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Percolation Transitions in Sticky Disk Systems. A Molecular Dynamics Study

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Molecular dynamics computer simulation was performed on the systems consisting of 100 two dimensional particles interacting with the hard core square well potential. Calculations were performed for various combinations of the parameters defining the attractive part of the potentials and for various densities. The pairs ϵ and Δ , denoting the depth and width of the potential well, were chosen in such a way that the systems approached Baxter's limit of sticky or adhesive potential with infinite depth and zero width of the well, provided that the product $\Delta \exp(\epsilon/kT)$ remained finite. The results of the simulation gave support to the claims based on the analysis of higher order virial coefficients that the system of adhesive particles does not possess thermodynamic stability. The results show that the approach of the system towards equilibrium slows down when approaching the limit of stickiness and, besides, systems close to the sticky limit show a tendency to aggregation and collapse towards the crystal structure, which raises doubts about the regularity of the percolation problem of sticky systems.

INTRODUCTION

In many scientific fields where a multitude of objects is treated and within this multitude the objects can form clusters, one observes an interesting phenomenon regarding cluster statistics.

If there exists a parameter upon which the connectivity of the objects depends, then there exists a value of this parameter beyond which the clusters become infinite and this limit is usually called the percolation threshold. Percolation transition possesses all the attributes of critical phenomena so that, besides the percolation threshold, one can define all the critical exponents.

The disciplines where the percolation phenomena are observed and studied range from epidemiology, ecology to physics and chemistry. The simplest model systems on which the percolation phenomena can be studied are either the objects positioned on regular lattices or the objects in continuous space (lattice or continuum percolations).¹ Lattice percolation problems are simpler than continuum percolation problems and for the majority of systems the lattice percolation problems have already been solved.² As

far as the continuum percolation is concerned, there are still many open questions and even the simplest system, such as the percolation of randomly centered spheres, does not possess an accurate solution.³ The problem of randomly centered spheres can be classified as noncorrelated percolation. The systems of physical particles that interact over some potential represent the problem of correlated percolation. In such a system, one should solve two hierarchically ordered problems. One should first solve the thermal problem, which means that the relation between the thermodynamic variables such as pressure, volume and temperature have to be determined. At each particular thermodynamic state, one can solve the percolation problem. If the connectedness criterion is unambiguously defined, then one can only ask whether the system is below or above the percolation threshold. In general, the criterion whether two particles are connected or not can be arbitrarily defined. In such a case, for each thermodynamic state, one can look for a connectedness criterion that would produce the percolation transition exactly at that point. This is the case of the system of particles interacting with the Lennard-Jones potential. For this type of potential, it was shown that, with several values of proximity criteria, one can observe a complete phenomenon of percolation transition.⁴ Some other types of interparticle interactions are more suitable for the study of percolation phenomena, such as the hard core square well (HCSQW) potential. In this case, it is quite easy to define the connectedness criterion. The hard core part of the potential does not allow two particles to penetrate so that they are held at separations greater than the diameter of the hard core. If the particles are at a distance greater than the diameter of the hard core increased for the width of the square well, they do not touch each other. What remains is the case in which two particles are bound by the square well part of the potential and it is straightforward to postulate that such a pair of particles is connected. After having defined the connectedness criterion, one can determine the size and the distribution of clusters, which are directly related to the percolation problem.

A special variant of the HCSQW potential was proposed by Baxter.⁵ If the depth of the well goes towards infinity and the width towards zero, one obtains the so called sticky or adhesive potential model due to which two particles are bound only when they are in contact. Intuitively, one can expect that such a potential may cause troubles, and only recently it was shown⁶ that the systems of adhesive disks or spheres do not possess thermodynamic stability.

Adhesive Disk Systems

Baxter's limit of the HCSQW potential is defined as that combination of square well width (Δ) and depth (ε) at which the product of $\Delta e^{\beta\varepsilon}$ remains constant when Δ tends towards zero and $e^{\beta\varepsilon}$ towards infinity. For such a potential, several low order virial coefficients have been well defined and, since also the Percus-Yevick approximation for the integral equation for the radial distribution function can be solved analytically, it led to the impression that the system of adhesive particles is a well defined statistical mechanical model. However, recently Stell and Williams have shown qualitatively that the expression for the pair correlation function contains terms that involve higher powers of Dirac δ function, which is certainly an irregular feature. Later, Borštnik and Stell⁷ performed a quantitative analysis of virial coefficients when approaching the adhesive disk limit. It was shown that the first six virial coefficients attain a regular limit when $\Delta \rightarrow 0$, and $e^{\beta\varepsilon} \rightarrow \infty$, while the seventh virial coefficient B_7 can be written as a polynomial of twelfth order in $e^{\beta\varepsilon}$

$$B_7 = \sum_{j=0}^{12} a_j e^{j\beta\epsilon}$$

The value of B_7 would attain a regular limit if all the coefficients a_j contained Δ raised to the power which may not be smaller than j . It turns out that this is not the case since a_{12} behaves like Δ^{11} , which means that when approaching the sticky limit, B_7 diverges linearly with $e^{\beta\epsilon}$.

