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Nontrivial extension of the two-dimensional Ising model: The *d*-dimensional ''molecular'' model

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A recently proposed molecular model is discussed as a nontrivial extension of the Ising model. For $d=2$ the two models are shown to be equivalent, while for $d>2$ the molecular model describes a peculiar second order transition from an isotropic high-temperature phase to a low-dimensional anisotropic low-temperature state. The general mean-field analysis is compared with the results achieved by a variational Migdal-Kadanoff real space renormalization group method and by standard Monte Carlo sampling for $d=3$. By finite size scaling the critical exponent has been found to be $\nu=0.44\pm0.02$, thus establishing that the molecular model does not belong to the universality class of the Ising model for $d>2$.

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I. INTRODUCTION

Most molecular liquids retain their molecular structure even in the solid phase, where some long range order usually shows up as a consequence of intermolecular interaction. However, in the solid the orientational order of the molecules may change according to the thermodynamic conditions, giving rise to quite rich phase diagrams as recently observed for hydrogen under high pressure [1].

The most studied theoretical models for orientational order describe a molecular interaction that arises from dipole fluctuation, is weak, and gives rise to the observed three-dimensional ordering of most molecular van der Waals solids. The thermodynamic behavior of such weakly interacting systems can be analyzed in terms of $O(3)$ symmetric vectorial models. Conversely, the ''molecular'' model was first motivated [2] by a description of almost covalent molecular solids where the interaction has a covalent main component and is characterized by some level of frustration (since the coordination number for the covalent bond is quite low). In such solids each molecule must choose a few partners and cannot accept any further invitation. The lower is the allowed coordination number, the higher the frustration, which gives rise to the low-dimensional structures observed in polymers (one dimensional) or in iodine [3–5] and hydrogen halides [6,7] (two dimensional). Moreover, we expect that a covalent interaction should show up for all molecular solids under high pressure [8], as the intermolecular distance approaches the intramolecular length, provided that some important structural transition does not occur first (like dissociation).

The ''molecular'' model is a simple frustrated lattice model which can describe some aspects of molecular orientation in covalently bound molecular solids. It consists of a *d*-dimensional hypercubic lattice with a randomly oriented linear molecule at each site. In its simplest version each molecule is allowed to be oriented toward only one of its nearest neighbors. There is an energy gain for any pair of neighbors that are oriented along their common bond (a covalent bond). The existence of preferred orientational axes breaks the rotational invariance of the single molecule, as is likely to occur for any real molecular system under pressure. In fact, even in hydrogen, the broken-symmetry phase transition observed under pressure [9] has recently been shown [10] to be affected by the presence of a crystal field which breaks the isotropy. Quite recently, similar lattice models have been used for describing the diffusion of particles and molecules inside a polymer, and the growth of one-dimensional islands (polymeric chains) [11].

The molecular model has already stimulated some recent work on molecular orientation in nitrogen [12,13] where some experimental data [14] confirm the existence of an orientational disordering temperature in the solid below the melting temperature. However, the molecular systems which seem to be more closely described by the molecular model are the hydrogen halides HX ($X=$F,Cl,Br,I). Their low-temperature structures are known to consist of planar chains of molecules in the condensed state, while a totally disordered structure has been observed with increasing temperature at ambient pressure [6]. The opposite transition, from orientational disorder to an ordered chain structure, has also been reported on increasing pressure [7].

In fact the molecular model undergoes a transition from an high-temperature (or weakly interacting) fully isotropic disordered system to a low-temperature (or strongly interacting) anisotropic low-dimensional broken-symmetry phase. As a consequence of frustration the breaking of symmetry is accompanied by a sort of decomposition of the system into low-dimensional almost independent parts, as observed in solid iodine and hydrogen halides. Such remarkable behavior requires a space dimension $d>2$, while for $d=2$ the model is shown to be equivalent to the exactly solvable two-dimensional Ising model [15]. As shown below by Monte Carlo calculations, in the broken-symmetry phase the system displays the presence of correlated chains of molecules (polymers) which point toward a common direction inside each two-dimensional subset of the lattice (plane). Such planes are weakly correlated in the low-temperature phase, and the system has a two-dimensional behavior even for $d>3$.

In this paper the relevance of the molecular model as a nontrivial extension of the Ising model is pointed out. Thus, apart from the physical motivations, the model is fully examined and the phase transition is described by several methods: mean field, real space renormalization group, and numerical simulations. Exactly solvable models are important for our understanding of more complex systems, and provide a test for approximate techniques. The *d*-dimensional molecular model shares with the Ising model the $d=2$ realization, since their equivalence for $d=2$ has been proved to be exact [2]. In this paper we will focus on the $d=3$ model, but we will take advantage of the existence of an exactly solvable realization for $d=2$. For $d>2$, as the frustration increases, the model shows a very different behavior from the Ising or Potts [16] models. These last show a fully *d*-dimensional broken-symmetry phase while the molecular model is characterized by a low-dimensional ordering inside the planes with negligible correlation among different planes. Moreover, for $d=3$ the molecular model is shown to belong to a different universality class, since its critical exponent ν turns out to be $\nu=0.44\pm0.02$ by finite size scaling. We expect that such a universality class should describe a broad group of isotropic physical systems characterized by a low-dimensional ordering in their low-temperature phase. Such a broad class of phase transitions should be explored by experiments in order to compare with the theoretical predictions for the critical universal properties. In this respect the driving parameter does not need to be the temperature, as the bond strength can be directly modified by a change of pressure in several systems.

This paper is organized as follows. Section II contains a formal definition of the *d*-dimensional molecular model, and a proof of its equivalence to the Ising model for $d=2$. In Sec. III the mean-field solution is discussed for the generic *d*-dimensional model. In Sec. IV a modified variational Migdal-Kadanoff method is presented and its application is discussed for $d=2$ and $d=3$. At variance with a previous calculation [17] which yielded a quite poor result, the variational method is shown to work very well provided that some assumptions are made about the nature of the broken phase. Section V contains the results of a numerical simulation by Monte Carlo sampling, and the numerical estimation of both critical temperature and exponent by finite size scaling. In Sec. VI the main findings are summarized and discussed.

