particles attract each other at some distances it is possible to order the system locally
even if globally the density is too low for that \( 11,15 \). In Fig. 2 we compare the coverage dependence of the diffusion coefficient plotted at two different temperatures for the interaction potential energies plotted in Fig. 1 (with the same parameters as there). It can be seen that the character of the curves corresponding to the interaction potential energies \( \varepsilon = \alpha/r^2 \) and the oscillating one [given in Eq. (18)] is similar at the same temperatures. The only significant qualitative difference between these two cases is seen around \( \theta = 1/3 \) at the lower of the two temperatures considered: the diffusion coefficient for the oscillating interaction exhibits a peak almost invisible for the system with a purely repulsive interaction at the same temperature despite the fact that for purely repulsive interaction the system does order at \( \theta = 1/3 \) at \( T = 0 \). It indicates that the presence of the inter–particle attraction for the system with oscillating interaction allows for an ordering corresponding to \( \theta = 1/3 \) already at temperatures much higher than those are needed for such ordering with the repulsive long range interactions only.

In fact, \( r = 3a \) is the preferred inter–particle distance (based solely on on the total interaction energy considerations) for the potential energy parameters selected in this example, so local ordered domains are preferentially formed which correspond to a local coverage \( \theta = 1/3 \). Attraction, creating the potential energy minimum, is a necessary condition for the formation of the local ordered domains. High diffusion coefficient within such domains aids in their formation because collective diffusion of particles effectively controls the system ability to create ordered phases \( 11,15 \). With purely repulsive interactions the ordering at \( \theta = 1/3 \) is possible only globally so the diffusion coefficient peak, very sharp at \( T = 0 \), is easily smeared out by thermal fluctuations. We can generalize our conclusions here: structures build by attractive inter–particle interactions are capable of creating local domains of ordered phases. Value of the ratio of the potential energy spatial oscillation period to the substrate lattice constant determines which of the diffusion coefficient peaks (present for \( T = 0 \) at \( \theta = 1/3 \) for purely repulsive long range interactions) is amplified or attenuated.

Analyzing Fig. 2 a bit more in detail for the case of lower temperatures we see that at coverages below \( \theta = 0.5 \) both the oscillating and the strictly repulsive interactions result in the diffusion coefficient of roughly the same magnitude except, however, around \( \theta = 1/3 \) where the broad peak for the oscillating interactions results in a somewhat faster diffusion for this case. Both types of interactions lead to a sharp increase of the diffusion coefficient at \( \theta = 1/2 \) – another coverage of a \( T = 0 \) ordered phase \( 28 \). For \( \theta > 0.5 \) the diffusion is more efficient for the purely repulsive interactions than it is for the oscillating ones. This can be traced back to the fact that the purely repulsive interaction has much stronger repulsive core at \( r = a \) than the oscillating interaction has (c.f. Fig. 1). All these features are largely washed out by thermal fluctuations at the higher temperature of the two considered here.

We show also in Fig. 2 the diffusion coefficient for the Lennard–Jones interaction. Here, the interactions favor the inter–particle distance of about \( 3a \), almost the same as the oscillating interaction does so it is not surpris-
strongly repulsive, as it is for $q_F$ (from $0.3/a$ up to $2.5/a$) and $\epsilon_F = 0.36$ (in the same arbitrary energy units as in the preceding figures.)

FIG. 3: (color online) Inter–particle potential energies [18] as a function of the inter–particle interaction distance $r$ for several values of $q_F$ (from $0.3/a$ up to $2.5/a$) and $\epsilon_F = 0.36$ (in the same arbitrary energy units as in the preceding figures.)

ing that at low concentrations both interactions result in almost the same value of the diffusion coefficient. At higher concentrations, however, the diffusion kinetics is controlled by a very steep repulsive core at short distances, much steeper for the Lennard–Jones than for any of the remaining two interactions. Consequently, the diffusion coefficient increases to very high values already at $\theta = 1/3$. More features unique to the Lennard–Jones interaction will be discussed in Sec. III B

In general, the character of the density dependence of the collective diffusion coefficient strongly depends on how closely the minima and the maxima of the oscillating interaction potential energy match the distances between particles which occupy the substrate lattice sites. In Fig. 3 the interaction potential energies for several values of $q_F$ are shown. It can be seen that the position of the first minimum moves towards higher inter–particle distances with decreasing $q_F$. Geometrically, the minimum inter–particle distance possible is $a$, the substrate lattice constant, and the overall character of the coverage dependence of the diffusion coefficient is to a major extent determined by the character of the interaction at this particular inter–particle distance.

