Revista Mexicana de Física **43**, *No. 3 (1997) 421–428*

Approximations to the configurational energy of dipolar particles on a 2D lattice

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Recibido el 16 de octubre de 1996; aceptado el 22 de abril de 1997

ABSTRACT. Current research on critical phenomena and minimum energy configurations of dipolar particles on a 2D lattice, usually approximates the infinite interaction range through a cutoff to carry out numerical simulations. In this work we compare the commonly reported procedure in literature, consisting of truncating the potential function from a given abscissa, to another proposed method, where the function is vertically shifted to zero after the truncation. We show that the first procedure renders more mistakes than the second, where mistakes still admittedly occur but their appearance notably decreases as a function of distance. We also examined the conditions necessary to consider discrete dipoles as being continuous beyond the cutoff position and found that the shifted procedure performs better than truncating alone.

RESUMEN. En la investigación teórica de los diagramas de fases y de los estados base configuracionales de partículas bajo interacción dipolar en una red bidimensional usando métodos numéricos, usualmente se aproxima el alcance infinito de esta interacción introduciendo una distancia de corte. En este trabajo comparamos el procedimiento reportado normalmente en la literatura, que consiste en un truncamiento simple contra el método de aproximación recientemente propuesto, en el que se efectúa una translación del origen del potencial después del corte en el alcance. Mostramos que con el primer procedimiento el número de fallas producidas es mayor, y este número decae para mayores distancias de corte que con el segundo. Estudiamos las condiciones necesarias para considerar la distribución discreta de dipolos más allá de la distancia de corte como continua y homogénea y verificamos que en el segundo procedimiento dichas condiciones se cumplen mejor.

PACS: 68.35.Rh

1. INTRODUCTION

There are systems that may be considered interacting elements on lattices, polymers, alloys, adsorbates, neural networks, etc. When only the interaction among first neighbors

is considered and the elements have two states, the systems can be studied using the Ising model. However, if the interaction range is longer, the situation becomes more intricate [1] as with the adsorption of alkali atoms on metal transition surfaces [2]. These systems are important for heterogeneous catalysis [3] and termoionic emission technologies [4]. From the theoretical point of view, they are important as two-dimensional systems able to show phase transitions [5].

There has been an intense discussion about the exact origin of the interaction among the alkali adsorbates [6–8] that extends from the traditional point of view which claims that the valence electron is stolen by the metallic substrate (creating dipoles across the surface) [9, 10], to a more recent view point which considers that the interaction is due to the alkali internal polarization [6]. In both cases, dipoles perpendicular to the surface will form [11, 12] that produce long range interaction among adsorbates. This situation makes it difficult to obtain phase diagrams or to calculate minimum energy configurations.

Monte Carlo calculations [13–15] and Exhaustive Inspection [16–18] are used to look for phase diagrams or minimum energy configurations. In both procedures, the dipolar potential is approximated by a cut-off followed by a continuous correction beyond the truncation distance [13, 14]. Muller [15] studied the system Cs/Rh(100) using a Monte Carlo simulation in which the dipolar interaction was truncated to the second lattice neighbor. The adsorption of Na over W(110) was also studied with Monte Carlo procedures, truncating after the third lattice parameter [13, 14]. Minimum energy configurations have been studied in fcc(100) and fcc(111) lattices with interaction up to the sixth lattice parameter [16–18]. In the case of Na/W(110), researchers claim that the particles beyond the cut-off position can be considered to be a continuous homogeneous distribution on the surface. This allows them to incorporate their contribution as an order-independent integral, resulting in the term $2\pi\theta/d_c$, where θ is the coverage particles array, and d_c the cutoff distance. Finally, in early works on Exhaustive Inspection [16–18], an energy shift was done in $1/d_c^3$ (Fig. 1), rendering a $3\theta/d_c$ correction term, in addition to the cutoff.

