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Orientational phase transitions in systems of adsorbed molecules

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We have applied the cluster variational method of Kikuchi and co-workers to systems with continuous degrees of freedom, in particular to planar rotor models, which we use for the study of orientational phase transitions in systems of adsorbed molecules. The method is based in approximated expressions for the free energy as a functional of the n-site distribution function, and the conditional minimum of the free energy is given by integral equations which are solved numerically. We apply the method to the herringbone transition of N_2 molecules on graphite and also to the orientational phase transition of molecules on a square lattice.

I. INTRODUCTION

Adsorbed monolayers of molecules on crystal surfaces present a large variety of structures. Besides the fluid, commensurate, and incommensurate phases classified according to the periodicity of the adsorbate with respect to the substrate, they may also appear as phases with different orientational order. The best known example[1-8] is that of N_2 molecules adsorbed in a commensurate $\sqrt{3}\times\sqrt{3}$ structure on graphite. The molecules are orientationally disordered above 30 K but below this temperature they form a herringbone structure as shown in Fig. 1, with six degenerate configurations. A similar orientational ordering may be predicted for molecules on a square lattice such as the surfaces of MgO, LiF, or certain noble metals, which would go from a high-temperature disordered phase to the low-temperature structure shown in Fig. 2, with two degenerate configurations.[9]

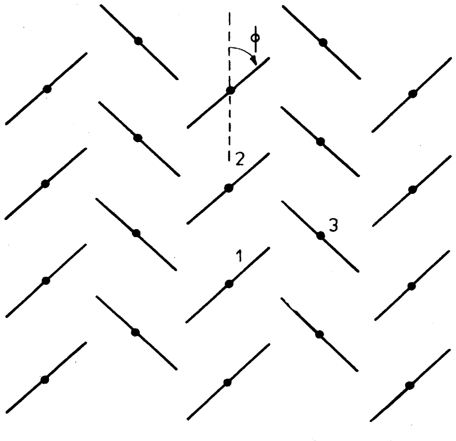

FIG. 1. The herringbone structure of N_2 molecules on graphite. The orientation of the molecules correspond to the minimum of the quadrupole-quadrupole interaction; there are six equivalent structures which may be obtained from the figure by rotation of $2\pi/3$ and by shifts of a lattice space. The labels 1,2,3 are used as reference in the text.

Computer simulations[9-15] have shown that these phase transitions may be understood with simplified models of planar rotors, with the center of the molecules fixed at the lattice sites and the rotation restricted to the substrate plane. These models also offer a good starting point for the different theoretical approaches. The mean-field approximation (MFA) has been applied to rotors on triangular[16] and square lattices,[17] but as it may be expected for systems in two dimensions, the success has been limited. The MFA predictions for the transition temperature are too far above the computer simulation results, and in the case of the herringbone structure, the MFA fails even to give the correct order of the phase transition. We have recently presented a study of these systems beyond the MFA,[18] partially based on the cluster variational method of Kikuchi and co-workers.[19-21] In this article we present a detailed account of the method applied to planar rotor models and show how it may be used to include in a systematic way the correlation effects at short range. We compare the results with two different computer simulation: the Monte Carlo calculation of Mouritsen and Berlinsky[11] for the herringbone transition of planar quadrupoles on a triangular lattice and the molecular dynamics simulation of site-site

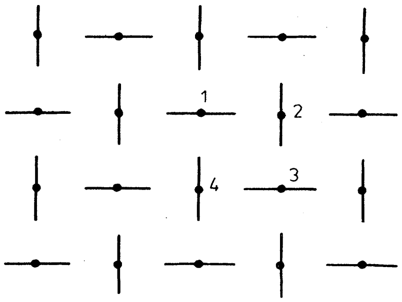

FIG. 2. Minimum energy configuration for molecules on a square lattice. There are two equivalent structures which may be obtained by rotation of $\pi/2$. The labels 1,2,3,4 are used as reference in the text.

Lennard-Jones (LJ) molecules on a square lattice done by Kalia *et al.*[9]

In the next section we give a summary of the MFA results for these models, in Sec. III we present the general lines of the Kikuchi approximation and develop it for the application to models with continuous degrees of freedom like the planar rotors, for which the free energy is written as a functional of the n-sites orientational distribution functions. Section IV deals with the study of the square and triangular lattice structures in the Bethe approximation which considers the basic cluster formed by two nearest-neighbor sites. In Sec. V we apply higher-order approximations which include the correlation between 3 and 4 sites in the triangular and square lattice, respectively. In the last section we conclude with an estimation of the method capabilities and possible extensions.

II. THE MEAN-FIELD APPROXIMATION

The simplest theoretical treatment of the planar rotor model is given by the MFA which may be formulated in terms of the orientational distribution function of the molecules $\rho_i(\phi)$, with the index i identifying the lattice site and the angle ϕ giving the molecular orientation. The free energy of the system is taken as a functional of $\rho_i(\phi)$ and approximated by

$$\beta F=\sum_i \int d\phi\, \rho_i(\phi)\{\ln[\rho_i(\phi)]-1\} + \sum_{(ij)} \int d\phi\, d\phi' \rho_i(\phi)\rho_j(\phi')\beta U_{ij}(\phi,\phi') , \quad (2.1)$$

