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Low-temperature orientational glass transition in molecular C_{60}

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We propose a model for the description of the low-temperature orientational glass transition in solid molecular C_{60} using the basic concepts and methods of spin-glass and multipole-glass theory. The physical origin of the frustration and the disorder is discussed. We obtain coexistence of orientational and glass orders in the glass phase and a broad maximum of the orientational specific heat in agreement with experimental data. The orientational ordering under pressure is discussed.

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I. INTRODUCTION

Among a lot of interesting features of solid molecular C_{60} (see, e.g., for reviews, Refs. 1–4 and the references therein), one of the most intriguing is the low-temperature phase transition into an orientational glass phase with a partly conserved orientational long-range order.[1–11] At this phase transition, the relaxation times increase and there is a broad maximum in the temperature dependence of the corresponding orientational specific heat contribution.

Almost immediately after the experimental discovery of the orientational glass phase in C_{60}, there appeared a purely phenomenological theory describing the transition as a "freezing" of an ensemble of two-level systems (see, e.g., Refs. 5 and 11). However, as far as we know, the microscopic explanation of the behavior of physical characteristics of the phenomena is absent till now. That is why we propose to consider the problem from a quite different point of view.

It is possible to imagine an analogy (although hidden) between the orientational glass state of molecular C_{60} and that of traditional spin glasses or, to more extent, orientational glass states in dilute systems of nonspherical molecules. The good candidates for such an analogy are ortho-para hydrogen mixtures and N_2-Ar mixture. So, the aim of this paper is to describe the orientational glass in C_{60} on a microscopic level in the spirit of spin-glass theory exploiting for this purpose our successful experience in the quadrupolar glass theory of ortho-para hydrogen given in Refs. 12 and 13, from one side, and in the microscopic description of the 260 K orientational ordering transition in molecular C_{60} given in the Ref. 14, on the other side. The main physical problem to be solved on this way is the following: how the states analogous to spin or moment bearing states (as orthomolecules of H_2) and that without moment (as paramolecules) can be identified in the case of "identical" C_{60} molecules. This separation in our approach is based on the consideration of the mutual molecule orientation types and a spin-glass-like model built with the appropriate linear combination of spherical harmonics playing the role of spins. (The large number of the nearest neighbor bonds allows for the spin-glass theory description of the problem.) Applying the methods of the spin-glass theory to the proposed model, we then obtain the results which are in agreement with the experiment: the coexistence of glass and long-range orders, the broad maximum in the specific heat temperature dependence, and the correct pressure and temperature dependences of the ratio of P and H states. As a by-product, we propose a model potential which is able to describe the physical properties of solid molecular C_{60} in a wide range of temperatures and pressures.

As is established in a number of experiments, C_{60} crystallizes in a face centered cubic (fcc) structure. At ambient temperature, the molecules rotate almost freely with centers on the fcc lattice sites, so that the space group is $Fm\bar{3}m$. When the temperature decreases to $T_c \approx 260$ K, the first order orientational phase transition takes place: The sites of the initial fcc lattice become divided between four simple cubic sublattices with its own preferable molecular orientation in each sublattice. The broken symmetry group is $Pa\bar{3}$.[15,16] Molecule C_{60} is the result of the cutting off the vertices of an icosahedron. As a result of this cutting procedure, 20 triangles transform into the hexagons and 12 (cut) vertices into 12 pentagons. The neutron-diffraction experiments have shown that the orientations in the ordered state are so that the electron-rich regions (the interpentagon double bonds) face the electron-deficient regions of the neighboring C_{60} molecule: the centers of pentagons or the centers of hexagons. The coexistence of these two configurations takes the form of the dynamical disorder. Every molecule reorientates rapidly between the two preferred orientations. The ratio of the number of molecules in those two states is about $\rho_P/\rho_H = 60/40$ at the phase transition temperature and it increases when the temperature decreases.