The convenience of working with continuous potentials in 1D systems is indisputable [19]. For this reason it has been applied to 2D systems to eliminate discontinuities that appear in the truncation distance. It has been suggested that this type of approximation could be useful in other kinds of procedures; *i.e.*, Monte Carlo calculations for alkali-metal systems [17].

As far as we know, there is no systematic discussion about the kind of approximation that could be used for dipolar interaction in these systems, excepting a commentary by Medvedev [13]. He analyzes $\theta = \frac{1}{4}$ orderings in bcc(110) for ranges between one to ten lattice parameters and consider that after three lattice parameters the contribution to the energy from particles beyond the cut-off would not depend on the specific arrangement which allows the approximation of their contribution by an integral. This affirmation, which we will refer to as *Medvedev's conjecture* has important effects on Monte Carlo calculations because the probability of transition among the different arrays depends on the difference in their energies. Thus, if the contribution to the energy of the particles beyond the truncation does not depend on their specific distribution, it is not necessary to calculate this contribution since it will be eliminated when the energy differences in the Boltzman factor are considered.

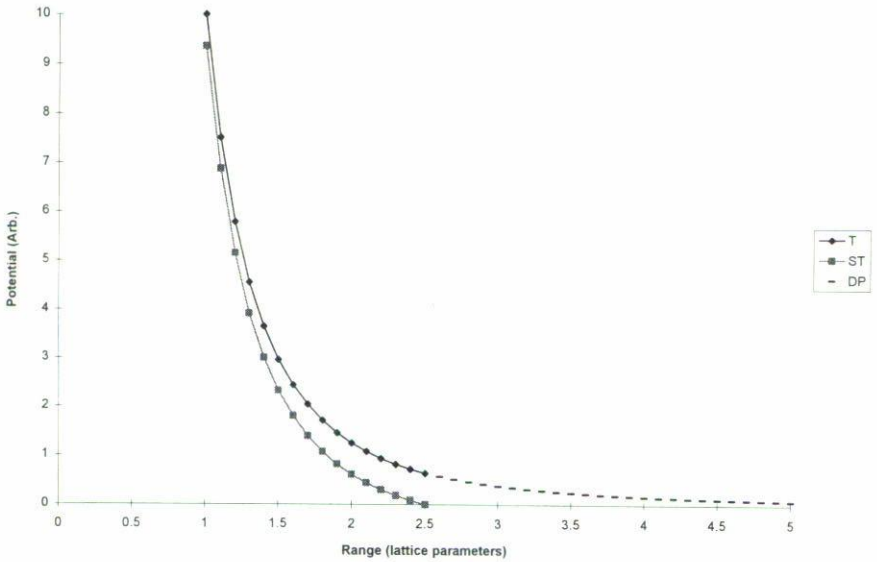


FIGURE 1. Display for Dipolar Potential and its approximations. Broken line corresponds to full dipolar potential (DP); black line with diamonds is draw to represent truncated approximation (T); and gray line with squares corresponds to shifted truncated approximation.

When the particles are ordered on a periodic array, the convergence of the sum of interactions over one particle depends on the form of the potential function as well as on the dimensionality of the embedding space. For instance, when the dimension is greater than the interaction's exponent of decay, the mentioned convergence cannot be guaranteed and it is necessary to use alternative techniques such as Ewald's sums [20]. Fortunately, this is not the case here: chemisorpted systems are two-dimensional and the interaction considered is dipolar (it decays as the cube of the distance).

In this study, we show that the shifted truncated approximation [17] performs better than the truncation commonly found in the literature. In addition, we explore the validity of Medvedev's conjecture when both types of approximations are considered. In Sect. 2 we describe our methods; results are shown in Sect. 3. Section 4 is devoted to the conclusions.