II. MOLECULAR MODEL

Let us consider a *d*-dimensional hypercubic lattice, with a randomly oriented linear molecule at each site. The molecules are supposed to be symmetric with respect to their center of mass which is fixed at the lattice site. Only a discrete number of space orientations are allowed for each molecule: we assume that each of them must point toward one of its $2d$ first neighbor sites. This choice can be justified by the existence of covalent interactions along preferred axes. Then each molecule has *d* different states corresponding to molecular orientation along the hypercube axes (molecules are symmetric). Finally, each couple of first neighbor molecules, when pointing one toward the other, are assumed to gain a bonding energy for their directional covalent bond (they touch each other). As shown in Fig. 1 for $d=2$, bonding in one direction excludes any possible bond along the other $(d-1)$ directions. The coordination number is 2 for any value of *d*, and the frustration increases with increasing *d*.

According to this description we introduce a versor variable $\hat{w}_{\mathbf{r}}$ for each of the *N* sites $\mathbf{r}$ of the lattice, with $\hat{w}_{\mathbf{r}} \in \{\hat{x}_1, \hat{x}_2, \dots, \hat{x}_d\}$ pointing toward one of the *d* hypercube axes x_α. The versors $\hat{x}_\alpha$ are assumed to be orthonormal: $\hat{x}_\alpha \cdot \hat{x}_\gamma = \delta_{\alpha\gamma}$. The partition function is

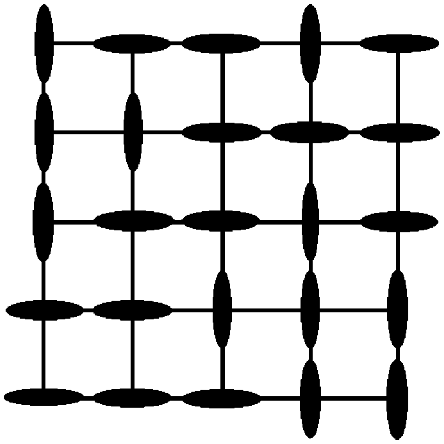

FIG. 1. An allowed configuration for $d=2$.

$$Z=\sum_{\{\hat{w}\}} e^{S}=\sum_{\{\hat{w}\}} \exp\left[4\beta\sum_{\mathbf{r},\alpha}(\hat{w}_{\mathbf{r}}\cdot\hat{x}_\alpha)(\hat{w}_{\mathbf{r}+\hat{x}_\alpha}\cdot\hat{x}_\alpha)\right], \tag{1}$$

where $\{\hat{w}\}$ indicates a sum over all configurations, α runs from 1 to *d*, and the lattice spacing is set to unity. The inverse temperature β (in units of the binding energy) can be negative for a *repulsive* model, but is assumed positive in the molecular context.

The model may be generalized by introducing an external *d*-dimensional vectorial field $\mathbf{h}(\alpha)$ at each link. The dependence on α means that the field differs according to the space direction α of the lattice link that joins the sites. The modified partition function reads

$$Z_h=\sum_{\{\hat{w}\}} e^{S_h}=\sum_{\{\hat{w}\}} \exp\Bigg\{4\beta\sum_{\mathbf{r},\alpha}\big[(\hat{w}_{\mathbf{r}}\cdot\hat{x}_\alpha)(\hat{w}_{\mathbf{r}+\hat{x}_\alpha}\cdot\hat{x}_\alpha) + \mathbf{h}(\alpha)\cdot\hat{w}_{\mathbf{r}}+\mathbf{h}(\alpha)\cdot\hat{w}_{\mathbf{r}+\hat{x}_\alpha}\big]\Bigg\}. \tag{2}$$

It is evident that if the field satisfies the condition

$$\sum_{\alpha} \mathbf{h}(\alpha)=\mathbf{0} \tag{3}$$

then S_h does not depend on $\mathbf{h}$ and $S_h \equiv S$. In such a case the extra degree of freedom provided by $\mathbf{h}$ can be regarded as a sort of internal symmetry of the model. This global symmetry can be made local by allowing the field $\mathbf{h}$ to depend on the site position $\mathbf{r}$. We will only take advantage of the global symmetry in this paper. We notice that such symmetry cannot be seen as a gauge invariance, since in lattice gauge models any gauge change leaves the energy gain unchanged at any link. Here the field $\mathbf{h}$ changes the energy gain of all the links while the whole action is invariant.

Adopting a more compact notation, the partition function reads

$$Z_h=\sum_{\{\hat{w}\}} e^{S_h}=\sum_{\{\hat{w}\}} e^{\Sigma_{r,\alpha}\mathcal{L}(\mathbf{r},\alpha)} \tag{4}$$

where the Lagrangian density $\mathcal{L}$ follows as

$$\mathcal{L}(\mathbf{r},\alpha)=\hat{w}_{\mathbf{r}}^{\dagger}M_{\alpha}(\beta,\mathbf{h})\hat{w}_{\mathbf{r}+\hat{x}_{\alpha}}. \tag{5}$$

Here the canonical d-dimensional column vector representation of R^d is employed with $\hat{x}_1\equiv(1,0,0,\dots)$, $\hat{x}_2\equiv(0,1,0,\dots)$, etc. The $d\times d$ matrix M_α does not depend on the configurations of the system, and entirely characterizes the model.