Higher virial coefficients diverge even more drastically and, consequently, there is no thermodynamic limit of sticky disk systems. The fact that, in spite of the absence of thermodynamic stability, there is a solution of the Percus-Yevick approximation of the integral equation for the pair distribution function can be explained by the fact that within this approximation the above mentioned singularities are left out. On the other hand, there are reports in the literature where the systems of particles bound by adhesive potentials are studied by the specially designed Monte Carlo method.⁸ The results obtained by this method show no pathological behaviour that would prevent determination of the equation of state and the percolation line which delimits the regions of phase diagram below and above the percolation threshold density.

According to the results of the analysis of higher virial coefficients, it is hard to believe that a clear picture provided by the Monte Carlo simulation is a real feature. Seaton and Glandt assert that certain moves are not permitted in their new Monte Carlo method. In particular, their method leaves aside the moves that build or destroy the fragments of close packed structure. The seventh virial coefficient, which we found to be singular, refers exactly to the above mentioned structures and this may be the source of the disagreement between the results of Seaton and Glandt's new Monte Carlo method and other approaches.

In this work, we would like to apply the molecular dynamics method to the HCSQW system with deep and narrow potential wells. The structure and time evolution of these systems might help us to understand the pathologies of sticky systems.

Molecular Dynamics Simulation of the HCSQW System Close to the Limit of Stickiness

Sticky potentials are not accessible to molecular dynamics simulation because Newtonian mechanics cannot deal with infinite depth of the potential well, since this would lead to infinite velocities of the particles.

According to our belief, the sticky system is irregular and, therefore, any effort to determine the structural, dynamic or thermodynamic properties will have a rather uncertain outcome. This is not true for the HCSQW systems which are approaching the sticky limit. As long as the width and the depth of the SQW potential is finite, it is natural to expect that any method should behave regularly. Molecular dynamics simulation is especially suitable as it provides structural as well as dynamical information. When studying the percolation phenomena, an insight into the dynamical processes is particularly important, since one can follow the time evolution of the cluster dynamics. In the system with narrow and deep square wells, one can expect that the clusters rearrange less frequently than in the systems where the depth of the potential is comparable to thermal energy. However, there is no information available about how the cluster dynamics depends upon the depth and width of the potential well. Therefore, the study of this phenomenon will be the primary concern of this paper.

Discontinuous potentials need special treatment in the molecular dynamics computer experiments. One cannot follow particle trajectories along uniformly spaced time intervals but should follow individual collisions. There is a standard numerical methodology how to treat the dynamics of hard core systems.⁹ One forms the matrix of collision times. The i, j element of this matrix tells at what time the particles i and j will collide if their motion is not interrupted by other particles. One finds the pair that is going to collide first and carries out the collision, then the matrix of collision times is updated and the next collision can proceed.

Each collision is carried out in the centre of the mass frame of the participating particles, which turns out to be a rather simple algebraic manipulation of particle velocities. It is interesting to point out that addition of the square well potential destabilizes the numerical procedure significantly. This can be demonstrated by a test in which a system of particles is followed until a certain number of collisions occur and then the velocities are reversed to move the particles backward.

If the number of collisions in such an experiment is beyond some threshold values, the particles do not reach their starting positions when moving backward for the same number of collisions as in forward motion. It turns out that the threshold number of collisions, is much lower in the system with the HCSQW potential than in the case when the interaction potential is of pure hard core type. This means that the increased complexity of the HCSQW potential, relative to the hard core potential, amplifies the round off numerical error. The round off error can be decreased if one increases the precision of numerical operations (double precision) but it can not be eliminated.

All the calculations were performed in two dimensions with 100 particles. Periodic boundary conditions were applied. Since our interest lies in the thermodynamic stability of the sticky disk system and in the study of properties relevant to the percolation phenomena, we decided to choose non-stationary initial conditions and study the approach towards equilibrium.