2. METHODS

When we work with the Monte Carlo method, Exhaustive Inspection or Genetic algorithms, we have to make decisions that depend on the configuration's energy. The Monte Carlo method, starts by selecting a configuration with known energy, usually from a periodic cell. The configuration is then modified at random, thus producing another configuration with its respective energy; if this energy is lesser than the first, we use the last configuration as an initial one. Otherwise, we use the Boltzman factor to decide whether the configuration is rejected or not. These steps are repeated many times to bring the system to and extract information from thermal equilibrium.

In the procedure described above, it would be convenient to have an ordered list of energy of all configurations consistent with the periodic cell, in which the energy was calculated using the full range of the interaction. This list could be named the *ideal list* and would provide the necessary information to select different configurations without having to perform the energy calculations. However the *ideal list* is impossible to calculate because we cannot calculate infinite range interactions with a computer. It is necessary to truncate the range of the interaction and this, of course, lead to change the order of energy configurations.

We can have a basic idea about the approximation's performance, counting the changes in position in the sorted energy list with respect to the *ideal list* and we will say that each of these changes is a *mistake*. Since the *ideal list* is impossible, we take 1000 lattice parameters to perform our calculations as compared to interaction ranges reported in the cited papers which are only up six lattice parameters.

To study sets of cases in an orderly way we will use those generated by Exhaustive Inspection [16–18]. This method was originally developed to find the ground configurational state for particles that interact dipolarly on a lattice in specific area and coverage. This procedure is based on the fact that in a given area and coverage the number of different orderings is finite. If we wish to study coverage p/q, with p and q relative primes, in a tq area, where the particles can only occupy positions on a lattice generated by the vectors $\mathbf{v}$ and $\mathbf{w}$, we build all the different cells generated by vectors $\mathbf{A}$ and $\mathbf{B}$ which correspond to linear combinations of $\mathbf{v}$, $\mathbf{w}$, such as $|\mathbf{A} \times \mathbf{B}| = tq$. Once all the possible cells are generated, we place one of the p particles on the vertexes of each cell, and construct all the possible arrangements by putting the remaining $p - 1$ particles in the internal position of the cells. If the minimum energy array is periodic, then this procedure allows us to obtain the ground configurational state.

In this work this method has been used to generate sets of arrays that allow us to show that the shifted truncated approximation is more effective than the pure truncation procedure. For this purpose, we studied square lattice with coverages $1/q$, with q ranging from 2 to 8 and values of t from 2 to 4.

Finally, we analyze the validity of Medvedev's conjecture by studying the deviations of energy increments as a function of the truncation distance. If the conjecture were true, all the configurations having the same coverage would increase their energies in the same amount for some distance and would therefore cancel the mentioned deviation. As expected, the value of these deviations are distance-dependent and, more importantly, this indicator drops faster in the case of the shifted truncated approximation than in the truncated one.

3. RESULTS AND DISCUSSION

The simpler results correspond to the analysis of minimum energy configurations for each coverage obtained with all the ranges considered. In Fig. 2a, hollow circles represent those cases where there is coincidence between the asymptotic behavior for the shifted truncated approximations and that of the range taken into consideration. Filled circles stand for those cases where there is no agreement. In Fig. 2b we have done the same