where $\beta=1/kT$, $U_{ij}(\phi,\phi')$ is the pair interaction potential between the molecules at lattice sites i and j and the sum over (ij) runs over all the pairs on the lattice. The MFA result is obtained by minimizing F with respect to all the possible functions $\rho_i(\phi)$, with the normalization requirement

$$\int d\phi\, \rho_i(\phi)=1 \quad (2.2)$$

(we do not consider vacancies in the system). The Euler-Lagrange equation corresponding to the conditional minimum may be easily written as

$$\rho_i(\phi)=\frac{\exp\left[-\beta\sum_j \int d\phi' \rho_j(\phi')U_{ij}(\phi,\phi')\right]}{\int d\phi \exp\left[-\beta\sum_j \int d\phi' \rho_j(\phi')-U_{ij}(\phi,\phi')\right]} , \quad (2.3)$$

which is very similar to the Maier-Saupe equation for a liquid crystal,[22] but with the orientation of the molecules restricted to a plane. The solution of the MFA is easier when the interaction potential is taken as the simple quadrupole-quadrupole interaction used in[11]

$$\beta U_{ij}(\phi,\phi')=K\cos(2\phi+2\phi'-4\theta_{ij}) , \quad (2.4)$$

where i,j are restricted to nearest-neighbor pairs and θ_{ij} is the angle formed by the ij direction on the lattice plane. In this case Eq. (2.3) may be rewritten as

$$\eta=\frac{\int d\phi \cos(2\phi)\exp[KC_h\eta\cos(2\phi)]}{\int d\phi \exp[KC_h\eta\cos(2\phi)]} , \quad (2.5)$$

in terms of the order parameter η defined as

$$\eta=\int d\phi\, \rho_i(\phi)\cos[2(\phi-\chi_i)] , \quad (2.6)$$

where χ_i gives the orientation of the molecule at site i when the system is in the minimum energy configuration. The constant C_h in (2.5) gives the highest number of "satisfied bonds" around a lattice site, that is, for the square lattice $C_h=4$ as it corresponds to the configuration of Fig. 2 in which all the nearest-neighbor pairs have a potential energy of $-K$. For the triangular lattice there is no way to fully satisfy the six bonds around each site, the herringbone structure does its best getting two pairs with energy $-K$ and the other four with $-K/2$, so that $C_h=4$ instead of 6. Equation(2.5) has always the trivial solution $\eta=0$, which corresponds to the disordered phase; notice that this is not to say that the angular distribution is completely uniform, $\rho_i(\phi)=1/2\pi$. In general $\rho_i(\phi)$ will have modulations compatible with the lattice symmetry. At large K (low temperature) a new solution with $\eta\neq 0$ may appear, which corresponds to the ordered phase. By expanding (2.5) for small η we can show that the phase transition is of second order (contrary to the three dimensions Maier-Saupe result) and the transition temperature in reduced unit of the interaction is $T\equiv 1/K=C_h/2=2$. The order parameter below the critical temperature may be easily obtained by numerical solution of (2.5), and it is presented in Fig. 3, together with the computer simulation results of Mouritsen and Berlinsky[11] for the herringbone phase transition. To compare with the simulation results of Kalia *et al.*[9] for the square lattice we have solved the general Eq. (2.3), with the pair interaction potential given by site-site Lennard-Jones used there. The result is shown in Fig. 4; in both cases the critical temperature is much larger than the simulation value and only at very

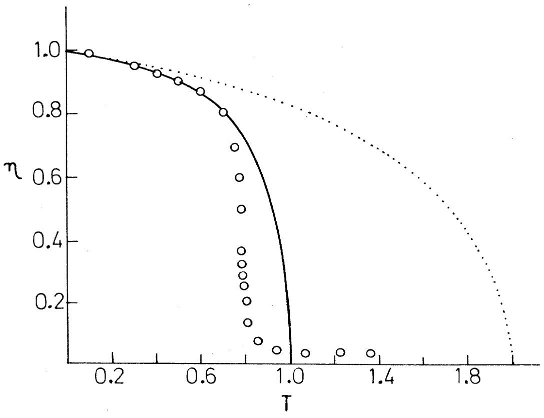

FIG. 3. Order parameter for the herringbone phase as a function of the reduced temperature, $T=K^{-1}$, circles are the Monte Carlo simulation results of Ref. 11; dotted line is the MFA; and solid line is the Kikuchi approximation presented here.

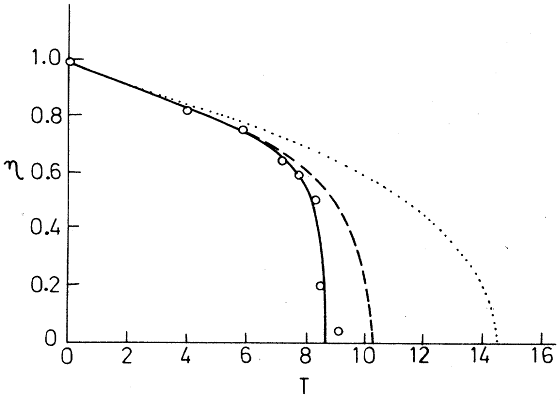

FIG. 4. Order parameter for the site-site Lennard-Jones molecules on a square lattice as a function of the reduced temperature in units of the LJ interaction. The circles are the result of the molecular dynamics calculation of Ref. 9; dotted line, MFA; dashed line, Bethe approximation; and solid line, Kramers-Wannier approximation.

low temperatures the order parameter is in good agreement with the simulation results. Moreover, in the case of the herringbone structure the MFA prediction of a second-order transition is in disagreement with the first-order phase transition found in the simulation and the renormalization-group analysis.[23] It becomes then clear that a study of the problem beyond the MFA is quite necessary before we may claim a full theoretical understanding of the problem.