If at the separation $a$ the inter–particle interaction is strongly repulsive, as it is for $q_F = 0.3/a, 0.35/a, 0.7/a$ or $1/a$, then the diffusion coefficient behaves as a function of coverage (for coverages between $\theta \approx 1/2$ and 1) simi-

larly to that corresponding to a purely repulsive interaction (as seen already in Fig. 2 for $q_F = 0.7/a$): it raises rapidly when the coverage approaches the value $\theta = 1/2$ from below, suffers a kink and then it decreases slowly with further increase of $\theta$. This behavior was already analyzed for a purely repulsive long–range interaction in Fig. 9 of Ref. 28. It can be traced back to the behavior of the diffusion coefficient static factor, proportional to $1/N$ (i.e. proportional to an inverse of an isothermal compressibility), modified by the behavior of the kinetic factor, proportional to $M$. For these values of $q_F$ the particles avoid occupying the nearest neighbor sites so for $\theta \approx 1/2$ they preferentially occupy every second lattice site. A substantial additional pressure is needed to compress the system above half occupation of the lattice, the isothermal compressibility is very low, i.e. the static factor goes through a sharp maximum at $\theta = 1/2$. The overall shape of the density dependence of the diffusion coefficient is determined, however, by both the static and the kinetic factor. With the hopping rates given in Eq. (16) the high value for interaction potential energy at the inter–particle distance $a$ results in a kinetic factor which also increases sharply at $\theta = 1/2$ but does not reach a maximum there. Instead, for $\theta > 1/2$ variations of the kinetic factor almost perfectly compensate for the variations of the static factor for these densities: the kinetic factor continues to increase (albeit, less dramatically than at $\theta = 1/2$), goes through a broad plateau and eventually decreases sharply as $\theta$ approaches the full coverage value of 1. The compensation between both factors for $1/2 < \theta \leq 1$ results in the diffusion coefficient which only slowly decreases as a function of $\theta$ over this coverage interval.

The structure observed in Fig. 4 at coverages below $\theta = 1/2$ (i.e. at $\theta \approx 1/3$ and smaller) for $q_Fa \leq 0.7$
may be understood in a similar way. In these cases the inter–particle interaction is strongly repulsive not only at a separation $a$ but also at the next possible one, $2a$, so at coverages close to $\theta \approx 1/3$ the particles preferentially occupy every third site with the resulting compressibility minimum at that coverage. We can see in Fig. 4 that locally, within the coverage interval $0.3 < \theta < 0.47$, the behavior of the diffusion coefficient for the interactions corresponding to $q_F = 0.7/a$ is quite reminiscent of that within the interval around $\theta = 1/2$ and above it (for the same values of $q_F$ and also $q_F = 1/a$): a sharp increase at $\theta = 1/3$ is followed by a slow diffusion coefficient decrease with increasing $\theta$ (until the singularity at $\theta = 1/2$ takes over). For still lower $q_F$’s similar structures are observed in Fig. 4 around $\theta = 1/6$ and even $1/7$ but due to their overlap they are not very well resolved at the temperature selected for the plots.

Comparing in Fig. 2 the diffusion vs. coverage curves evaluated at the same temperatures for the $\varepsilon(r) = \alpha/r^2$ interaction with the ones for the corresponding to it (as defined in Fig. 1) $q_F = 0.7/a$ oscillating interaction [15] we see that the presence of inter–particle attraction for the latter results in more pronounced structures in $D(\theta)$. The diffusion maximum around $\theta = 1/3$, very broad and almost unnoticeable for the purely repulsive interaction, becomes quite obvious and sharp for the corresponding to it oscillating interaction. The $\theta = 1/3$ diffusion coefficient peak is clearly visible in Fig. 4 also for $q_F = 0.35/a$ and $0.3/a$. The diffusion coefficient increase at some adsorbed layer densities (here $\theta = 1/3$) is due to the attraction felt by particles at specific distances. The overall shape, however, of the coverage dependence of diffusion curves is always a result of several different, often compensating each other factors, like a character of interaction at different distances (which affect both the static and the kinetic factor), a relative height of the interaction potential energy barrier which a hopping particle must overcome between adsorption sites (which enters the kinetic factor). It is not possible, therefore, to guess from the interaction potential energy curves alone whether maxima of the diffusion coefficient at certain coverages do exist or do not. Only analyzing the diffusion coefficient vs. density curves we may rationalize the existence of certain characteristic features.

