Multiphase behaviour of the plane quadratic lattice gas with nearest-neighbour exclusion and next-nearest-neighbour finite interaction

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E V Aksenenko and Yu V Shulepov

Institute of Colloid Chemistry and Chemistry of Water, Academy of Sciences of the Ukrainian SSR, 42 Vernadsky Avenue, Kiev 252 180, USSR

Abstract. The plane quadratic lattice gas with nearest-neighbour exclusion and next-nearest-neighbour finite interaction is considered in the framework of the double-site and single-square approximations of the cluster variation method and in the branched lattice approximation. In addition to the disordered and hard-core-ordered phases only one extra phase is shown to exist which arises at low temperatures near the half-maximum density. This phase which is due to the next-nearest-neighbour repulsion exhibits both first- and second-order transitions to the disordered phase.

1. Introduction

In this paper we derive the closed-form approximations for the plane quadratic lattice gas model with nearest-neighbour exclusion and next-nearest-neighbour weak pair interaction. The previous studies of the model were based on the closed-form approximations (Kaye and Burley 1974a, Aksenenko and Shulepov 1978), the exact finite method (Runnels et al 1970), the series expansions (Springgate and Poland 1975, 1979, Aksenenko and Shulepov 1979, 1981); in all these investigations the finite next-nearest-neighbour attraction was treated. The phase diagram calculated for this case contains the disordered and ordered phases which are separated by the coexistence region below the tricritical point and by the continuous phase transition line above this point. More recently the next-nearest-neighbour repulsion was treated by Kinzel and Schick (1981) using the phenomenological scaling method of Nightingale (1979); the procedure involved also the exact finite calculations. In addition to the disordered and hard-core-ordered phases mentioned above, the phase diagram constructed for this case contains the third phase which exists at low temperatures and is located in the vicinity of the half-maximum density. In fact this phase was first detected by Bellemans and Nigam (1967) who studied, among other models, the plane quadratic lattice gas with nearest- and next-nearest-neighbour exclusion, which can be regarded as a low-temperature limit for the lattice gas considered here, if a repulsion exists between the next-nearest neighbours.

The models in which hard-core exclusion is attended by soft repulsion of more distant neighbours are interesting but not only in their own right. There is a wide variety of systems which can be described thermodynamically by such models, namely the localised adsorption monolayers.

The state of an atom adsorbed on a metal surface depends on the nature of the adsorption bond. Referring to Schrieffer (1972), Lyo and Gomer (1975), Bol'shov *et al* (1977) for the detailed reviews of chemisorption bonding, we shall point out here that in the case of either physisorption or chemisorption the adsorbed atom together with its electron distribution can form a dipole directed perpendicularly to the surface. Then for physical adsorption a dispersion attraction between the adsorbed atoms is superimposed on the dipole–dipole repulsion, the latter prevailing at large distances. If an ionic bonding exists between the chemisorbed atom and the surface, then the dipole–dipole interaction dominates at almost all distances, acting through the vacuum half-space. In addition there exists a long-range oscillating exchange interaction via the electron gas of the adsorbent (Grimley 1967, Grimley and Walker 1969).

If the size of the adsorbed atom does not exceed the distance between the adsorption centres on the surface, then the thermodynamics of such an adsorbed monolayer may be represented using Ising-type plane lattice gas models with extended interactions (see e.g. Domany *et al* 1978, Shulepov and Aksenenko 1981). Here we particularise to the less extensively studied case when the hard-core diameter of an adsorbed species exceeds the lattice spacing, and a soft interaction exists between next-nearest-neighbouring atoms. These are for example the atoms possessing considerable electric charge (alkaline or alkali-earth elements) or dipole moments (rare gases) adsorbed on a metal surface, the dipole–dipole repulsion being, in this case, the major contributor to the interaction. In the framework of the same model the next-nearest-neighbour attraction which may correspond to the dispersion forces existing between the atoms of gases adsorbed on, say, a graphite surface, can be treated similarly.

The closed-form approximation methods used here are to complement the more accurate calculations for the following two reasons. Firstly, irrespective of their quantitative roughness, they provide a qualitatively correct description of the thermodynamics of the system by means of relatively simple analytical solutions. Secondly, the transfer matrix methods (Kinzel and Schick 1981) or the series-expansion technique can be used only provided the existence of the phase (the manner of the decomposition of the system) is established. In § 2 we shall show that the three phases mentioned above exhaust the variety of the phases available for the system. Section 3 contains the results and the phase diagram of the system.