III. KIKUCHI APPROXIMATION FOR PLANAR ROTOR MODELS

The cluster variational method developed by Kikuchi and co-workers,[19–21] includes earlier approximations, like Bethe[24] and Kramer-Wannier,[25] into a systematic treatment where the free energy of a lattice model is calculated as a function of the probabilities for the different configurations in a cluster of n sites. The MFA may be regarded as the $n=1$ case, the Bethe or quasichemical approximation, which considers configurations of nearest-neighbors pairs, is the $n=2$ case. The Kramers-Wannier approximation for the Ising model in a square lattice corresponds to $n=4$, with a cluster formed by the four sites of the elementary square in the lattice. The method may be applied to any lattice model and any cluster size with the only limitation of the computational feasibility. In any case the entropy of the system is approximated, with probabilistic arguments, by an expression like

$$S=a_p \sum_{i=1}^{m_p} p_i \ln(p_i)+a_q \sum_{j=1}^{m_q} q_j \ln(q_j) + a_r \sum_{k=1}^{m_r} r_k \ln(r_k)+\cdots , \tag{3.1}$$

where p_i are the probabilities of finding any of the m_p possible configurations for the n-sites cluster and $q_j, r_k, \ldots$ are the probabilities for the $m_q, m_r, \ldots$ configurations of smaller clusters up to a single site. The values of $q_j, r_k, \ldots$ may be obtained as a sum of p_i's. The constants $a_p, a_q, a_r, \ldots$ depend on the lattice structure and the cluster size, we refer the reader to the original works of Kikuchi *et al.*[19–21] for different ways to determine them. The internal energy of the system is given in terms of the pair interaction potential and the pair distribution probabilities, so that together with (3.1) one may obtain the free energy of the system, F, as a function of the set of p_i's. The equilibrium cluster configuration probabilities are found by minimizing F with respect to the p_i's. The Kikuchi approximation has been applied to a large variety of lattice models and although it is not good to study the long-range fluctuation effects, like nonclassical critical exponents, it certainly gives a systematic way to improve the predictions for the critical temperature, order parameter, and thermodynamic properties. In the application to Ising or Potts models the number of different configurations is relatively small and it is possible to reduce the number of independent variables by using all the symmetries which imply some degeneracy in the configurations. Thus, for the Ising model in a square lattice the Bethe approximation ($n=2$) requires two independent variables, and Kramers-Wannier ($n=4$, $2^n=16$ configurations) requires at most five independent probabilities. However, in the application to planar rotor models we have a continuum of configurations which cannot be treated separately. Instead we propose to describe the system in terms of the n-sites angular distribution functions $\rho_{ij\cdots l}(\phi,\phi',\ldots,\phi'')$ and to transform the sums in (3.1) into integrals over the angles

$$\sum_i p_i \ln(p_i) \rightarrow \int d\phi \cdots d\phi'' \rho_{ij\cdots l}(\phi,\ldots,\phi'')\ln[\rho_{ij\cdots l}(\phi,\ldots,\phi'')] , \tag{3.2}$$

where we drop additive constants which together with the kinetic energy contribution will only give a shift to the free-energy axis. The distribution functions of the smaller clusters may be obtained by integration of $\rho_{ij\cdots l}(\phi,\ldots,\phi'')$ with respect to some angles and the potential energy may be obtained in terms of the pair potential $U_{ij}(\phi,\phi')$ and the pair distribution function $\rho_{ij}(\phi,\phi')$, so that finally we will get the free energy of the system as a functional of the n-sites distribution function.

IV. THE BETHE APPROXIMATION

The first step beyond the MFA is the Bethe approximation which in our case becomes

$$\begin{aligned}\beta F=&\sum_{(ij)} \int d\phi\, d\phi' \rho_{ij}(\phi,\phi')\ln[\rho_{ij}(\phi,\phi')]\\ &-(\nu-1)\sum_i \int d\phi\, \rho_i(\phi)\ln[\rho_i(\phi)]\\ &+\beta \sum_{(ij)} \int d\phi\, d\phi' \rho_{ij}(\phi,\phi')U_{ij}(\phi,\phi') ,\end{aligned} \tag{4.1}$$

where ν is the coordination number in the lattice, the sums over (ij) run over all the lattice bonds, i.e., pairs of nearest neighbors (which we consider as the only interacting sites), and the sum over i runs over all the lattice sites. The equilibrium pair distribution and free energy is obtained by minimizing F with respect to $\rho_{ij}(\phi,\phi')$. In the orientationally disordered phase all the lattice bonds and sites are equivalent, so that the function $\rho_{ij}(\phi,\phi')$ should only depend on the bond index ij through a trivial shift of the angular origin, to take into account the orientation of the bond. The minimum of F may then be calculated with respect to a single function, say $\rho_{12}(\phi,\phi')$ to represent all the bonds. There are some restrictions on this function: The symmetry of the single site distribution, $\rho_1(\phi)=\rho_2(\phi)$, has to be guaranteed, so that

$$\rho_1(\phi)=\int d\phi'\rho_{12}(\phi,\phi')=\int d\phi'\rho_{12}(\phi',\phi)=\rho_2(\phi) \ . \tag{4.2}$$