Note that the structure observed around $\theta = 1/3$ disappears when $q_F$ increases from $0.7/a$ to $1/a$. Upon further increase of $q_F$ also the structure around $\theta = 1/2$ disappears. Apparently, the repulsion at the inter–particle distance of $2a$ and $a$, respectively, ceases to be a factor controlling behavior of diffusion. Indeed, we see in Fig. 3 that upon increasing $q_F$ above $q_F = 0.7/a$ the repulsion at an inter–particle distance of $2a$ weakens and is gone for $q_F = 1/a$ – consequently any structure around $\theta = 1/3$ is no longer present. Then, with further increase of $q_F$ above $q_F = 1/a$ the repulsion at a separation of $a$ also weakens and, consequently, no structure around $\theta = 1/2$ is observed for $q_F = 1.5/a$. It was checked that upon increasing $q_F$ gradually up from $0.7/a$ the structure around $\theta = 1/3$ in Fig. 5 evolves initially into the locally concave dependence around $\theta = 1/3$ and then into the locally convex one, as seen in Fig. 4 for $q_F = 1/a$. Further increase of $q_F$ washes out the only remaining structure around $\theta = 1/2$, $D(\theta)$ becomes a structureless concave function (as seen for $q_F = 1.5/a$) and then it evolves into a convex one (as seen for $q_F = 2.5/a$). It is worth noting that the evolution of the $D(\theta)$ from a function with the structure at $\theta = 1/2$ for $q_F = 1/a$ through the concave structureless function for $q_F = 1.5/a$ and then to the convex one for $q_F = 2.5/a$ parallels the evolution of $D(\theta)$ observed in Figs. 3 and 4 of Ref. [25] for the short range interaction changing from the strongly repulsive, through the weakly repulsive, to the attractive one. Indeed, as seen in Fig. 3 the inter–particle interaction at a distance $a$ is strongly repulsive for $q_F = 1/a$, weakly so for $q_F = 1.5/a$ and somewhat attractive for $q_F = 2.5/a$.

Convex $D(\theta)$ is characteristic for systems with dominant attractive inter–particle interactions which cause them to bond and to form clusters. When particles stay on average at distances that minimize the total interaction energy, the jump rates are lowered according to [7] resulting in a decrease of the diffusion coefficient kinetic factor. Diffusion for $q_F = 2.5/a$ oscillating interaction decreases generally as a function of density. The decrease, quite fast at low coverages, slows down at higher ones.

We have argued above that a sudden change of slope of $D(\theta)$ observed in Fig. 4 at certain characteristic coverages can be understood as due to strong inter–particle repulsion at very short distances. This, however, cannot be the only reason for such a behavior because, except at $\theta = 1/2$, such sudden slope changes are much less pronounced for purely repulsive interactions, certainly the attraction must also play a role. We note also that all $D(\theta)$ curves in Fig. 4 for $q_F \leq 1/a$ start as convex functions of coverage already at $\theta = 0$ and the characteristic smallest coverage at which they suffer a sudden decrease of its slope is $\theta_1 = 1/7, 1/6, 1/3$, and $1/2$ for $q_F a = 0.3, 0.35, 0.7$, and $1$, respectively. In each case, the corresponding value of $a/\theta_1$ is equal to the inter–particle distance at which the potential energy [13] with the appropriate value of $q_F$ has the first deepest minimum in Fig. 5. The convex character of $D(\theta)$ at coverages $\theta < \theta_1$ is a signature of the attractive character of the inter–particle interactions at distances beyond the minimum, i.e. the distances larger than $a/\theta_1$. At $\theta \approx \theta_1$ the system tends to order with inter–particle distances being, on average, equal to $a/\theta_1$. For $\theta > \theta_1$ the average inter–particle distances are small enough for the repulsion being the dominant interaction and ordering is still possible at some coverages resulting in $D(\theta)$ going through the second maximum at $\theta = 1/3$ (for $q_F \geq 0.35/a$) and $\theta = 1/2$ (for $q_F \geq 0.7/a$). In short, for a particular oscillating interaction (i.e. particular $q_F$), the smallest coverage $\theta_1$ at which $D(\theta)$ ceases to be a convex function is a boundary between the coverages ($\theta < \theta_1$) for which the inter–particle attraction dominates and the ones ($\theta > \theta_1$)
for which the repulsion does dominate. For $q_F = 2.5/a$ the interaction is effectively equivalent to a short range attraction (the first minimum of the interaction potential energy is at $r < a$) while for $q_F = 1.5/a$ the repulsion at $r = a$ competes with attraction at $r = 2a$. For this intermediate case the character of $D(\theta)$ resembles, as observed earlier, the one appropriate for the weak repulsive interactions.