The global symmetry of the action provides a simple way to show the equivalence between molecular and Ising models for $d=2$. For the two-dimensional lattice the condition (3) is satisfied by the field $\mathbf{h}(1)=h(\hat{x}_1-\hat{x}_2)$, $\mathbf{h}(2)=-\mathbf{h}(1)$. The matrix M_α follows:

$$\begin{aligned} M_1&=\begin{pmatrix} 4\beta(1+2h) & 0 \\ 0 & -8\beta h \end{pmatrix}, \\ M_2&=\begin{pmatrix} -8\beta h & 0 \\ 0 & 4\beta(1+2h) \end{pmatrix}. \end{aligned} \tag{6}$$

Then for $h=-1/4$, $M_1\equiv M_2$, and $\mathcal{L}$ reads

$$L(\mathbf{r},\alpha)=\beta+\hat{w}_{\mathbf{r}}^{\dagger}\begin{pmatrix} \beta & -\beta \\ -\beta & \beta \end{pmatrix}\hat{w}_{\mathbf{r}+\hat{x}_{\alpha}}. \tag{7}$$

Identifying the two-dimensional column versors $\hat{w}$ with spin variables, apart from an inessential factor, Z reduces to the partition function of a two-dimensional Ising model,

$$Z=e^{2\beta N}Z_{Ising}, \tag{8}$$

and is exactly solvable. For $\beta\rightarrow+\infty$ a ground state is approached with all the molecules oriented along the same direction, and with formation of one-dimensional polymeric chains [Fig. 2(a)]; for $\beta\rightarrow-\infty$ the repulsive model approaches a zero-energy (no bonds) ground state analogous to the antiferromagnetic configuration of the Ising model [Fig. 2(b)].

For $d\geqslant 3$ the analogy with the Ising model breaks down, and this is evident from a simple analysis of the ground state configuration. Due to frustration the model has an infinitely degenerate ground state in the thermodynamic limit $N\rightarrow\infty$. For instance, in the case $d=3$, the minimum energy is obtained by orienting all the molecules along a common direction, as for $d=2$. However, the ground state configuration is not unique: the number of molecular bonds does not change if we rotate together all the molecules belonging to an entire layer that is parallel to the original direction of orientation. As a consequence of frustration the total degeneracy is $3(2^{(N^{1/3})})$, and the system could even behave like a glass for the large energy barriers that separate each minimum from the others. The phase diagram is expected to be quite rich, with at least a transition point between the high-temperature disordered phase and an ordered broken-symmetry low-temperature phase.

III. MEAN-FIELD APPROXIMATION

For the generic d-dimensional model, some analytical results can be obtained in mean-field (MF) approximation: neglecting second order fluctuation terms

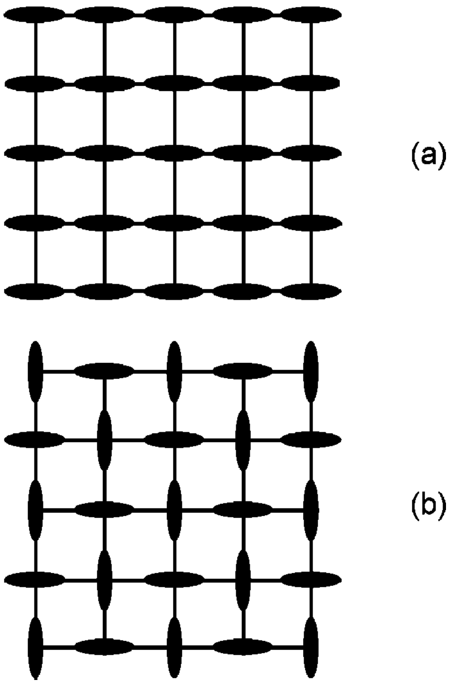

FIG. 2. Ground state configurations for the two-dimensional *attractive* (a) and *repulsive* (b) models.

$$(\hat{w}_{\mathbf{r}}\cdot\hat{x}_\alpha)(\hat{w}_{\mathbf{r}+\hat{x}_\alpha}\cdot\hat{x}_\alpha)\approx\Delta_\alpha(\hat{w}_{\mathbf{r}}\cdot\hat{x}_\alpha)+\Delta_\alpha(\hat{w}_{\mathbf{r}+\hat{x}_\alpha}\cdot\hat{x}_\alpha)-\Delta_\alpha^2, \tag{9}$$

where $\Delta_\alpha=\langle\hat{w}_{\mathbf{r}}\cdot\hat{x}_\alpha\rangle$ is an average over the configurations, and $\Sigma_\alpha\Delta_\alpha=1$ (with the obvious bounds $0\leqslant\Delta_\alpha\leqslant 1$). Here the order parameter Δ_α gives the probability of finding a molecule oriented along the direction of $\hat{x}_\alpha$. The partition function factorizes as

$$Z_{MF}=\left(\sum_\alpha e^{8\beta\Delta_\alpha}\right)^N\exp\left(-4N\beta\sum_\alpha\Delta_\alpha^2\right) \tag{10}$$

and the free energy follows as

$$F_{MF}=-\frac{1}{N\beta}\ln Z_{MF}=4\sum_\alpha\Delta_\alpha^2-\frac{1}{\beta}\ln\left(\sum_\alpha e^{8\beta\Delta_\alpha}\right). \tag{11}$$

The derivative with respect to Δ_μ yields, for the stationary points,

$$\Delta_\mu=\frac{e^{8\beta\Delta_\mu}}{\Sigma_\alpha e^{8\beta\Delta_\alpha}}, \tag{12}$$

which satisfies the condition $\Sigma_\alpha\Delta_\alpha=1$.