Moreover, the function $\rho_{12}(\phi,\phi')$ has to be normalized

$$\int d\phi\, d\phi'\rho_{12}(\phi,\phi')=1 \ . \tag{4.3}$$

These conditions may be introduced through Lagrange multipliers $\xi(\phi)$ and μ so that the Euler-Lagrange equation for the problem is obtained by setting equal to zero the functional derivative of

$$\Omega=\beta F/N-\mu\int d\phi\, d\phi'\rho_{12}(\phi,\phi') - \int d\phi\, \xi(\phi)\int d\phi'[\rho_{12}(\phi,\phi')-\rho_{12}(\phi',\phi)] \ , \tag{4.4}$$

N being the number of lattice sites. The result is

$$\rho_{12}(\phi,\phi')=C[\rho_1(\phi)\rho_2(\phi')]^{(\nu-1)/\nu} \times\frac{a(\phi)}{a(\phi')}\exp[-\beta U_{12}(\phi,\phi')] \ , \tag{4.5}$$

where we have defined $C=\exp(2\mu/\nu)$ and $a(\phi)=\exp[2\xi(\phi)/\nu]$, which should be used to satisfy the conditions (4.2) and (4.3). This leads to the integral equations

$$a(\phi)=\left[\frac{\int d\phi'\rho_1(\phi')^{(\nu-1)/\nu}a(\phi')\exp[-\beta U_{12}(\phi',\phi)]}{\int d\phi'\rho_2(\phi')^{(\nu-1)/\nu}\frac{1}{a(\phi')}\exp[-\beta U_{12}(\phi,\phi')]}\right]^{1/2} , \tag{4.6}$$

and

$$\rho_1(\phi)=\frac{\int d\phi'[\rho_1(\phi)\rho_2(\phi')]^{(\nu-1)/\nu}\frac{a(\phi)}{a(\phi')}\exp[-\beta U_{12}(\phi,\phi')]}{\int d\phi\, d\phi'[\rho_1(\phi)\rho_2(\phi')]^{(\nu-1)/\nu}\frac{a(\phi)}{a(\phi')}\exp[-\beta U_{12}(\phi,\phi')]} , \tag{4.7}$$

which should be solved consistently. This may be done by an iterative process which only involves the one-site functions $a(\phi)$ and $\rho_1(\phi)=\rho_2(\phi)$. Starting from $a(\phi)=1$ and $\rho_1(\phi)=1/2\pi$ the process converges in few iterations. The resulting $a(\phi)$ and $\rho_1(\phi)$ are used in (4.5) and (4.1) to obtain the pair distribution and the free energy. For the study of the ordered phases we have to take into account the existence of different kinds of sites and bonds. The number of independent functions $\rho_{ij}(\phi,\phi')$ in (4.1) depends on the lattice structure. In the square lattice all the bonds are equivalent (with the appropriate rotations and/or reflections) while in the herringbone structure on the triangular lattice there are two different types of bond distributions which should be kept as independent variables. In any case the problem may be solved along the same lines that for the disordered case, with equations similar to (4.5)–(4.7) but reflecting the symmetry of the structure.

A. The ordered phase in the square lattice

In the low-temperature structure shown in Fig. 2 all the nearest-neighbors pair distribution functions are equivalent, e.g., with the index 1,2,3 referring to the positions marked in Fig. 2, we have $\rho_{23}(\phi,\phi')=\rho_{12}(\phi+\pi/2,\phi'+\pi/2)$. However, the relation (4.2) is not valid any more and it should be substituted by

$$\rho_1(\phi)=\int d\phi'\rho_{12}(\phi,\phi') =\int d\phi'\rho_{12}(\phi'+\pi/2,\phi+\pi/2)=\rho_2(\phi+\pi/2) \ , \tag{4.8}$$

this changes the equation for the Lagrange multipliers so that (4.5)–(4.7) with $\nu=4$, become

$$\rho_{12}(\phi,\phi')=C[\rho_1(\phi)\rho_2(\phi')]^{3/4}\frac{a(\phi)}{a(\phi'+\pi/2)}\exp[-\beta U_{12}(\phi,\phi')] \ , \tag{4.9}$$

$$a(\phi)=\left[\frac{\int d\phi'\rho_1(\phi')^{3/4}a(\phi')\exp[-\beta U_{12}(\phi',\phi-\pi/2)]}{\int d\phi'\rho_2(\phi')^{3/4}\frac{1}{a(\phi'+\pi/2)}\exp[-\beta U_{12}(\phi,\phi')]}\right]^{1/2} , \tag{4.10}$$

and

$$\rho_1(\phi)=\frac{\int d\phi'[\rho_1(\phi)\rho_2(\phi')]^{3/4}\frac{a(\phi)}{a(\phi'+\pi/2)}\exp[-\beta U_{12}(\phi,\phi')]}{\int d\phi\, d\phi'[\rho_1(\phi)\rho_2(\phi')]^{3/4}\frac{a(\phi)}{a(\phi'+\pi/2)}\exp[-\beta U_{12}(\phi,\phi')]}\ . \tag{4.11}$$

The numerical solution of these equations is very similar to those of the disordered case, the only difference is that the initial guess for the iterative process should break the symmetry between the two degenerated structures, this is easily done by starting with a one-site orientational distribution with the inhomogeneity associated to one of the structures. At low temperature it is more effective to initialize both $\rho_1(\phi)$ and $a(\phi)$ with the results of a previous run for higher temperature. The disordered phase may also be recovered from the more general Eqs. (4.9)–(4.11), above the critical temperature the iterative process will destroy any asymmetry in the initial guess and converge towards the disordered phase. The critical temperature obtained is $T_c=10.3$ to be compared with the MFA value of 14.8 and the computer simulation between 8.75 and 9, all in the reduced units of the Lennard-Jones interactions. The order parameter below T_c is presented in Fig. 4. It presents good agreement with the simulation for $T\le 6$.