Character of the inter–particle interaction at closest possible separations, i.e. repulsion, attraction, or the potential energy minimum, determines the overall shape of the $D(\theta)$ dependence. For small $q_F a$’s, the particles that reside at closest possible separations from their neighbors experience the interaction induced repulsion. With increasing $q_F a$ they find themselves first at the interaction potential energy minimum, then experience attraction and then the interaction energy maximum. The cycle repeats with further increase of $q_F a$. Such a cycle of successive repulsions and attractions at a given separation should lead to a non–monotonic dependence of the diffusion coefficient on the parameter $q_F$ at a particular fixed coverage: we expect that after a monotonic $q_F a$ dependence of $D$ for $q_F a$ up to about 1 the diffusion coefficient should pass through a series of minima and maxima as $q_F a$ further increases. Indeed, this is observed in Fig. 5 in which $D$ is plotted against $q_F a$ for fixed coverage. Following the curve for $\theta = 1/3$ we observe a monotonic decrease of $D$ until a minimum is reached for $q_F a \approx 1$. With further increase of $q_F a$ the maximum is reached for $q_F a \approx 1.4$, followed by a broad minimum around $q_F a \approx 2.13$, a maximum around $q_F a \approx 3.55$, and a minimum again, at $q_F a \approx 5$. The oscillations of $D$ continue with increasing $q_F a$ but their amplitude decreases mirroring the decreasing amplitude of oscillations of the interaction potential energy $\epsilon(r = \text{const})$ with increasing $q_F a$ [c.f. Eq. (18)]. For $\theta = 1/2$ the $q_F$ dependence of $D$ is very similar to that for $\theta = 1/3$ except that the former starts with much higher value for small $q_F a$, has an inflection point around $q_F a \approx 1.4$ rather than a narrow minimum followed by a narrow maximum. Beyond $q_F a \approx 2$ both curves follow closely each other.

### B. Diffusion of particles interacting via Lennard–Jones potential

Neutral particles are known to interact via long-range Lennard–Jones potential energy \( \epsilon_{LJ} \). Its repulsive core falls off more rapidly than \( 1/r^2 \) (in fact, it falls as \( 1/r^{12} \), reaches an equilibrium position minimum at \( r_{\text{min}} = 2^{1/6}\sigma \), and is attractive at larger distances, falling off like \( 1/r^6 \)). A staircase of ordered phases at coverages \( \theta = 1/n \) is supported by such an interaction (similarly like for a purely repulsive interaction), the most prominent ones being \( \theta = 1/2 \) and \( 1/3 \), and due to huge repulsion at short distances the diffusion coefficient of particles ordered in such phases is abnormally large in comparison to that when the system is not ordered. We plot in Fig. 6 the coverage dependence of the diffusion coefficient at fixed temperature in a system with Lennard–Jones interactions corresponding to several values of \( \sigma \) (the other parameter in Eq. (19), \( \epsilon_{LJ} \), is not varied). The overall shape of the presented curves is determined by an interplay between two length parameters in the system: the distance \( r_{\text{min}} = 2^{1/6}\sigma \) below which particles repel each other, and the substrate lattice permitted minimum separation \( a \) between interacting particles.