Two kinds of non-equilibrium initial conditions were used. In the first category of calculations, the starting configuration was that of randomly positioned disks in such a configuration that no bonds between them were formed. This was achieved by the following preparation of the system. The particles were positioned on the grid points of a regular square lattice. The particles were allotted random initial velocities and the system was let to evolve in time. In this period, the interaction potential was modelled as a hard sphere potential with the diameter $\sigma + \Delta$, where σ and Δ are the parameters of the HCSQW potential, which is used in the main calculation to be described later. The randomization took 200 collisions per particle.

Another class of calculations started from the configuration of particles in the form of a single cluster of compact form, as seen in Figure 1. In this cluster, 100 atoms are arranged in such a way that the number of bonds is maximized. All the neighbours on the lattice are bound by the square well.

All the productive runs were started with one of the above mentioned initial configurations and the systems were followed until a large number of collisions occurred. The configurations of particles that appeared during the time evolution of the system were analyzed in order to control the cluster statistics, total energy and pressure in the system.

The simulations were run at isothermal conditions at $T = 1$. Each 100 collisions, the velocities were rescaled so that the temperature was returned to the required value.

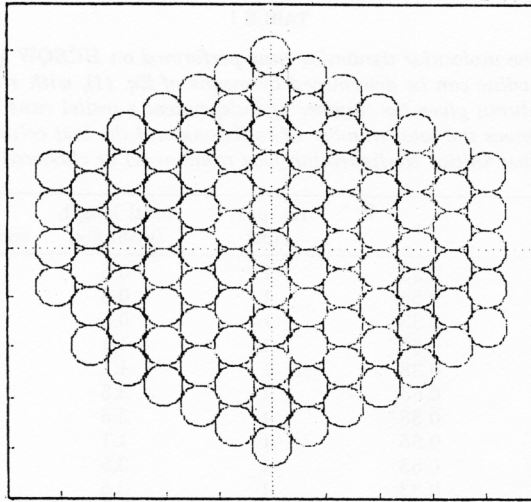


Figure 1. The arrangement of disks which served as a starting configuration for molecular dynamics runs.

During the simulation, we observed an undesired feature manifested in the non-conservation of momentum. The accumulation of round off numerical errors had the consequence that the kinetic energy split into two parts: kinetic energy due to the translation of the centre of mass and real thermal energy. This means that some of our calculations were, in fact, run at a lower temperature than it had been anticipated. The situation was cured by projecting out the centre of mass motion.

RESULTS AND DISCUSSIONS

In what follows, the unit of length will be the hard core diameter σ , the particles will have unit mass ($m = 1$) and the depth of the potential will be expressed in terms of energy unit $\epsilon_0 = 1$, which also served as the unit of average thermal energy (T) which is the measure of temperature. The unit of time is equal to $\text{sqrt}(m\sigma^2/2\epsilon_0)$.

The calculations were performed at two values of number density, $\rho_1 = 0.33$ and $\rho_2 = 0.55$. The values of the depth of the potential for which the calculations were performed were $\epsilon = 0.5, 1, 2, 3, 4$, and 5 . The corresponding widths of the well were determined by the expression which guarantees the approach towards Baxter's limit:

$$\Delta = \sigma e^{-\beta\epsilon} / (4\tau) \quad (1)$$

where τ is the dimensionless indicator of the temperature in sticky limit and $\beta = 1/T$. All the calculations performed are listed in Table I. The information made available by all these calculations is still not sufficient to get a clear picture of the possible states that the HCSQW system can take. When studying the percolation properties, it is important to know the equation of state because, only in that case, one can locate those points in the phase diagram where it is meaningful to look for the percolation threshold line. For the case of the two dimensional HCSQW system, only a limited information regarding the equation of state is available.¹⁰ Therefore, we rely on the

TABLE I

List of the molecular dynamics runs performed on HCSQW systems. The Δ value can be determined by means of Eq. (1), with $\tau = 0.3$. Third column gives the number of independent parallel runs. Fourth column gives the total number of collisions and the last column tells whether initial configuration was random (r) or clustered (c).