B. The Bethe approximation for the herringbone structure

The application of the Bethe approximation to the herringbone phase in the triangular lattice requires the use of two different functions for the nearest-neighbor pair distribution functions. The pair 12 in Fig. 1 is clearly different from the pairs 23 and 31, the two later are related by appropriate reflections and rotations. The functional minimization of F in (4.1) has to consider $\rho_{12}(\phi,\phi')$ and $\rho_{23}(\phi,\phi')$ as independent functional variables. They have to satisfy the symmetry conditions related to the one-site distribution functions

$$\rho_1(\phi)=\int d\phi'\rho_{12}(\phi,\phi')=\int d\phi'\rho_{12}(\phi',\phi)=\rho_2(\phi)\ , \tag{4.12}$$

$$\begin{aligned}\rho_2(\phi)&=\int d\phi'\rho_{23}(\phi,\phi')\\&=\int d\phi'\rho_{23}(\phi'+\pi/2,\phi+\pi/2)=\rho_3(\phi+\pi/2)\ ,\end{aligned} \tag{4.13}$$

and the normalization condition (4.3), the main difference with the square lattice is that two different Lagrange multipliers $a_{12}(\phi)$ and $a_{23}(\phi)$ are required. The result is again a set of integral equations relating $\rho_1(\phi)$, $a_{12}(\phi)$, and $a_{23}(\phi)$, which have to be solved numerically. The result of this calculation is that the system never stabilizes the ordered phase, even at very low temperature the minimum free energy is given by a phase with order parameter $\eta=0$ [defined as in (2.6)]. This may be analyzed in terms of the two-sites correlation function in the disordered phase given by the Bethe approximation (4.5) at very low temperature. In that case the Boltzmann factor of the pair potential has a very narrow maximum at the orientations giving the minimum of (2.4). At $T=0$ ($\beta\rightarrow\infty$) the potential energy contribution to F in (4.1) is $-K$ per lattice bond, so that $\beta F/N=-3$ K. This is lower than the exact ground-state configuration given by the herringbone structure, with $\beta F/N=-2$ K. So, even at $T=0$ the free energy in Bethe approximation is minimized by the disordered phase. This failure is due to the treatment of the bond distribution as an independent variable in the Bethe approximation so that the frustration effects of triangular lattice are not taken into account. The herringbone structure corresponds to the exact minimum energy configuration, in which all the bonds cannot be satisfied at the same time. In summary, the Bethe approximation provides a good improvement over the MFA for the square lattice, but not for the triangular lattice, for which it fails even to predict the presence of a phase transition. This failure should be regarded as a peculiarity of the herringbone structure in the triangular lattice which responds to the frustration effects created by the interaction potential (2.4) on a triangular lattice. It is then clear the need for a treatment which, within the Kikuchi scheme, considers a larger cluster including three-sites correlations.

V. BEYOND THE BETHE APPROXIMATION

A. The triangular cluster approximation for the herringbone structure

Along the line of the Kikuchi scheme, the next step beyond the Bethe approximation for the herringbone problem is to consider the clusters of three-sites forming the basic triangle in the lattice. We may expect that this is enough to take into account the frustration effects which invalidate the Bethe approximation. This approximation was derived in the original works of Kikuchi[19–21] for the Ising model, in our case the free energy is written as

$$\begin{aligned}\beta F=&\sum_{(ijk)}\int d\phi\, d\phi' d\phi''\rho_{ijk}(\phi,\phi',\phi'')\ln[\rho_{ijk}(\phi,\phi',\phi'')]\\&-\sum_{(ij)}\int d\phi\, d\phi'\rho_{ij}(\phi,\phi')\{\ln[\rho_{ij}(\phi,\phi')-\beta U_{ij}(\phi,\phi')]\}+\sum_{i}\int d\phi\,\rho_i(\phi)\ln[\rho_i(\phi)]\ ,\end{aligned} \tag{5.1}$$

where the function $\rho_{ijk}(\phi,\phi',\phi'')$ refers to the triplets of nearest-neighbors forming the basic triangle on the lattice. The sum over (ijk) runs over all those triangles, the sum over (ij) runs over all the nearest-neighbors pairs, and the sum over i is over all the lattice sites. In the disordered phase all the triangles, bonds, and sites have the same distribution functions, while in the herringbone phase there are two different kinds of sites [although their distribution function $\rho_i(\phi)$ is made similar by a rotation of $\pi/2$], and several kinds of bonds, which may be expressed in terms of two independent functions, $\rho_{12}(\phi)$ and $\rho_{23}(\phi)$ as we saw above. All the triangles may be referred to a single function $\rho_{123}(\phi,\phi',\phi'')$. The free energy F in (5.1) has to be minimized with respect to $\rho_{123}(\phi,\phi',\phi'')$ with the bond and site distributions given by the corresponding integrals. There are some symmetry conditions to be satisfied by $\rho_{123}(\phi,\phi',\phi'')$, with the structure shown in Fig. 1 the bond 12 has to be symmetric

$$\rho_{12}(\phi,\phi')=\int d\phi''\rho_{123}(\phi,\phi',\phi'')=\int d\phi''\rho_{123}(\phi',\phi,\phi'')=\rho_{12}(\phi',\phi) , \tag{5.2}$$

and the bonds 23 and 31 are related by

$$\rho_{31}(\phi,\phi')=\int d\phi''\rho_{123}(\phi',\phi'',\phi)=\int d\phi''\rho_{123}(-\phi'',-\phi,-\phi')=\rho_{23}(-\phi,-\phi') . \tag{5.3}$$