2. Summary of calculations

To account for the periodical density distributions over the lattice we define the sublattices into which the whole lattice can be decomposed. The existence of the hard cores implies the decomposition of the plane quadratic lattice into two interpenetrating quadratic sublattices a and b in such a way that the a sublattice site has four of its nearest neighbours on the b sublattice and vice versa. Each of these sublattices can be decomposed in a similar way, with sublattices 1 and 3 corresponding to the a sublattice, and sublattices 2 and 4 to the b sublattice. Since the interactions of the model extend to the second neighbours, further decomposition is unnecessary. Finally, the sublattices 1,2 and 3,4 may be composed to form the sublattices c and d representing alternate parallel rows or columns on the lattice. The number density ρ_i, $i = a, b, c, d, 1, 2, 3, 4$ can be associated with each of the sublattices, the value of ρ_i being equal to the probability of occupation of the ith sublattice site. These probabilities are normalised to unity; they are related to each other and to the total density ρ via

the equations

$$2\rho = \rho_a + \rho_b = \rho_c + \rho_d, \qquad 2v = \rho_a - \rho_b,$$

$$2\rho_a = \rho_1 + \rho_3, \qquad 2s_a = \rho_1 - \rho_3, \qquad (1)$$

$$2\rho_b = \rho_2 + \rho_4, \qquad 2s_b = \rho_2 - \rho_4.$$

Here we have introduced ordering variables v, s_a and s_b, which describe the preferential occupation of certain sublattices. The potential energy E_2 of the next-nearest-neighbour interaction enters the calculations through the Boltzmann factor

$$t = \exp(-E_2/kT), \qquad (2)$$

and the activity is to be introduced,

$$z = j_0 \exp(-E_1/kT), \qquad (3)$$

where j_0 is the partition function for the internal degrees of freedom of the adsorbed particle, and E_1 is the potential energy of interaction between the adsorbed particle and the adsorbent surface.

2.1. Finite-cluster-variation approximations

To obtain state equations which describe the thermodynamic behaviour of the lattice gas, one can use the finite cluster variation (FCV) method. To avoid duplication we refer to Hijmans and De Boer (1955), Woodbury (1967) and Shulepov and Aksenenko (1981) for detailed discussion of the procedure. Since the method is familiar and the calculations are not especially involved, we present here only the brief summary of the treatment.

To construct the expression for the free energy function $f = F/kT$, where F is the Helmholtz free energy per lattice site, in the single-square approximation of the FCV method it is necessary to introduce two extra spanning variables w_a and w_b which represent the occupation of the square basic figure by two molecules on the a and b sublattices respectively. The minimisation of the free energy function with respect to the five variables v, s_a, s_b, w_a, w_b leads to a set of five simultaneous phase equations. It can be seen that some homogeneous and periodic density distributions (hereafter referred to as 'phases') can be generated from these equations, leaving the resulting set well defined:

$$
\begin{array}{lll}
\text{Phase I (disordered)} & v = 0, & s_a = s_b = 0, \\[4pt]
\text{Phase II } (\sqrt{2} \times \sqrt{2}) & v \neq 0, & s_a = s_b = 0, \\[4pt]
\text{Phase III } (2 \times 1) & v = 0, & s_a = \pm s_b \neq 0, \qquad (4) \\[4pt]
\text{Phase IV} & v \neq 0, & s_a \neq 0, s_b = 0, \\[4pt]
\text{Phase V} & v \neq 0, & s_a \neq 0, s_b \neq 0, s_a \neq s_b.
\end{array}
$$

In the following the Roman subscripts refer to the corresponding phases.