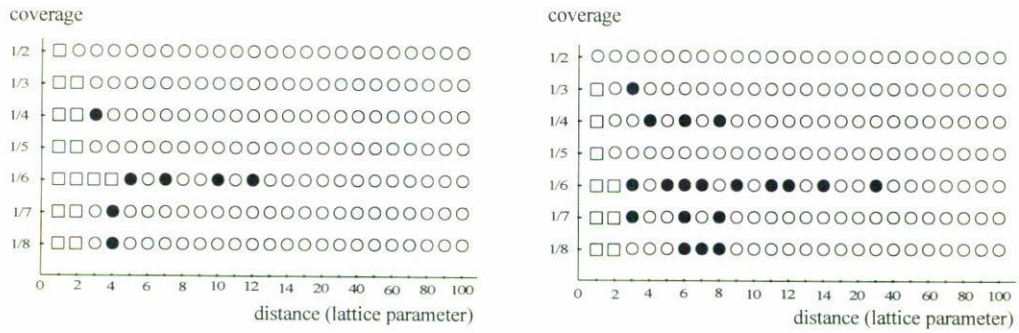


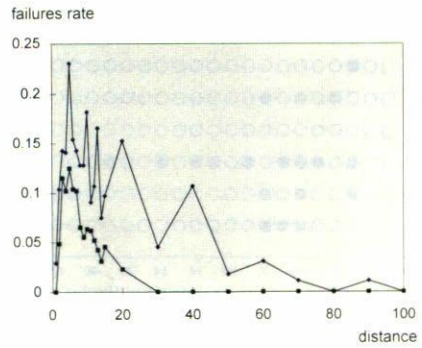
FIGURE 2. Hollow circles correspond to cases where there is coincidence between asymptotic behavior and truncated range. Full circles represent those cases where the ground state reported in the respective cutoff distance is incorrect. Squares indicate degeneration among several configurations at the minimum energy. Fig. 2a is drawn for shifted truncated approximation and Fig. 2b for the truncated one.

report but for the truncated approximation. As can be seen, the amount of failures increases with cut-off distances for the latter type of approximation.

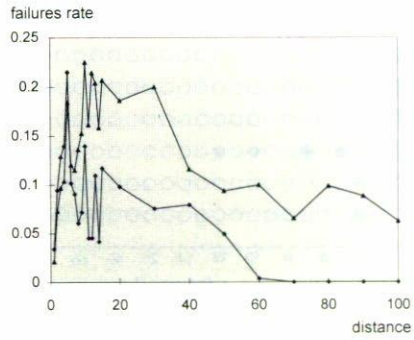
In Fig. 3, some of the graphs that correspond to the analysis of the complete data have been displayed; for each coverage and area we have detected the amount of mistakes that occur for each range, plotting the ratio of these to the amount of total cases. In Fig. 3a we show for the shifted truncated approximation (squares) and for the truncated approximation (diamonds) the rate of failures for coverage $\frac{1}{6}$ and area 18. For every range the rate of failure is greater for the truncated case. In Fig. 3b we show the rate of failures for the truncated potential with coverage $\frac{1}{5}$ and area 15 (diamonds) and area 20 (triangles); in Fig. 3c we draw the same cases for the shifted truncated potential. Again, this type of approximation markedly produces less errors and they tend to disappear for shorter ranges. This behavior is the same for every studied coverage and area.

Finally, in Fig. 4, the evolution of the energy increment deviations in logarithmic scales are plotted. The plot corresponds to coverage $\frac{1}{4}$ with an area of 12; the squares correspond to the shifted truncated approximation and the diamonds represent the deviations of the truncated potential. The slope of the first line has a value of -3.77 ± 0.08, while in the second one, it is equal to -2.55 ± 0.02. Even with different slope values, the deviations in the energy increments of the shifted truncated approximation in all the studied cases drop faster with the ranges than those of the truncated. Medvedev's conjecture is better performed by the shifted truncated potential.

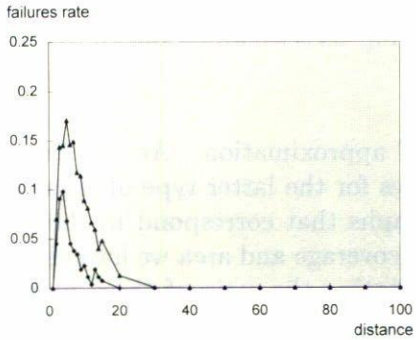
After studying many cases in which mistakes occur in the order of configuration arrangements, we notice that the crossing of the arrays occur when the potential cutoff affects the density of the particles within the cutoff radius. We explain this situation with the example shown in Fig. 5, in which we calculate the interaction of all the array particles of the array, with the central particle shaded in black. Of all the particles, we have only drawn four in gray, which are at distance d from the central particle. We can dissect the energy interaction as $E = E_i + 4p^2/d^3 + E_e$, where E_i corresponds to the contribution of the particles which are within the radius d, E_e to the contribution to the