These relations introduce some Lagrange multipliers which are functions of two angles. There is also a constant Lagrange multiplier associated to the normalization of $\rho_{123}(\phi,\phi',\phi'')$. By using the equivalent to (4.4), we may write the Euler-Lagrange equation for this problem as

$$\rho_{123}(\phi,\phi',\phi'')=CY_{12}(\phi,\phi')Y_{23}(\phi',\phi'')Y_{31}(\phi'',\phi) , \tag{5.4}$$

where

$$Y_{ij}(\phi,\phi')=\left[\frac{\rho_{ij}(\phi,\phi')A_{ij}(\phi,\phi')\exp[-\beta U_{ij}(\phi,\phi')]}{[\rho_i(\phi)\rho_j(\phi')]^{1/6}}\right]^{1/2} \tag{5.5}$$

The functions $A_{ij}(\phi,\phi')$ are related to the Lagrange multipliers used to satisfy (5.2) and (5.3) and the C is the normalization constant. These equations may be applied to the disordered phase or to any of the six degenerated herringbone structures; the particular structure is chosen by the relation which should satisfy the functions A_{ij}. For the structure in Fig. 1, $A_{12}(\phi,\phi')=A_{12}(\phi,\phi')^{-1}$ has to be used to guarantee (5.2) and $A_{23}(\phi,\phi')=A_{31}(-\phi,-\phi')^{-1}$, to get (5.3). This leads to a set of coupled integral equations for the functions A_{ij} and ρ_{ij} which may be written as

$$A_{12}(\phi,\phi')=\left[\frac{R_{12}(\phi',\phi)}{R_{12}(\phi,\phi')}\right]^{1/2} ,$$

and

$$A_{23}(\phi,\phi')=\left[\frac{R_{23}(-\phi,-\phi')}{R_{31}(\phi,\phi')}\right]^{1/2} , \tag{5.6}$$

with

$$R_{ij}(\phi,\phi')=\int d\phi''Y_{jk}(\phi',\phi'')Y_{ki}(\phi'',\phi) , \tag{5.7}$$

the index ijk running on cycles over 123, and by integration of (5.4),

$$\rho_{ij}(\phi,\phi')=CY_{ij}(\phi,\phi')R_{ij}(\phi,\phi') . \tag{5.8}$$

Equations (5.5)–(5.8) may be solved iteratively, from an initial guess which breaks the symmetry between the different structures. The calculations are now heavier than for the Bethe approximation, because we have to deal with functions of two variables, and perform the convolutions in (5.7), but it is still possible to carry on the computation in a personal computer. A simplified version of the equations may be obtained for the disordered phase, by taking into account the full symmetry of that case, but this may also be studied with the general equations above, which in that case converge towards a symmetric solution. The result of this calculation with the quadrupole interaction (2.4) is that the phase transition, missing in the Bethe approximation, appears now at a temperature, $T\equiv 1/K=0.998$, must closer to the simulation result,[11] $T=0.775$, than the MFA value $T=2$. However, the transition is continuous (as in the MFA) contrary to the simulation prediction of a first-order phase transition. The order parameter (2.6) as a function of the temperature is shown in Fig. 3, the result is very close to the simulation values up to the first-order transition observed in the latter. As a result of our calculation we also obtain the distribution functions of two and three sites in both the ordered and the disordered phases. In Fig. 5(a) we show the two-sites distribution at a temperature slightly above the phase transition, the maxima are along the line $\phi+\phi'=\pi/2$ as it corresponds to the minimum of the potential energy (2.4) (with $\theta_{ij}=0$) and the minima are along the line $\phi+\phi'=\pi$, which gives the maximum of $U_{ij}(\phi,\phi')$. In the Bethe approximation the shape of $\rho_{ij}(\phi,\phi')$ is mainly given by the Boltzmann factor in (4.5), so that the contour lines will be nearly straight lines with constant $\phi+\phi'$. The modulations along these lines which are observed in the results of the present approximation, are the signature that the frustration effects are taken into account. In Figs. 5(b) and (c) we show the distribution functions for the two different kinds of bonds at $T=0.8$, below the phase transition. The function $\rho_{12}(\phi,\phi')$ has a very narrow maximum at $\phi=\phi'=\pi/4$, as it corresponds to the pair of parallel molecules in the herringbone structure, the shape of the maximum is still extended along the $\phi+\phi'=\pi/2$ line, showing that the main fluctuations will kept the pair distribution along the minimum of the potential energy, as in the disordered case. The function $\rho_{23}(\phi,\phi')$ has a narrow maximum at $\phi=\pi/2$ and $\phi'=3\pi/2$, so that this is the nonsatisfied bond with a potential energy of a half of the minimum value. All this suggests that the Kikuchi approximation is good to describe the short range correlation effects, including the frustrations effects which were missing in the Bethe approximation. However, there are long-range effects, responsible for the change of the transition order, which are still missing in this approximation.