In the high-temperature limit $\beta\rightarrow 0$ Eq. (12) has the unique solution $\Delta_\mu=1/d$ which reflects the completely random orientation of molecules. In the opposite limit $\beta\rightarrow\infty$, apart from such a solution, Eq. (12) is satisfied by the broken-symmetry field $\Delta_\mu=1$, $\Delta_\alpha=0$ for $\alpha\neq\mu$, which obviously corresponds to a minimum for F_{MF}. Thus at a critical point $\beta=\beta_c$ the high-temperature solution must become unstable toward a multivalued minimum configuration. The Hessian matrix is easily evaluated at the stationary points by using Eqs. (12) and (11):

$$H_{\mu\nu}=\frac{1}{8}\frac{\partial^2 F_{MF}}{\partial\Delta_\mu\,\partial\Delta_\nu}=\delta_{\mu\nu}(1-8\beta\Delta_\mu)+8\beta\Delta_\mu\Delta_\nu . \quad (13)$$

In the high-temperature phase ($\beta<\beta_c$), inserting $\Delta_\mu=1/d$, the eigenvalue problem

$$\det|H_{\mu\nu}-\lambda\,\delta_{\mu\nu}|=0 \quad (14)$$

yields

$$\left(1-\frac{8\beta}{d}-\lambda\right)^{d-1}(1-\lambda)=0. \quad (15)$$

Thus the Hessian matrix is positive definite if and only if $\lambda=(1-8\beta/d)>0$. Beyond the critical point $\beta=\beta_c=(d/8)$ the solution $\Delta_\mu=1/d$ is not a minimum, and a multivalued minimum configuration shows up. Such a result obviously agrees with the MF prediction for the Ising model, $\beta_{Ising}=1/(2d)$, only for the special dimension $d=2$. For $d>2$ we observe an increase of β_c with d, to be compared to the opposite trend shown by the Ising model. Such behavior may be interpreted in terms of the low dimensionality of the ordered phase. Due to frustration the ordering may occur only on a low-dimensional scale: for instance, in three dimensions each layer has an independent internal ordering. Thus we expect a larger β_c for $d>2$ since the increase of d only introduces larger fluctuations, with each molecule having $(d-2)$ allowed out-of-plane orientations. For $d=3$ the low-temperature phase can be regarded as a quenched disordered superposition of layers that are internally ordered along different in-plane directions. As a consequence of frustration the system shows a two-dimensional character below the critical point while behaving as truly three dimensional in the high-temperature domain. In a MF analysis the neglecting of some fluctuations usually leads to a critical temperature that overestimates the exact value (i.e., the critical inverse temperature β_c is underestimated). For $d=2$ the MF prediction is $\beta_c=0.25$ to be compared with the exact value $\beta_c=0.4407$. For $d=3$ the MF prediction $\beta_c=d/8=0.375$ should provide a lower bound to the unknown exact value.

IV. VARIATIONAL MIGDAL-KADANOFF APPROXIMATION

According to the Migdal-Kadanoff [15,18] method, a link displacement may be introduced by considering that the configurational average of the Lagrangian density $\mathcal{L}$ in Eq. (5) must be translationally invariant,

$$\langle\mathcal{L}(\mathbf{r},\alpha)\rangle=\langle\mathcal{L}(\mathbf{r}',\alpha)\rangle. \quad (16)$$

Then defining

$$\Gamma_\alpha(\mathbf{r},\mathbf{r}')=\mathcal{L}(\mathbf{r},\alpha)-\mathcal{L}(\mathbf{r}',\alpha) \quad (17)$$

we can state that $\langle\Gamma_\alpha(\mathbf{r},\mathbf{r}')\rangle=0$ and the same holds for any sum Γ over an arbitrary set of such terms,

$$\Gamma=\sum\,\Gamma_\alpha(\mathbf{r},\mathbf{r}'). \quad (18)$$

Replacing the action S_h by the sum $S_h+\Gamma$, and assuming that the condition (3) is satisfied (so that we can drop the h in S_h and Z_h which are invariant), the modified partition function Z_Γ can be approximated by cumulant expansion as

$$Z_\Gamma=\sum_{\{\hat{w}\}}e^{S+\Gamma}=Z\langle e^\Gamma\rangle\approx Z[e^{\langle\Gamma\rangle}e^{(\langle\Gamma^2\rangle-\langle\Gamma\rangle^2)/2}]; \quad (19)$$

then, since $\langle\Gamma\rangle=0$,

$$Z_\Gamma\approx Ze^{\langle\Gamma^2\rangle/2}. \quad (20)$$

For instance, the sum in Eq. (18) could run over all $\alpha\neq1$, and for appropriate values of the vectors $\mathbf{r},\mathbf{r}'$, in order to yield a displacement of links that are orthogonal to $\hat{x}_1$. To second order in Γ, the error introduced by link displacement is controlled by the exponential factor in Eq. (20).

Link displacement breaks the internal symmetry of the model, so that Z_Γ is no longer invariant for any field change subject to the condition (3). Thus we may improve the approximation by using the extra freedom in the choice of $\mathbf{h}$ for minimizing the difference between the approximate partition function Z_Γ and the exact Z.

If $\mathbf{h}$ satisfies the condition (3) then $a\mathbf{h}$ satisfies such a condition as well for any choice of the scalar parameter a. Then a special class of invariance transformations can be described by a change of the strength parameter h, assuming the field $\mathbf{h}$ as proportional to h. The following discussion can easily be generalized to other classes of transformations described by more than one parameter. Since Γ is linear in the field $\mathbf{h}$, then in general

$$\Gamma^2=[A+hB]^2, \quad (21)$$

where A and B depend on the configuration of the system. For the average we have

$$\langle\Gamma^2\rangle=\langle A^2\rangle+2h\langle AB\rangle+h^2\langle B^2\rangle. \quad (22)$$

This last equation, inserted in Eq. (20), leads to the following considerations: (i) the coefficient $\langle B^2\rangle$ is positive definite, so the average $\langle\Gamma^2\rangle$ always has a minimum for an appropriate value of $h=h_0$; (ii) in general $\langle AB\rangle\neq0$, so $h_0\neq0$, and a direct use of the Migdal-Kadanoff method on the original model (with no field considered) would yield a larger error; (iii) to the considered order of approximation Z_Γ is stationary at $h=h_0$ and is symmetric around that point, so all the physical properties described by such a partition function must be symmetric with respect to h_0. Moreover, at the same order of approximation, any physical observable f will acquire an unphysical dependence on h, and the symmetry around h_0 requires that $df/dh=0$ for $h=h_0$. Thus we expect that all such observables should be stationary at $h=h_0$, and their best estimate should coincide with the extreme value.