We can systematically analyze shapes of the $D(\theta)$ curves in Fig. 6. For $\sigma = 0$ there are no inter–particle interactions (except for site blocking) and $D(\theta)/W^0a^2 = 1$ as seen in Fig. 6. For $\sigma = 0.89a$ we have $r_{\text{min}} = a$ so when $0 < \sigma < 0.89a$ the interaction between particles separated by $a$ is attractive. Consequently, it is energeti-
cally preferable for particles to be as close to each other as possible and for such values of \( \sigma \) the \( D(\theta) \) dependence is convex (as seen for \( \sigma = 0.7a \) and 0.89a in Fig. 4), typical for systems for which the inter–particle attraction dominates (c.f. Fig. 4 in Ref. 23). For \( \sigma > 0.89a \) the interaction at the closest separation \( r = a \) becomes repulsive and, indeed, for \( \sigma = a \), the \( D(\theta) \) dependence becomes concave resembling qualitatively \( D(\theta) \) for weakly repulsive short range interaction in Fig. 3 of Ref. 23. With further increase of \( \sigma \) the repulsion at \( r = a \) increases: for \( \sigma = 1.1a \) we note a characteristic maximum of \( D \) around \( \theta = 1/2 \) also observed already for stronger short range interactions in Fig. 3 of Ref. 23. For \( \sigma = 1.3a \) the repulsion at \( r = a \) is strong enough to induce a preferential occupation of every second site (note that the interaction at the \( r = 2a \) separation is still weakly attractive in this case) causing the diffusion coefficient to suddenly raise by many orders of magnitude as \( \theta \) approaches 1/2 from below.

With further increase of \( \sigma \) we reach, at \( \sigma = 2a/2^{1/6} = 1.78a \), the point beyond which the interaction at \( r = 2a \) is no longer attractive. For \( \sigma \) somewhat lower than 1.78a we have a very strong repulsion at \( r = a \) and a much weaker one at \( r = 2a \). We see in Fig. 6 that for \( \sigma = 2.2a \) a local maximum of \( D(\theta) \) develops for \( \theta \approx 1/3 \) hinting at a preferential occupation of every third site around this coverage due to repulsion for \( r = 2a \), followed by a sharp, almost discontinuous raise of \( D \) at \( \theta = 1/2 \) due to an extremely strong repulsion at \( r = a \). With further increase of \( \sigma \) the repulsion at \( r = 2a \) becomes stronger so the structure around \( \theta = 1/3 \) becomes as sharp as that around \( \theta = 1/2 \). The examples are curves for \( \sigma = 2.3a, 2.6a \) and 2.8a in Fig. 7. For the latter, however, the interaction at the separation \( r = 3a \) is also repulsive. In fact, with further increase of \( \sigma \) features similar to those around \( \theta = 1/2 \) and 1/3 develop also around \( \theta = 1/4 \), as seen for \( \sigma = 3.4a \). This is because for \( \sigma > 3a/2^{1/6} = 2.67a \) the interaction at the separation \( r = 3a \) becomes repulsive and, when strong enough, it leads to a preferential occupation of every fourth site for \( \theta \approx 1/4 \). This structure is not present yet for \( \sigma = 2.8a \) at the temperature selected in Fig. 6.

The character of the coverage dependence of the diffusion coefficient changes qualitatively every time when the interaction between particles becomes repulsive at any of the inter–particle separations permitted by the substrate lattice: i.e. every time when \( \sigma \) increases through \( na/2^{1/6} \). For \( \sigma \) such that \( n/2^{1/6} < \sigma/a < (n + 1)/2^{1/6} \) the particles separated by distances \( r = a, 2a, \ldots, na \) repel each other (with the repulsion being stronger for shorter separations) while they attract each other for separations \( r = (n + 1)a \) and larger. In such case one expects at \( T \approx 0 \) a sharp increase of the diffusion coefficient at coverages \( \theta = 1/2, 1/3, \ldots, 1/(n + 1) \) due to the low temperature structural organization of the adsorbate at these coverages to minimize the total interaction energy in the system. In our runs done at lowest temperatures for which the calculations are feasible we see such structures for \( \theta = 1/2, 1/3 \) and 1/4. Still, one expects that as the parameter \( \sigma \) is varied one should observe a non monotonic oscillatory changes of the diffusion coefficient at low enough coverages. Indeed, this is seen in Fig. 7 in which \( D(\theta = 1/5) \) is plotted as a function of \( \sigma/a \). The maxima are noted for \( \sigma/a \) approximately halfway between \( \sigma = na/2^{1/6} \) for \( n = 1, 2, 3, 4, \ldots \), i.e. for \( \sigma/a \approx 1.3, 2.2, 3.1, \ldots \) for which the interaction is already strongly repulsive for all inter–particle separation up to \( a, 2a, 3a, \ldots \), respectively.