ε	ρ	no. par. runs	total length (millions)	initial configuration
0.5	0.33	1	0.5	c
1.0	0.55	1	0.5	c,r
1.0	0.33	1	0.5	c,r
2.0	0.55	1	1.1	c,r
2.0	0.33	1	1.1	c,r
3.0	0.55	4	3.5	r
3.0	0.33	4	3.5	r
3.0	0.55	1	1.1	c
5.0	0.55	4	3.5	r
5.0	0.33	4	3.5	r

results of our own calculations. The minimum information needed is the location of the spinodal decomposition curve that separates the metastable and unstable regions in the phase diagram. In the temperature-density plane, the points of interest lie above the spinodal decomposition curve. One can expect the position of the spinodal curve to be different for each combination of ε , Δ values and it would be an enormous task to give proper attention to the problem of determination of spinodal curves. We have chosen a limited number of points, as given in Table I. The calculations performed at these points reveal the character of the systems and on this basis we shall try to draw the conclusions about the thermal as well as percolation properties.

Thermal properties of the systems were estimated on the basis of the calculated total energy, pressure and on the basis of the visual inspection of pictorial illustrations of particle configurations. Pressure was determined by calculating the virial of the system which is obtained by summing up the momentum transfers in binary collisions.

The quantities that we used for the clarification of percolation properties of the systems were deduced from the distribution of clusters. Every so often, we calculated the size of the largest cluster (n_{\max}), the distribution of coordination numbers and the distribution of clusters according to their size (n) for $n = 1$ to 10.

A general impression which emerges on the basis of molecular dynamics results is the following. At a relatively shallow well ($\varepsilon \leq 1$), the results are in agreement with the results of other authors.¹⁰ In this case, it is easy to determine the spinodal decomposition curve and the percolation threshold curve. At a deeper well ($\varepsilon \geq 2$), things begin to be complicated because the number of collisions necessary for the system to approach the equilibrium configuration goes beyond the limit that can be reached by standard computer technology. For that reason, the results are slightly uncertain. In spite of this difficulty, we succeeded in determining the trend of changes that take place when the sticky limit is approached. The most important dynamical characteristic is the slowing down of the equilibrium process. As far as the structural characteristics are concerned, the results seem to be compatible with the findings that higher order virial coefficients diverge, which makes the aggregated state the only stable configuration.

A greater part of the calculations was performed for the value of Baxter's temperature parameter $\tau = 0.3$, but the calculations were also performed below this value. The limit of stickiness was approached from a relatively shallow and wide potential well with $\varepsilon = 1$, $\Delta = 0.3$, and then we proceeded towards deeper wells with $\varepsilon = 2, 3, 4$ and 5 , and with the corresponding widths following from Eq. (1). At $\varepsilon < 3$, the systems equilibrate after a few hundreds of collisions per particle. This is shown in Figure 2, where the total energy of the system at $\varepsilon = 2$, $\Delta = 0.11036$, $\rho = 0.55$ and $T = 1$ is shown as a function of time. Two runs were performed. One was started from a clustered configuration of particles (as in Figure 1) and the other from a random configuration. A typical configuration of particles taken from the equilibrium part of the history of the system is depicted in Figure 3. We can see that the system is in the vicinity of the percolation threshold. The particles marked by crosses are members of a cluster that extends across the system and, due to the cluster boundary conditions, they form a cluster with infinite extension. In the course of time evolution, such clusters decompose and form again. This process is compatible with the definition of the percolation threshold.

At deeper and narrower potential wells ($\varepsilon = 3$, $\Delta = 0.0406$, $\rho = 0.553$; Figure 4 and $\varepsilon = 5$, $\Delta = 0.00549$, $\rho = 0.55$; Figure 5), the structure of the system changes qualitatively. The clusters attain a more compact shape in the form of fragments of a closed packed structure. As far as the percolation properties are concerned, we can see that the systems are close to the percolation threshold. As it can be seen in Table I, the calculations were also performed for the density $\rho = 0.33$. At this density, all the systems are below the percolation threshold.

The calculations at $\varepsilon = 3$ and $\varepsilon = 5$, fragments of which are displayed in Figures 4 and 5, were started from randomized configurations. After more than one million collisions had occurred, we were not sure whether the systems had reached equilibrium.