As a consequence of the above statements, the Migdal-Kadanoff method can be improved by taking advantage of the global symmetry of the model. By use of the approximate partition function Z_Γ the critical temperature acquires a nonphysical field dependence, but the best estimate of β_c is its stationary value corresponding to $h=h_0$. The method can be seen as a variational method with the best approximation achieved by the minimum in the inverse temperature.

Such a stationary condition resembles the principle of ‘‘minimum sensitivity’’ introduced by Stevenson [19] for determining the best renormalization parameters whenever the physical amplitudes depend on them (and they should not). In our context, since the critical temperature should not depend on the choice of the field strength h, the best value for such a field is the one that makes the critical temperature less sensitive, i.e., the stationary point. However, according to Eqs. (20) and (22), here we have a formal proof of the stationary condition up to second order of the cumulant expansion.

The method may be used by performing a displacement of links that are orthogonal to $\hat{x}_1$ and then a one-dimensional decimation along the $\alpha=1$ axis. According to such a program let us define the $d\times d$ matrix $t_\alpha(\beta,h)$,

$$e^{\mathcal{L}(\mathbf{r},\alpha)}=\hat{w}_{\mathbf{r}}^{\dagger}t_\alpha(\beta,h)\hat{w}_{\mathbf{r}+\hat{x}_\alpha}. \tag{23}$$

The partition function follows:

$$Z_h=\sum_{\{\hat{w}\}}\prod_{\mathbf{r},\alpha}[\hat{w}_{\mathbf{r}}^{\dagger}t_\alpha(\beta,h)\hat{w}_{\mathbf{r}+\hat{x}_\alpha}]. \tag{24}$$

After link displacement and decimation along the $\alpha=1$ axis, the modified partition function reads

$$Z_\Gamma=\sum_{\{\hat{w}\}}\prod_{\mathbf{r},\alpha}[\hat{w}_{\mathbf{r}}^{\dagger}\tilde{t}_\alpha(\beta,h)\hat{w}_{\mathbf{r}+\hat{x}_\alpha}], \tag{25}$$

where the sum and the product run over the configurations and the sites of the new decimated lattice, and

$$\tilde{t}_1(\beta,h)=[t_1(\beta,h)]^\lambda, \tag{26}$$

$$\tilde{t}_\alpha(\beta,h)=t_\alpha(\lambda\beta,h)\quad \text{for} \quad \alpha\neq 1, \tag{27}$$

with λ being the scale factor between the new and the old lattice. A renormalized inverse temperature $\tilde{\beta}_\alpha$ may be defined according to

$$\tilde{t}_1(\beta,h)=t_1(\tilde{\beta}_1,h), \tag{28}$$

$$\tilde{\beta}_\alpha=\lambda\beta \quad \text{for} \quad \alpha\neq 1. \tag{29}$$

Eventually, the same scaling operation should be performed consecutively for all the directions in order to obtain a hypercubic lattice again. For any finite scaling parameter $\lambda>1$ the renormalized inverse temperature is anisotropic, but an isotropic fixed point can be recovered in the limit $\lambda\to 1$. Equations (28) and (29) define the flow of the renormalized inverse temperature, which changes for different values of the field strength h. Equation (28) has a more explicit aspect in the representation of the common eigenvectors of the matrices t_1 and $\tilde{t}_1=[t_1]^\lambda$. The rank of such matrices is 2 for any space dimension d, as is expected from the definition of the model. Then both the matrices can be represented in terms of the two nonvanishing eigenvalues η_1,η_2, which are functions of β and h. Assuming that $\eta_2\neq 0$ and defining

$$f(\beta,h)=\eta_1/\eta_2, \tag{30}$$

apart from a regular multiplicative factor for the partition function, the scaling equation (28) reads

$$[f(\beta,h)]^\lambda=f(\tilde{\beta}_1,h). \tag{31}$$

For any fixed h, the fixed points follow through the standard Migdal-Kadanoff equations

$$[f(\lambda^{\alpha-1}\beta_\alpha,h)]^\lambda=f(\lambda^{\alpha-d}\beta_\alpha,h). \tag{32}$$

When λ is analytically continued up to 1 such equations give the same isotropic fixed point β_c. In fact, the expansion of Eqs. (32) around $\lambda=1$ implies (up to first order in $\lambda-1$)

$$\ln f(\beta_c,h)=-(d-1)\beta_c\left[\frac{1}{f}\frac{df}{d\beta}\right]_{\beta_c}, \tag{33}$$

which is an implicit equation for β_c. Such equations yield their best estimate of β_c when the strength of the field h is set to the stationary value h_0.

It is instructive to evaluate the stationary point h_0 for the case $d=2$, which is equivalent to the two-dimensional Ising model for the choice $h=h_I=-1/4$, as shown in Sec. II. The h invariance of the exact partition function guarantees the equivalence of the two models for any choice of $h\neq h_I$. However, the mere application of the Migdal-Kadanoff equations (32) to the simple $h=0$ molecular model fails to predict even the existence of the fixed point. On the other hand, for $h=h_I$, the very same recurrence equations (32) are known to predict the exact fixed point in the limit $\lambda\to 1$. That can also be checked by inserting in Eq. (33) the exact expression for the fixed point of the two-dimensional Ising model. Such contradictory results are not surprising since, as already discussed, link displacement breaks the h invariance of the model, and the approximate solution is thus dependent on the choice of h. It can be checked [17] that in this case, by use of Eq. (6), the solution of Eq. (33) is stationary at $h=-1/4=h_I$ for any β. As expected, this is the value required in order to recover the Ising model. Thus the Migdal-Kadanoff approximation gives an improving estimate of the critical point as we move from the *molecular* toward the *Ising* representation (where the approximation yields the exact fixed point). We stress that all such representations are equivalent due to the h invariance of the action.