(a)



(b)



(c)

FIGURE 3. Comparison between shifted truncated approximation and truncation. In Fig. 3a the triangles represent the truncated approximation and the diamonds represent the shifted truncated for coverage $\frac{1}{6}$ and area 18. In Fig. 3b we draw data only for the truncated approximation with $\theta = \frac{1}{5}$; triangles correspond to area 15 and diamonds to area 20. Fig. 3c is only for shifted truncated at $\theta = \frac{1}{5}$; diamonds for area 20 and squares for area 15.

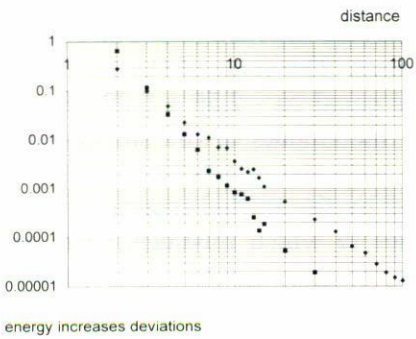


FIGURE 4. Behavior for the energy increment deviations. Coverage $\frac{1}{4}$ and area 12. Diamonds represent truncation, squares correspond to the shifted truncated approximation.

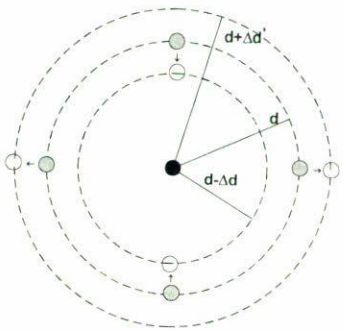


FIGURE 5. See text.

particles outside the cutoff radius, and p is the dipolar moment of the adsorbates. Due to the concavity of the dipolar potential and not dependent upon of the substrate lattice, we can find a new configuration with greater energy, by bringing half of the particles in gray Δd closer and moving the other half of the particles by Δd from the center particle. We have plotted this new situation by representing the particles as hollow circles. Now we have energy $E' = E_i + 2p^2/(d - \Delta d)^3 + 2p^2/(d + \Delta d')^3 + E_e$. If we do a truncation of the interaction at a distance slightly greater than d, we would have for some Δd, an inverted ordering of the energies. This is due to the fact that two particles disappear from the E' calculation. This situation can repeat itself with different distances and distinct configurations. The latter effect shown is softened by shifting the zero of the potential, because when $1/d^3$ is subtracted from each particle within the cutoff radius, the energy E suffers a more severe subtraction than E'. Since both approximations lead to the same asymptotic energy value, it is be preferable to use the shifted truncated approximation.

4. CONCLUSION

We examined the effect of different approximations on the behavior of the energy of particle configurations on a lattice that interacted dipolarly. These approximations are common when the interaction among the particles is of dipolar character and, calculations such as the Monte Carlo and Exhaustive Inspection are performed and would be necessary if the Genetic algorithm where used. We developed Medvedev and Yakovkin conjecture [13] by carrying out our analysis through thousands of cases generated with the Exhaustive Inspection method [17] and considering ranges for the potential of units up to one thousand lattice parameters. We took into account the effect on the value of the configurational energy when either simple truncation [13–15] or shift and truncation of the potential [16–19] is made. We found that simple truncation accumulates errors that can degrade the results obtained and, furthermore, these errors persist for greater ranges. Since both approximations lead asymptotically to the same values of the energy (also taking into consideration that the errors source is lattice-independent for the truncation procedure) we conclude that it is preferable to use the proposed shifted truncated approximation in any kind of spatial array.

ACKNOWLEDGMENTS

This work was partially supported by DGAPA-UNAM through grants No. IN-104594 and IN-104694. We thank Susan Moore for technical support in the preparation of the manuscript.

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