B. The Kramers-Wannier approximation for the square lattice

The next step for the square lattice is the Kramer-Wannier approximation which considers the cluster formed by a basic square on the lattice. The free energy may be written as

$$\beta F=\sum_{(ijkl)}\int d\phi\, d\phi' d\phi'' d\phi''' \rho_{ijkl}(\phi,\phi',\phi'',\phi''')\ln[\rho_{ijkl}(\phi,\phi',\phi'',\phi''')] - \sum_{(ij)}\int d\phi\, d\phi' \rho_{ij}(\phi,\phi')\{\ln[\rho_{ij}(\phi,\phi')]-\beta U_{ij}(\phi,\phi')\} + \sum_{i}\int d\phi\, \rho_i(\phi)\ln[\rho_i(\phi)] , \tag{5.9}$$

as a function of the four-sites distribution function $\rho_{ijkl}(\phi,\phi',\phi'',\phi''')$, from which all the lower-order functions $\rho_{ij}(\phi,\phi'),\rho_i(\phi)$, may be obtained. Both in the ordered and the disordered phases, all the basic squares can be made equivalent by the appropriate rotations, so that we have to consider a single function $\rho_{1234}(\phi,\phi',\phi'',\phi''')$ (with the indices referred to Fig. 2). There are some restrictions on this function which have to be imposed through the corresponding Lagrange multipliers, the normalization and the bond symmetries

$$\rho_{12}(\phi,\phi')=\rho_{23}(\phi+\pi/2,\phi'+\pi/2)=\rho_{34}(\phi,\phi')=\rho_{41}(\phi+\pi/2,\phi'+\pi/2) , \tag{5.10}$$

which require Lagrange multipliers which are functions of two angles. By using the appropriate symmetries we can finally write the Euler-Lagrange equation as

$$\rho_{1234}(\phi,\phi',\phi'',\phi''')=CY_{12}(\phi,\phi')Y_{23}(\phi',\phi'')Y_{34}(\phi'',\phi''')Y_{41}(\phi''',\phi) , \tag{5.11}$$

where C is fixed to satisfy the normalization and

$$Y_{ij}(\phi,\phi')=\left[\frac{\rho_{ij}(\phi,\phi')A_{ij}(\phi,\phi')\exp[-\beta U_{ij}(\phi,\phi')]}{[\rho_i(\phi)\rho_j(\phi')]^{1/4}}\right]^{1/2} , \tag{5.12}$$

where the functions $A_{ij}(\phi,\phi')$ are associated to the Lagrange multipliers used to satisfy (5.10) and have the symmetry

$$A_{12}(\phi,\phi')=\frac{1}{A_{23}(\phi+\pi/2,\phi'+\pi/2)}=A_{34}(\phi,\phi')=\frac{1}{A_{41}(\phi+\pi/2,\phi'+\pi/2)} . \tag{5.13}$$

The two-sites distribution functions may be obtained from $\rho_{1234}(\phi,\phi',\phi'',\phi''')$ by integration over two angles as

$$\rho_{ij}(\phi,\phi')=CY_{ij}(\phi,\phi')T_{ij}(\phi,\phi') ,$$

with

$$T_{ij}(\phi,\phi')=\int d\phi'' d\phi''' Y_{jk}(\phi',\phi'')Y_{kl}(\phi'',\phi''')Y_{li}(\phi''',\phi) , \tag{5.14}$$

with $ijkl$ running on cycles over 1234. The symmetries (5.10) imply the equations

$$A_{ij}(\phi,\phi')=\frac{T_{jk}(\phi+\pi/2,\phi'+\pi/2)}{T_{ij}(\phi,\phi')} , \tag{5.15}$$

for the Lagrange multipliers $A_{ij}(\phi,\phi')$, which together with (5.12)–(5.14) form a set of coupled integral equations for $\rho_{12}(\phi,\phi')$ and $A_{12}(\phi,\phi')$ which may be solved iteratively from an appropriate initial guess. The calculations are similar to the herringbone case, with functions of two variables, but now there are double convolutions (5.14). A simplified version of these equations for the disordered phase may be also obtained, by using the full symmetry of that phase. The results for the order parameter as a function of the temperature are given in Fig. 4 and compared with the previous approximations and with the computer simulation. The agreement with the later is perfect, within the precision of the simulation results, of course a detailed analysis very close to the transition temperature should evidence the failure of any Kikuchi approximation to describe the nonclassical critical behavior, but this is also beyond the accuracy of the computer simulation.[9]

VI. CONCLUSIONS

We have developed an extension of the Kikuchi approximation to study systems with continuous degrees of freedom, applying it to planar rotor models. In this case the method is expressed in terms of approximated forms for the free energy as a functional of the n-sites distribution functions. The conditional functional minimum gives a set of Euler-Lagrange integral equations which may be solved numerically. The methods gives a systematic way to go beyond the mean-field approximation, including the correlations at short distance. In this work we have used this scheme to study the orientational phase