For $d>2$ no equivalence to standard studied models has been found, and the behavior seems to be dictated by the strong frustration which does not allow a higher coordination number than 2, even for higher dimensions. We will focus on the $d=3$ model in order to compare the results with the Monte Carlo findings of the next section. First of all the fields $\mathbf{h}(\alpha)$ must be defined. An isotropic choice would be

$$\begin{aligned}\mathbf{h}(1)&=h(\hat{x}_1-\tfrac{1}{2}\hat{x}_2-\tfrac{1}{2}\hat{x}_3),\\ \mathbf{h}(2)&=h(\hat{x}_2-\tfrac{1}{2}\hat{x}_3-\tfrac{1}{2}\hat{x}_1),\\ \mathbf{h}(3)&=h(\hat{x}_3-\tfrac{1}{2}\hat{x}_1-\tfrac{1}{2}\hat{x}_2).\end{aligned} \tag{34}$$

Now Eq. (30) reads

$$f(\beta,h)=\frac{\eta_1}{\eta_2}=\frac{(bx^3+2)-\sqrt{(bx^3-2)^2+8x^3}}{(bx^3+2)+\sqrt{(bx^3-2)^2+8x^3}}, \tag{35}$$

where $b=\exp(4\beta)$ and $x=\exp(4\beta h)$. Differentiating with respect to x we find that the derivative of f vanishes only for

$$h=h_m=-\frac{1}{3}+\frac{1}{12\beta}\ln 2, \tag{36}$$

which depends on β. For such a field strength $h_m(\beta)$ the ratio between the eigenvalues reduces to

$$f(\beta,h_m)=\tanh(\beta), \tag{37}$$

which is exactly the same expression holding for the Ising model [15]. However, we must point out that in such a case h_m is not the stationary point h_0. Since h_m depends on β, the vanishing of the derivative of f does not imply that the solution of Eq. (33) is stationary. In fact, for $d=3$, the choice $h=h_m$ yields the known [17] poor result $\beta_c=0.1398$ by insertion of Eq. (37) in Eq. (33). On the other hand, by insertion of the general expression for f, Eq. (35), the scaling equation (33) can be numerically solved for β_c as a function of h. At the stationary point β_c has a minimum, and thus the variational method yields an even worse prediction ($\beta_c \approx 0.12$ at the stationary point). These shortcomings show that the isotropic $d=3$ variational method does not suit the molecular model. Actually, both MF and Monte Carlo methods predict a larger β_c and, as pointed out at the end of the previous section, the exact β_c should be larger than the MF prediction $\beta_{MF}=0.375$.

We could have guessed such a disagreement since we are using an isotropic version of the variational Migdal-Kadanoff method for a system that is not isotropic in its ordered phase. At the transition point the system chooses a direction, as is usual for any symmetry breaking mechanism. However, at variance with the usual models, in the ordered phase the correlation length cannot be isotropic: order occurs inside all layers that are orthogonal to the chosen direction, while there is a negligible correlation along that direction. It would be more sensible to describe the ordering that takes place inside a single layer, thus neglecting any correlation among different layers. Inside each layer the correlation length is isotropic, and the $d=2$ variational Migdal-Kadanoff method should give a better description of the transition. The same argument should hold for the generic d-dimensional molecular model. Moreover, despite the cost of this further approximation, the Migdal-Kadanoff method is known to work better for lower dimensions, and a $d=2$ variational method could provide a tool for describing the generic d-dimensional molecular model even for $d>3$.

A $d=2$ version of the variational method requires a different choice for the fields $\mathbf{h}(\alpha)$ which do not need to be isotropic any more. Let us take the same field we used in Sec. II, namely, $\mathbf{h}(1)=h(\hat{x}_1-\hat{x}_2)$, $\mathbf{h}(2)=-\mathbf{h}(1)$, and $\mathbf{h}(3)=\mathbf{0}$. The matrix t_1 is

$$t_1=\begin{pmatrix} e^{4\beta+8\beta h} & 1 & e^{4\beta h} \\ 1 & e^{-8\beta h} & e^{-4\beta h} \\ e^{4\beta h} & e^{-4\beta h} & 1 \end{pmatrix}. \tag{38}$$

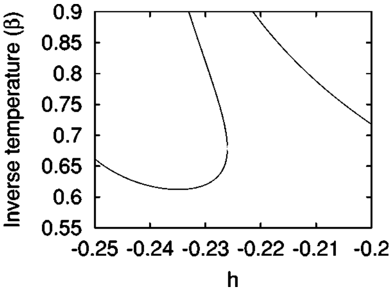

FIG. 3. Numerical solutions of the two-dimensional Migdal-Kadanoff equations for a single layer of the three-dimensional molecular model. The critical temperature β is reported as a function of the field strength h. The stationary point is at $h=h_0=-0.2349$ where $\beta=\beta_c=0.6122$. For $h>-0.226$ there is no physical solution.

Notice that this is a 3×3 matrix since we are using the $d=2$ method but we are still dealing with a $d=3$ molecular model. The two matrices t_1 and t_2 share the same eigenvalues. Their ratio is

$$f(\beta,h)=\frac{(bx^2+1+1/x^2)-\sqrt{(bx^2-1-1/x^2)^2+4(1+x^2)}}{(bx^2+1+1/x^2)+\sqrt{(bx^2-1-1/x^2)^2+4(1+x^2)}} \tag{39}$$

Inserting this result in the scaling equation (33) evaluated at $d=2$ yields an implicit equation for β_c versus h. The numerical solutions are reported in Fig. 3. They share most of the features of the $d=2$ molecular model: (i) There are several solutions but there is no repulsive fixed point for $h=0$; (ii) the physical solution starts at a negative h which in this case is $h\approx-0.226$; (iii) the physical solution has just one stationary point h_0 where β_c reaches its minimum value. However, in this case the stationary point is at $h_0=-0.2349$ where $\beta_c=0.6122$. This best estimate of the critical point is not too far from the finite size scaling prediction of the next section, $\beta_c=0.53$. The result is encouraging, and gives us more confidence in our understanding of the physics described by the molecular model. Strictly speaking, this $d=2$ variational method describes the transition occurring in a single layer of molecules. However, at variance with the $d=2$ molecular model, each molecule is now allowed to be oriented along three different axes (two in-plane and one out-of-plane orientations). Thus this reasonable prediction for β_c could be regarded as an indirect proof that the correlation between two different layers is negligible, and that in the ordered phase the system behaves as a truly two-dimensional one.