To obtain the solution it is most convenient to eliminate the spanning variables between the equations in favour of four new reduced variables defined as follows:

$$x_i = \frac{t(\rho \pm v - w_i)}{1 - 4\rho + w_a + w_b}, \qquad y_i = \frac{ts_i}{1 - 4\rho + w_a + w_b}, \qquad i = a, (+) \text{ or } b, (-). \qquad (5)$$

Phase I corresponds to $x_a = x_b$, $y_a = y_b = 0$, and may be calculated via the quadratic solution. Phase II was studied in single-square and double-square approximations by Kaye and Burley (1974 a, b) for the $t > 1$ case. To perform the calculations it is convenient to introduce $2x = x_a + x_b$, $2q = x_a - x_b$. Then eliminating q from the phase equations in favour of density one obtains the result via the cubic solution. This phase coexists with phase I along the line $t = (3 - 8\rho)/4\rho(1 - 2\rho)$.

Phase III can be obtained from the phase equations with $y = y_a = \pm y_b$ and $x = x_a = x_b$. To obtain the solution one has to eliminate y^2 in favour of density. This procedure leads to a seventh-power equation in x with the coefficients dependent on ρ and t. The solution corresponding to phase III exists inside a region bounded by the phases I and III separation line $t = -(3 - 14\rho + 12\rho^2)(1 - 6\rho + 4\rho^2)/16\rho(1 - \rho)^2(1 - 2\rho)$. With the numerical solution of the seventh-power equation and the $y^2(\rho, t)$ function, one can calculate the 'adsorption isotherm' $\ln z_{\mathrm{III}}(\rho, t)$ and the equation-of-state curve $\Gamma_{\mathrm{III}}(\rho, t) = \rho \ln z_{\mathrm{III}}(\rho, t) - f_{\mathrm{III}}(\rho, t)$. When tabulating these we found a loop occurring on the Γ_{III} versus ρ and z_{III} versus ρ isotherms in the vicinity of the high-density branch of the separation line as shown in figure 1, indicating a first-order transition existence in this single-square approximation between phases I and III.

It is evident from (4) that the region of phase IV existence, if any, is to be located within the phase II region, because the limiting case of phase IV, corresponding to $s_a = 0$ is just the definition of phase II. Similarly phase V can exist only inside the phase IV region. Expanding the phase equations at $s_a \approx 0$, $s_b = 0$ to calculate the phase II and IV separation line coordinates, one obtains a set of two simultaneous equations, the first of them being just the equation for phase II. Then tabulating the LHS of the second equation we found that, throughout the whole region of phase II existence, this expression never changes its sign. Thus phase IV and consequently phase V do not exist in this approximation.

For completeness we performed similar FCV calculations using a pair of nearest-neighbouring sites as a basic figure and the mean-field-type approximation for energy, and were surprised by the variety of non-physical phenomena taking place along the phase I and II separation line at $t < 1$, including a first-order transition at sufficiently low temperatures and a discontinuity in the ordering parameter v. These unusual features stem from the low order of the approximation; they are not produced by the single-square calculations. On the contrary, no phase I and III coexistence region was detected; phase IV was shown not to exist in this approximation.

2.2. Branched lattice approximation

There is another approximate procedure for calculation of the thermodynamic properties of the lattice gas, termed the branched lattice (BL) method. The essence of this method is as follows: instead of calculation of the approximate expressions for the thermodynamic functions of the lattice gas considered, one can calculate these properties exactly for some branched lattice, which is 'locally equivalent' to the original lattice. The values obtained in such a way are expected to provide a satisfactory approximation to the solution sought for.