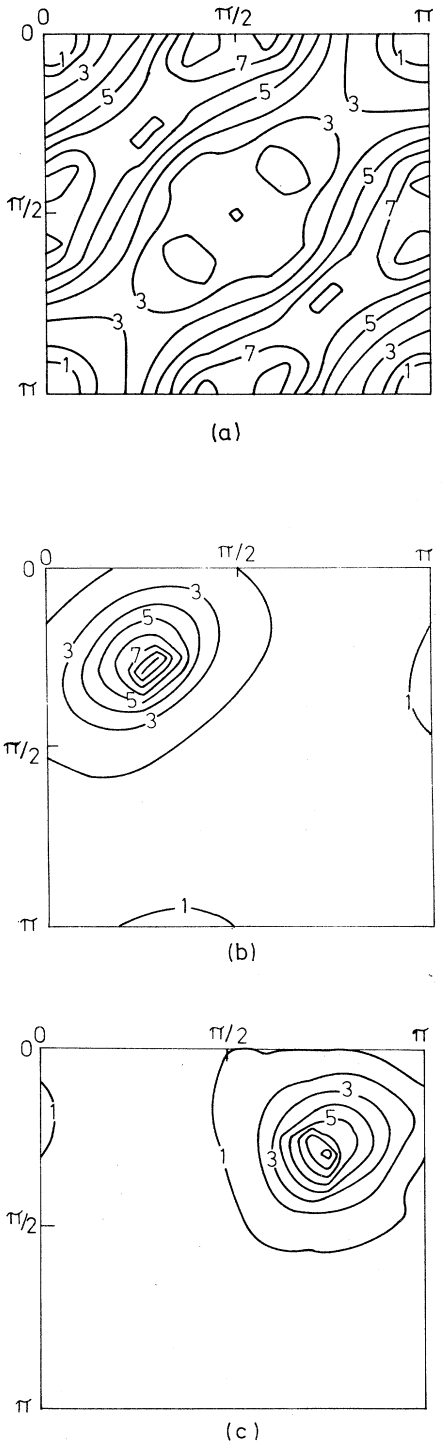

FIG. 5. The two-site distribution functions for the N_2 molecules on graphite in the Kikuchi approximation developed here. (a) is at $T=1$, just above the phase transition with all the bonds being equivalent. The curves correspond to values from 0.008 (level 1) with interval 0.005. (b) and (c) correspond to $T=0.8$ in the herringbone phase, and they represent the two kinds of different bonds. (b) is $\rho_{12}(\phi,\phi')$ and (c) is $\rho_{23}(\phi,\phi')$ referring to the labels in Fig. 1. The curves correspond to values from 0.02 (level 1) with intervals of 0.04.

transitions of adsorbed monolayers of molecules on a crystal surface. We have performed the calculations for two different models which have been used in previous computer simulation: The herringbone structure of quadrupoles on a triangular lattice (to mimic N_2 molecules on graphite) and the site-site Lennard-Jones molecules on a square lattice. There are striking differences between the results obtained for these two systems. For the second one the results within the Kikuchi scheme improve with the degree of the approximation, i.e., with the size of the basic cluster used as a functional variable. The Bethe approximation ($n=2$) compares with the simulation much better than the MFA (which may be regarded as the $n=1$ case), and the Kramers-Wannier approximation (which corresponds to $n=4$) is in perfect agreement with the simulation results (letting aside the nonclassical critical behavior very close to the continuous phase transition). However, for the triangular lattice the use of the Bethe approximation fully destroys the phase transition, which is predicted by the MFA (at a rather inaccurate temperature). This may be understood in terms of the frustration imposed by the quadrupole-quadrupole interaction on the triangular lattice, which is taken into account in the low-temperature herringbone structure, but which are missed by the Bethe approximation in which the distribution function of all the nearest neighbors is optimized independently. The next step along the Kikuchi scheme for this problem uses the three-sites cluster forming a triangle on the lattice, so that the configurational restrictions for the bond structures are considered. This takes back the phase transition and it compares with the simulation result much better than the MFA. However, the predicted phase transition is still continuous (as in the MFA), contrary to the simulation results and to the renormalization-group calculations.[18,23] The first-order character of the phase transition has to be induced by longer ranged correlations which are missing in our calculation. In this respect, the difference between the regular behavior of the square lattice model and the peculiar herringbone system should be produced by the high degeneracy of the ground state, with six equivalent configurations, while the square lattice has only two degenerated states at low temperature. Thus, the herringbone phase should be somehow similar to the six states Potts model (although some qualitative differences have been pointed in Ref. 18), for which it is well known that the fluctuations play an important role in determining the order of the transition.[26] The square lattice problem, being similar to the Ising model does not present these effects.

In summary, the Kikuchi approach may be successfully used to describe the orientational phase transitions of adsorbed molecules, although it may miss some of the peculiarities of the herringbone structure. It is worth comparing our results with the capability of the Kikuchi approximation to describe the q-states Potts model, for which the transition is known to be continuous for $q<4$ and first order for $q>4$. The mean-field approximation gives a first-order transition for any $q>2$, and this is not changed by the use of Bethe or Kikuchi approximation, although they improve the value of the transition temperature. For $2<q<4$, the continuous character of the phase transition is due to the long-range fluctuations and cannot be obtained with a finite cluster approximation. For the herringbone case we have the opposite: The mean-field prediction of a continuous transition contrasts with the real first order character, so that the fluctuations are very important but they are not of infinite range. In this case, one could hope to get the correct result with approximations including the correlations up to a finite distance. However, this is still not the case for the Kikuchi triangle approximation which we have used here.

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