V. MONTE CARLO SAMPLING

In order to check the prediction achieved by different approximate methods it would be desirable to have an accurate numerical estimate of the critical temperature. That can easily be obtained by finite size scaling. Moreover, according to the scaling hypothesis, the critical exponent ν can be extracted from the numerical data with good accuracy.

Cubic samples $N\times N\times N$ with $N=10,15,20,25,30$ have been considered. All the averages have been evaluated by Monte Carlo sampling with no special boundary conditions.

In this model any ordering is characterized by the presence of some degree of correlation along one-dimensional chains of molecules. For $d=3$ there are $3\times N\times N$ different chains in each sample. Each chain may be labeled by its direction $\alpha=1,2,3$ and by two integer coordinates I_1,I_2 running over a lattice layer orthogonal to the axis $\hat{x}_\alpha$. For any chain we define an order parameter

$$m(\alpha,I_1,I_2)=\frac{1}{N}\sum_{J_\alpha=1}^{N}[\hat{w}(J_\alpha,I_1,I_2)\cdot\hat{x}_\alpha], \tag{40}$$

where $\hat{w}(J_\alpha,I_1,I_2)$ is the versor $\hat{w}_{\mathbf{r}}$ at the chain site $\mathbf{r}$ whose integer coordinates are determined by J_α along the chain and by the couple I_1,I_2 in the orthogonal directions. If there is no correlation at all ($\beta\rightarrow 0$) then $m(\alpha,I_1,I_2)\approx 1/3$ for any chain in the sample. By averaging over all the chains of each sample and over all the configurations, we obtain $\langle m\rangle=1/3$. For large N, according to the central limit theorem, in this statistical ensemble the variable m follows a Gaussian distribution centered at its average value. In the opposite limit ($\beta\rightarrow\infty$) one-third of the chains in each sample have a large $m\approx 1$, while $m\approx 0$ for two-thirds of them. Since any intermediate value of m is unlikely, the statistical distribution of m can be regarded as the superposition of two different peaked distributions centered at $m=0$ and $m=1$. If N is large enough, and for a large number of configurations, such distributions are very peaked and their width is very small. Actually, just below the critical point the Gaussian distribution already splits into a double-peak distribution. We can monitor the transition by use of the new variable γ,

$$\gamma=\frac{m-\langle m\rangle}{\sqrt{\langle m^2\rangle-\langle m\rangle^2}}. \tag{41}$$

By its definition the configurational average of γ is vanishing $\langle\gamma\rangle=0$ and the second moment $\langle\gamma^2\rangle=1$. The variable γ differs from m only by a shift and a rescaling; thus the statistical distribution for γ follows the same trend already discussed for m. However, the fourth moment $s=\langle\gamma^4\rangle$ is now strongly dependent on the number of peaks characterizing the statistical distribution. For a single Gaussian $s=3$ exactly. Below the critical temperature the distribution splits. In the thermodynamic limit $N\rightarrow\infty$ the width of each peak vanishes, while the two peaks separate by a finite quantity. For instance, assume that just below the critical point one-third of the chains yield $m\approx 1/3+\epsilon$ where ϵ is a very small increase in the chain correlation that breaks the symmetry of the sample. The other two-thirds of the chains must yield $m\approx 1/3-\epsilon/2$ since by its definition $\langle m\rangle=1/3$ exactly. Neglecting the width of the peaks we may approximate the statistical distribution for m as the superposition of two δ functions with weight factors

$$P(m)=\frac{2}{3}\delta\left(m-\frac{1}{3}+\frac{\epsilon}{2}\right)+\frac{1}{3}\delta\left(m-\frac{1}{3}-\epsilon\right). \tag{42}$$

By use of such an approximate statistical distribution the calculation of the fourth moment $s=\langle\gamma^4\rangle$ is straightforward and gives $s=1.5$ for any ϵ, no matter how small. This is one-half of the single Gaussian value. Thus in the thermodynamic limit we expect that the fourth moment s should behave like a step function with constant values $s=3$ and $s=1.5$, respectively, above and below the critical temperature, and a sharp jump at the critical point. For finite size samples the fourth moment is expected to be continuous across the transition, but according to the scaling hypothesis the critical value should not depend on the sample size if we assume a one-parameter scaling law across the critical point:

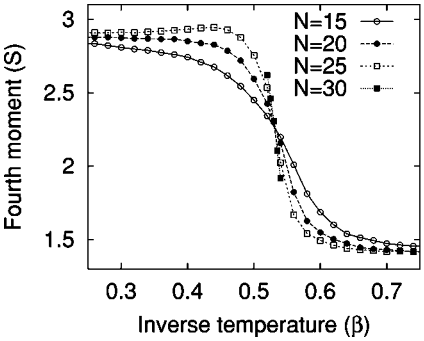

FIG. 4. The fourth moment $s=\langle\gamma^4\rangle$ versus the inverse temperature β for $N=15,20,25,30$. For $N=30$ only a few points around the critical point have been evaluated. The curves are a linear interpolation between points and are reported as a guide for the eye.

$$s=s(L/\xi(\beta)), \tag{43}$$

where L is here the sample length, and ξ is the correlation length, which is a function of temperature. According to such a scaling law $s=s(0)$ at the critical point for any L.