![Image](image_url)

**FIG. 7:** (color online) Dependence of the diffusion coefficient at \( \theta = 1/5 \) on the Lennard–Jones interaction parameter \( \sigma \) for \( \beta = 20 \) and \( \epsilon_{LJ} = 0.031 \) (same as in Fig. 6).

**IV. CONCLUSIONS**

Variational approach has been applied to examine collective diffusion in a one dimensional lattice gas systems with two type of long–range inter–particle interaction: the electron–gas–mediated interaction described by the oscillating Friedel–like potential energy (18), and the Lennard–Jones interaction corresponding to the potential energy (19). We have discussed the features of the coverage (adsorbate density) dependence of the diffusion coefficient for both these interactions and compared them with those investigated in detail for purely repulsive long–range interaction(28) corresponding to the potential energy \( \propto 1/r^2 \) as well as with the behavior typical for short–range repulsive and attractive interactions(23).

In general, at densities above half coverage \( (\theta > 1/2) \), at which the inter–particle repulsion at short distances plays a main role, the diffusion coefficient for the repulsive and the oscillating interaction behaves, as a function of coverage, qualitatively similarly: the diffusion coefficient is much higher than without interactions and depends on coverage relatively weakly. This is true even for the Lennard–Jones interaction, except that a very steep repulsive core in this case, making creation of a high density adsorbate energetically very costly, results in huge values of the diffusion coefficient at such densities.
At lower densities, the behavior of the coverage dependence of diffusion coefficient for the Lennard–Jones interaction, repulsive for inter–particle separations \( r < r_{\min} \) and attractive for \( r > r_{\min} \), is quite easy to understand. At sufficiently low temperatures, it experiences for increasing \( \theta \) a finite series of progressively sharper increases at “critical” coverages \( \theta = 1/n \) (\( n = n_{\max}, n_{\max} - 1, \ldots, 2 \)). The first one, for \( \theta = 1/n_{\max} \), corresponds to the largest inter–particle distance \( r = r_{\max}^{\theta} \), which the interaction between the particles is still repulsive (i.e. at the separation \( r = (n_{\max} + 1)/n_{\min} \) the interaction is already attractive). As temperature increases, the structures at lower densities of this series are usually smoothed out. In fact, we observe for the Lennard–Jones interaction a delicate interplay between two length scales: the lattice constant \( a \), which determines what actual distances between particles are possible, and the characteristic length of the interaction potential, \( r_{\min} \), separating the short range repulsion from the attraction at larger distances. When \( r_{\min} < a \) then the repulsive core of the interaction is irrelevant and the diffusion coefficient exhibits features similar to those observed for short–range attractive interactions.

Features of diffusion for the oscillating interaction are somewhat more difficult to explain in simple terms due to the existence of multiple interaction potential energy minima and, consequently, alternating regions of inter–particle attraction and repulsion. Still, a sudden raise of the diffusion coefficient at \( \theta = 1/2 \) has origin similar to that for such structure for the purely repulsive and Lennard–Jones interaction. The structures for \( \theta < 1/2 \) are, however, masked by the influence which attraction alternating with repulsive interactions has on diffusion.

We must note also that interpreting features of the diffusion coefficient in terms of the features of the inter–particle interaction is deficient in that respect that it necessarily is limited to the interpretation of the kinetic phenomenon (diffusion) in terms of the static properties of the system, i.e. in terms of the static (or thermodynamic) factor commonly used in theories of diffusion. The kinetic factor is known, however, to be capable of compensating for very often drastic behavior of the static factor as a function of density. This is also the case here: a slow variation of the diffusion coefficient as a function of coverage for several curves in Figs. 4 and 9 for \( \theta \) immediately larger than 1/2, 1/3, and 1/4 is the result of a delicate compensation between a sharp drop of the static factor (which at these particular coverages suffers a sharp cusp–like maximum corresponding to a sharp drop in an isothermal compressibility) and a strong increase of the kinetic factor when the coverage is increased through these values.

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