The BL approximations for phases I and II were obtained by Aksenenko and Shulepov (1978); these solutions were reproduced also in Aksenenko *et al* (1978) and Shulepov and Aksenenko (1981). To construct the solution for phase III we need to perform a similar procedure with an improved account for next-nearest-neighbour interaction.
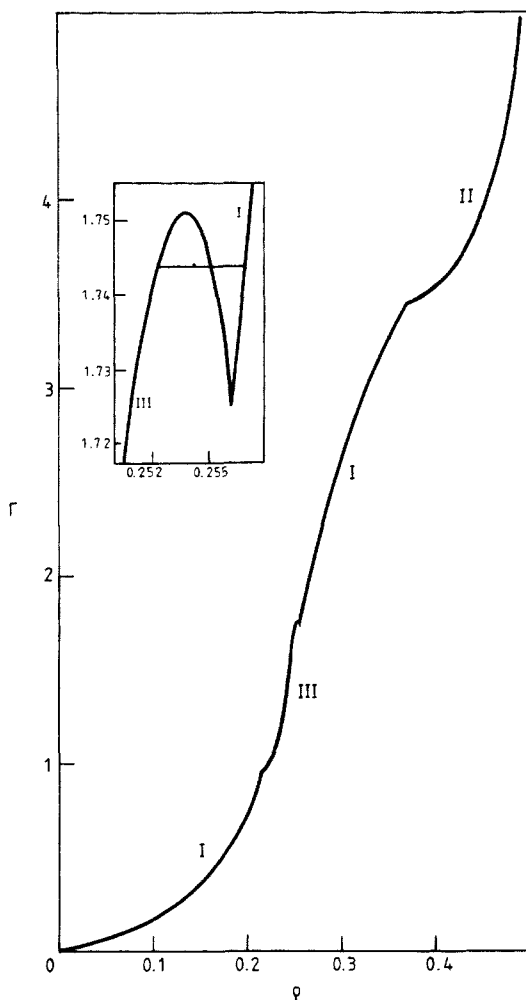
Figure 1. The Γ versus ρ isotherm in single-square approximation for $t = 0.05$, showing three phases of system. Inset: magnified section of isotherm near the phase I and III separation line. The horizontal line connects coexisting phases.

The main point in the procedure of the BL method used here is the assumption that the lattice is built out of the two-site clusters step by step, the probabilities of occupation of preceding step clusters being related to those of current step cluster according to the interactions and the activities of the atoms involved in the cluster-to-cluster transfer. Then, assuming a homogeneous sublattice density distribution throughout the lattice one can close the chain of the expressions for the probabilities, thus obtaining the phase equations. To be concise we refer here to figure 2 of Aksenenko and Shulepov (1978) or figure 2.2.13 of Shulepov and Aksenenko (1981) where the procedure is described, noting that (i) the interactions are to be accounted for all four clusters involved, and (ii) since only three of four possible next-nearest-neighbour interactions can be represented in this branched lattice, another Boltzmann factor $t_1 = t^{4/3}$ is to be introduced to remove in part this error.

We performed the calculations along these lines and obtained the solutions for phases I and II, and the equations for the phases I and II and I and III separation lines. As the accuracy of the BL approximation will be shown in § 2.3 to be intermediate between those of double-site and single-square approximations, but the phase equations are much more involved, we did not attempt to calculate the thermodynamic properties for phase III and restricted ourselves to the construction of the phase diagram only.

2.3. Accuracy of the approximations

In spite of the qualitative similarity of the phase diagrams derived by means of various approximate treatments, the particular values of characteristic phase transition parameters are rather different. To estimate the validity of approximate methods used it is a common practice to compare the solutions obtained using these methods for some limiting case of the problem considered, with an exact solution, if one exists. Unfortunately this is not the case, the only exact solution for the lattice gas with hard molecular cores being that of Baxter (1980) for the hard hexagons triangular lattice gas. Nevertheless we can compare our solutions with the results obtained for case B of Bellemans and Nigam (1967), which represent the low-temperature limit of the model considered here. Inasmuch as the double-site approximation cannot reproduce the thermodynamic functions of the next-nearest-neighbour exclusion model, we performed the calculations for another two approximations. The analytical solutions are available for phases I and III. Comparing the first few terms of an exact series expansion for phase III derived by Bellemans and Nigam,

$$(1-4\rho)_{\mathrm{exact}} \approx \tfrac{1}{2} z^{-1/2} (1 + 2z^{-1/2} + \ldots),$$

with the expansions of the same quantity which can be obtained from our approximate solutions,

$$(1-4\rho)_{\mathrm{single\ square}} \approx \tfrac{1}{2} z^{-1/2} (1 + z^{-1/2} + \ldots),$$

$$(1-4\rho)_{\mathrm{branched\ lattice}} \approx (6\,z)^{-1/2} (1 + 11 \times 6^{-3/2} z^{-1/2} + \ldots),$$

we conclude that single-square approximation provides a better estimate for phase III thermodynamic behaviour.

3. Results and discussion

We have shown that three phases can exist in the plane quadratic lattice gas with nearest-neighbour exclusion and next-nearest-neighbour finite interaction. Among them phase I is disordered in the sense that no periodical density distribution exists across the lattice, and phases II and III are ordered.