Therefore, we also performed runs with the initial structure in the form of a close packed cluster in order to see whether the time evolution would lead to the same struc-

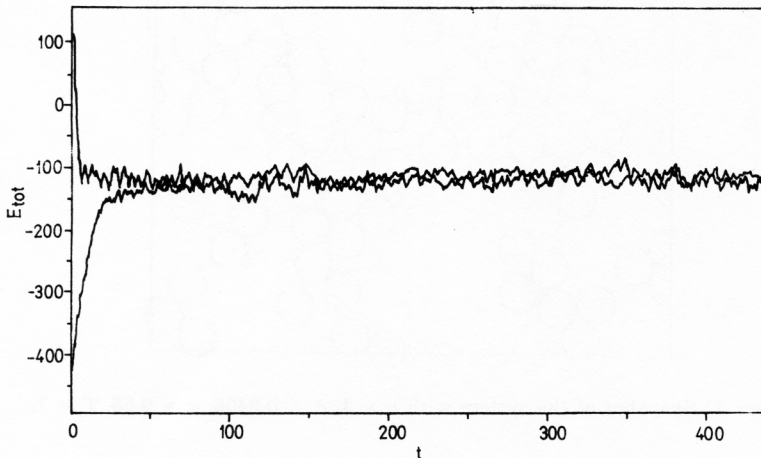


Figure 2. Total energy of the system of HCSQW disks with $\varepsilon = 2$, $\Delta = 0.11036$, $\rho = 0.55$, $T = 1$ as a function of time. One can see that, after approximately 70 time units, the system which started from random configuration (upper curve at $t < 70$), and the system which started from clustered configuration (lower curve at $t < 70$) converge.

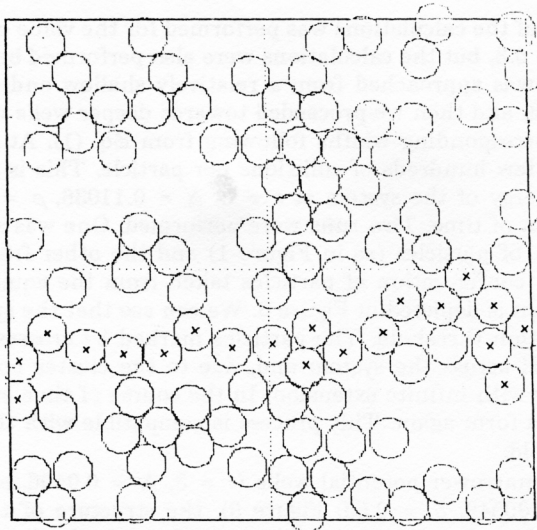


Figure 3. A snapshot of particles taken from the equilibrium part of the calculation mentioned in the caption of Figure 2. The particles marked by crosses belong to a cluster which percolates in the infinite system of replicas of the central square implemented by periodic boundary conditions.

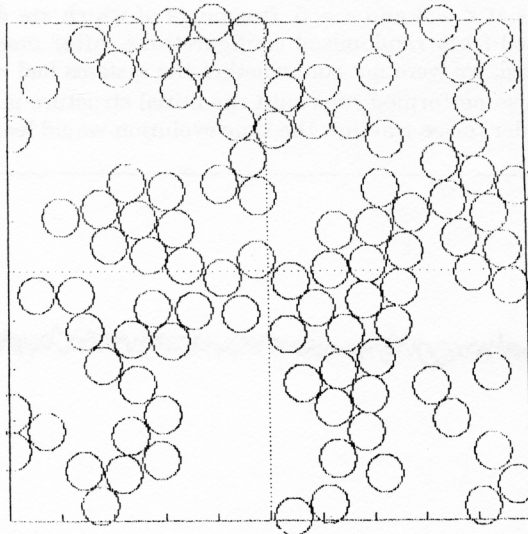


Figure 4. Snapshot of the system with $\varepsilon = 3$, $\Delta = 0.0406$, $\rho = 0.55$, $T = 1$.

ture as in the case of the calculations started from random configurations. It turned out that the clustered configurations was very stable. The stability decreases with decreasing depth of the well, but even at $\rho = 3$, $\Delta = 0.0406$ and $T = 1$, the cluster did not decompose within 800000 collisions. In Figure 6, we can see that the total ener-

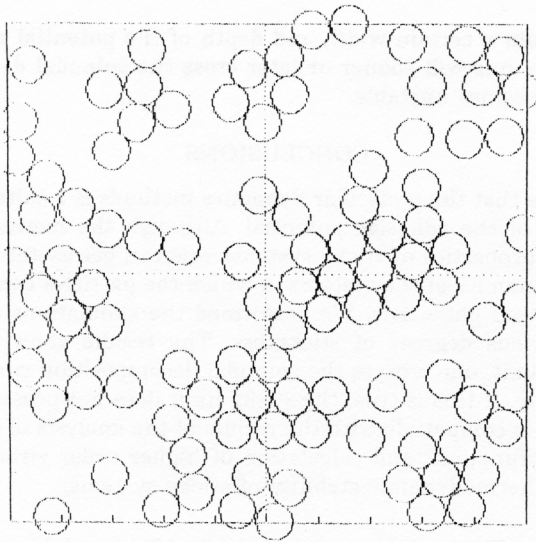


Figure 5. Snapshot of the system with $\varepsilon = 5$, $\Delta = 0.00549$, $\rho = 0.55$, $T = 1$.

gies of the two runs started with random and clustered configurations do not meet at a common point and, consequently, the question whether the equilibrium configuration of the system at $\varepsilon = 3$, $T = 1$, $\rho = 0.55$ is fluid or solid-like cannot be answered with certainty.