We have checked this prediction by standard Monte Carlo sampling. For any fixed sample size, we have taken a completely random initial configuration, and thermalized it at a very high temperature ($\beta\approx 0.02$) by 5×10^4 complete sweeps. The temperature is then decreased by steps of $\Delta\beta=0.02$. At each step a good thermalization is achieved by 8×10^3 complete sweeps, and then the averages are evaluated over the successive 2×10^3 sweeps. Once a sufficiently low temperature is reached ($\beta\approx 1$), the process is reversed and the temperature increased up to the initial value. We have checked that the hysteresis is small in the whole range of temperature considered. Moreover, the small differences observed in going up and down give a measure of the errors on the configurational averages that have been approximated by the mean values. The fourth moment s is reported in Fig. 4 for $N=15,20,25,30$. All the curves cross at the same point $\beta_c=0.53\pm 0.01$ as predicted by the one-parameter scaling hypothesis. Moreover, for very large or very small temperatures the correlation length becomes very small and the fourth moment s should approach its thermodynamic-limit value $s\rightarrow s(\infty)$, which is expected to be $s(\infty)=3$ at high temperature and $s(\infty)=1.5$ at low temperature. As shown in Fig. 4 the measured s approaches such limits far away from the critical point.

According to the usual definition of the critical exponent,

$$\xi\sim\frac{1}{(\beta-\beta_c)^\nu}, \tag{44}$$

the scaling equation (43) allows for an accurate estimate of its value: linearizing s around the critical point yields

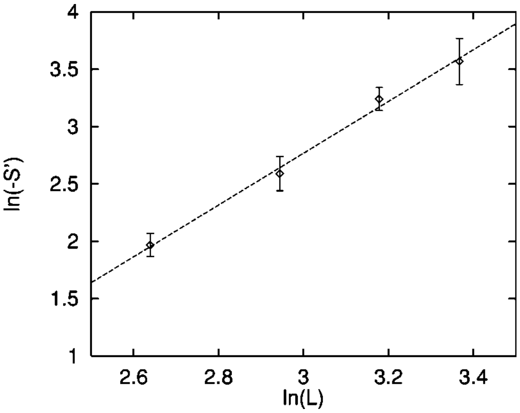

FIG. 5. Linear fit for the critical exponent according to Eq. (45). The points have been evaluated for $N=15,20,25,30$.

$$\ln L=\nu \ln|s'(\beta_c)|+\text{const}, \tag{45}$$

where $s'(\beta_c)$ is the derivative of s as a function of β. In Fig. 5 a best fit by the least squares method is reported yielding $\nu=0.44\pm 0.02$. Here the error is the statistical one coming from the linear fit.

Of course this Monte Carlo calculation is far from being the best numerical simulation that can be achieved by modern computing machines. Our sample sizes are relatively small and a slight shift of the critical point cannot be ruled out. However, the estimates for the critical temperature and exponent are accurate enough for a comparison with experimental findings and for a check of the analytical results of the previous sections, and that is just what we needed at the moment. More refined calculations are called for in order to establish more accurate predictions.

VI. DISCUSSION

Here we summarize and discuss the main findings of the previous sections. According to mean-field calculations and finite size scaling the three-dimensional molecular model has a second order continuous transition from an isotropic disordered high-temperature phase to an anisotropic two-dimensional ordered low-temperature phase. The $d=3$ realization of the model is the one that more closely describes real molecular systems. For this reason the $d=3$ model has been studied by the variational Migdal-Kadanoff method and by numerical Monte Carlo simulation. The transition point is characterized by a diverging correlation length according to the one-parameter scaling hypothesis, which seems to be fulfilled as shown by the data of the previous section. On the other hand, the $d=2$ model is special in itself for its equivalence to the two-dimensional Ising model, and for the existence of exact analytical results. Thus the $d=3$ model can be seen as a nontrivial extension to higher dimension of the two-dimensional Ising model. Here ‘‘nontrivial’’ means that the $d=3$ molecular model does not belong to the universality classes of the standard $d=3$ extensions of the Ising model (three-dimensional Ising and Potts models). The difference is evident from a comparison of the ground state $T=0$ configurations: highly degenerate and anisotropic in the molecular model (with a two-dimensional character even for higher dimensions); with a small degeneration and fully isotropic in the Potts models (including the Ising one as a special case). By considering the two-dimensional character of the low-temperature phase, the molecular model could be thought to belong to the universality class of the simple two-dimensional Ising or three-state Potts models. However, in the high-temperature unbroken-symmetry phase the molecular model is fully isotropic and has a three-dimensional character.

A formal proof of such statements comes from a comparison of the critical exponents. For the three-dimensional molecular model the finite size scaling calculation of the previous section yields $\nu=0.44$ to be compared to the two-dimensional two-state (Ising) and three-state Potts models, whose exponents are $\nu=1$ and $\nu=0.83$, respectively [15], to the three-dimensional Ising model whose exponent is $\nu=0.64$ [15], and to the three-state three-dimensional Potts model which is known to undergo a first-order transition [20,21].

The molecular model belongs to a universality class characterized by a sort of dimensional transmutation. In fact, order occurs in chains that are arranged in layers, and the disorder-order transition requires a decrease of the effective dimensionality of the system. In the ordered phase the molecules are correlated inside layers, but there is no correlation between molecules that belong to different layers. This understanding of the ordered phase is in agreement with our finding that the two-dimensional Migdal-Kadanoff variational method for a single layer yields a better prediction for the critical point than the three-dimensional method applied to the whole lattice. On the other hand, the very same two-dimensional variational method provides a convenient analytical tool for describing the generic d-dimensional molecular model by a straightforward generalization.

From such arguments the critical point has been given an upper bound by the variational method, which yields $\beta_c=0.61$, while a lower bound is usually provided by mean-field analysis, which in this $d=3$ case gives $\beta_c=0.375$. The numerical estimate of the previous section $\beta_c=0.53$ fits nicely inside such bounds.

Having discussed some formal aspects of the molecular model and a few approximate methods that throw some light on its phase transition, we would like to make contact with the phenomenology. Our main finding—that the order-disorder transition described by the model belongs to a different universality class—deserves some experimental test. Transitions of this kind have been observed in several systems, as discussed in the Introduction. Since the critical properties should not depend on the microscopic details of the system we expect that the simple molecular model could predict the correct critical exponent of real orientational transitions occurring in complex real molecular systems especially under pressure. New experiments are called for in order to test such ideas and explore this broad universality class.

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