Phase II or $(\sqrt{2} \times \sqrt{2})$ can exist due to the molecular hard cores at high densities, when one of the sublattices a or b is preferentially occupied, the other being nearly empty.

Phase III or (2×1) arises at low temperatures in the vicinity of the $\rho = \tfrac{1}{4}$ point, when the second-neighbour repulsion leads to the existence of an ordered state with one of the two sublattices c or d, say c, almost close-packed; in every c row, in turn, one of the two sublattices, 1 or 2, which result from the decomposition of sublattice c, is occupied preferentially, but in such a way that $\rho_1 = \rho_2$ throughout the whole

lattice. In single-square approximation this phase coexists with phase I along the low-density branch of the coexistence curve; close to the high-density branch the coexistence region is located as shown in figure 2.
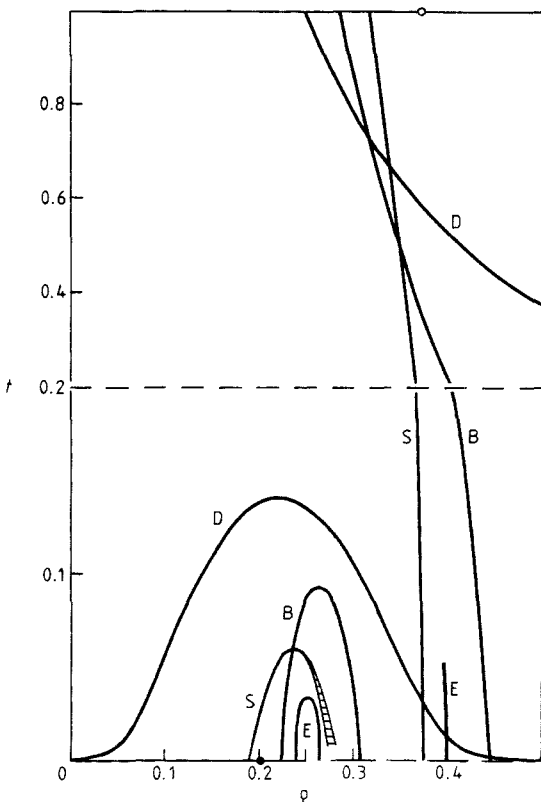

Figure 2. The *t* versus *ρ* phase diagram obtained in (D), double-site; (B), branched lattice; (S), single-square approximations and (E) exact finite method–phenomenological scaling (Kinzel and Schick 1981) calculations. Also shown are (○) the exact series expansions result obtained by Gaunt and Fisher (1965) and Baxter *et al* (1980), and (●) the approximate transition point location calculated by Bellemans and Nigam (1967). The vertical scale changes at *t* = 0.2.

In all the approximations used, no other phases were detected to exist. Since a well known feature of the closed-form approximations is the overestimation of the lattice system ability to undergo the phase separation, we believe this result to be valid in general.

Phase transitions in the lattice gas with intermolecular attraction were discussed elsewhere (see e.g. Kaye and Burley 1974a, b, Runnels *et al* 1970, Springgate and Poland 1979), and we concentrate here on the repulsion case $t < 1$. The phase diagrams obtained by various approximate methods are shown in figure 2. The less accurate double-site approximation (curves D) considerably distorts the phase diagram: the region of phase II existence is bound by the minimum value $t = \exp(-1)$, while phase III at extremely low temperatures extends over the whole range of density available for the system. This last feature is an expected one in view of the mean-field type of

the approximation used for the energy of the system. The phase diagrams obtained in the branched lattice and in the single-square approximation, curves B and S respectively, are more realistic. Also shown is the phase diagram obtained by Kinzel and Schick (1981) using the exact finite method–phenomenological scaling approach (curves E).

Maybe the most interesting feature of the model is the probable existence of the phase I and III coexistence region located close to the high-density branch of the phase separation line in the single-square approximation. Kinzel and Schick (1981) noted a first-order-like behaviour of the thermal exponent; by examining the isotherms it has been ascertained, however, that no first-order transition occurs at finite temperature. No serious doubts can be expressed against these considerations; it should be kept in mind, however, that the exact finite calculations (with lattice circumferences 14 and less) might possibly not be precise enough to detect a rather narrow coexistence region.

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