Most probably, both the liquid-like and the crystal-like phases represent the equilibrium states and, consequently, the states at $\varepsilon = 3$, $T = 1$ find themselves below the spinodal decomposition curve. This is also true of the states with $\varepsilon = 4$ and $\varepsilon = 5$. These findings are important when the approach towards the limit of stickiness is analyzed, since on this basis we can anticipate the following scenario. If one proceeds towards the sticky limit by choosing a certain value of Baxter's indicator of tempera-

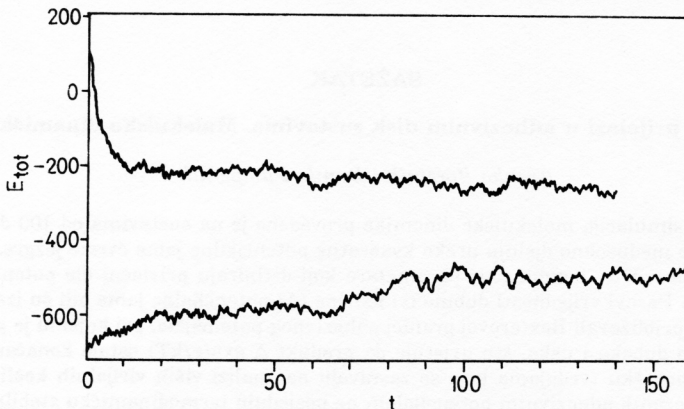


Figure 6. Total energy of the system with $\varepsilon = 3$, $\Delta = 0.0406$, $\rho = 0.55$, $T = 1$. Upper curve—random initial configuration; lower curve—clustered initial configuration.

ture and starting from a certain width and depth of the potential above the spinodal decomposition curve, one will sooner or later cross the spinodal decomposition curve where the system becomes unstable.

CONCLUSIONS

We can conclude that the molecular dynamics methods is a suitable tool for studying the real nature of the adhesive potential. Although the method does not give a direct access to the properties of sticky systems, one can get useful information about the structure and dynamics of the systems in which the particles can be bound by deep and narrow square-well potentials. We performed the simulations on a series of systems exhibiting various degrees of stickiness. The results show that, on the way towards the sticky limit, one crosses the spinodal decomposition curve, where the system is no more stable. If this is true, the sticky limit does not possess thermodynamic stability. This belief is compatible with the results of the analysis of the terms defining the pair correlation function⁶ and calculation of higher order virial coefficients both of which deny the thermodynamic stability of sticky systems.

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SAŽETAK

Perkolacijski prijelazi u adhezivnim disk sustavima. Molekulsko-dinamička studija

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Numerička simulacija molekulske dinamike provedena je na sustavima od 100 dvodimenzij-skih čestica, koje međusobno djeluju preko kvadratne potencijalne jame čvrste jezgre. Računanja su provedena za različite kombinacije parametara koji definiraju privlačni dio potencijala, te za različite gustoće. Parovi vrijednosti dubine (ϵ) i širine (Δ) potencijalne jame bili su izabrani tako, da su se sustavi približavali Baxterovoj granici adhezivnog potencijala, pri kojemu je potencijalna jama beskonačno duboka i uska, što uvjetuje da produkt $\Delta \exp(\epsilon/kT)$ ostaje konačan. Rezultati simulacije daju podršku tvrdnjama koje se zasnivaju na analizi viših virijalnih koeficijenata, da sustavi čestica vezanih adhezivnim potencijalom ne posjeduju termodinamičku stabilnost. Rezultati pokazuju da približavanje sustava ravnoteži usporava približenjem granici ljepljivosti. Osim toga sustavi uz granicu ljepljivosti pokazuju tendenciju agregacije čestica do prijelaza u kristalnu strukturu, što povećava sumnju u regularnost perkolacijskog problema ljepljivih sustava.