Solid C_{60} at $T_g = 90$ K undergoes the orientational glass transition when no reorientational motion can usually be detected. Below T_g, the fraction of more favorable orientation is essentially frozen at the value of $\approx 84\%$. This partial static orientational disorder persists down to very low temperatures. The thermal energy is too small compared with the large energy barrier (250–300 meV) that separated the two orientational configurations for further reorientation to be possible.[1,2,5–8,11,17–19]

II. FORMALISM OF ORIENTATIONAL ORDERING

Let us first note briefly the construction of the model orientational potential introduced in Ref. 14. The general form of the angular part of the largely used intermolecular potential[20] is

$$\Phi_{ij}(\omega_i,\omega_j) = \sum_{l;\nu,\tau} C^l_{\nu,\tau}(\omega_{ij}) u_{l\nu}(\omega_i) u_{l\tau}(\omega_j), \qquad (1)$$

where $l=6,10,12,16,18,\ldots$, according to the icosahedral molecular symmetry I_h,[21] ω_i are the angles describing the orientation of the molecule on site i [for example, Euler angles], ω_{ij} describes the orientation of the bond, and here u are harmonics of some kind.

However, we do not use the multipole series *per se* but simplify the problem and develop a model orientational interaction exploiting the symmetry properties to maximal extend. We follow the main ideas of Refs. 6, 22, and 23 and use the restricted number of allowed orientations instead of free continuous rotations. We take into account in the energy, Eq. (1), only the orientations with pentagons, hexagons, or double bonds directed toward 12 nearest neighbors in fcc lattice. It is important that the C_{60} molecule is constructed in such a way that if six of its 12 pentagons (or 6 of its 20 hexagons) face six nearest neighbor double bonds (P and H states), then six of its 30 interpentagon double bonds face the remaining six nearest neighbors. Now, the energy matrix elements can take only three values: J_0—the energy of the general mutual position, J_P—pentagon versus double bond, and J_H—hexagon versus double bond. These energies of our model can be compared with those calculated in Refs. 17 and 24–26 as functions of the angular displacements of the molecule at (0,0,0). Following Ref. 22 and putting $J_0=0$, we obtain from the Fig. 2b of Ref. 17 the following: $J_P=-300$ K and $J_H=-110$ K. So, only allowed linear combinations of $u_{l\nu}$ enter the energy. The theoretical curve in Ref. 17 makes no difference between the number l of harmonics and describes the effect of all of them. In the framework of our model calculation, it is possible to build up the allowed functions using only the harmonics with $l=6$; we need only their transformation properties. However, the coefficients J_P and J_H are not some of $C^6_{\nu,\tau}$ given in Eq. (1) but effectively take into account higher order terms.

The allowed linear combinations of $u_{l\nu}$ are just the P and H. Now, we construct the corresponding functions $P_n(\omega_i)$ and $H_n(\omega_i)$ explicitly in terms of the cubic harmonics $K_m \equiv K_{6,m}$, $m=1,2,\ldots,13$. Here, n is the number of the sublattices with the site i and ω are the corresponding angles. The states $P_i(H_i)$ have six pentagons (hexagons) and six double bonds directed toward the 12 nearest neighbors along different [100] axes. All functions P_i and H_i are the sums of K_m, invariant under the icosahedral symmetry of the molecule (i.e., belonging to the A_{1g} representation of the icosahedral group I_h) if icosahedrons are naturally oriented in one of the eight properly chosen coordinate systems. If we choose the z axis along the fivefold icosahedral axis, the initial function $A_1(\omega)$ can be written as[27]

$$A_1(\omega) = a_0\{Y_{6,0}(\omega) + a_5[Y_{6,5}(\omega) - Y_{6,-5}(\omega)]\}, \qquad (2)$$

where $Y_{lm}(\omega)$ are spherical harmonics, $a_0=-\sqrt{11}/5$, and $a_5=-\sqrt{7}/\sqrt{11}$. After rotating the icosahedron clockwise about the y axis by the angle $\phi=58.282\,53$, it occurs in the position with its three twofold axes parallel to the Cartesian axes. This is the so-called standard B orientation.[28] $P_1(\omega)$ describes the molecule rotated from the standard orientation B about the [111] axis through the angle $\psi=97.761\,25°$ (clockwise). The three fivefold icosahedron axes after the rotation occur to be directed along $[\mp 1,0,\mp 1]$, $[0,\mp 1,\mp 1]$, $[\mp 1,\mp 1,0]$, that is, in the directions of the six nearest neighbors. The functions $P_2(\omega)$, $P_3(\omega)$, and $P_4(\omega)$ are obtained from $P_1(\omega)$ by the subsequent counterclockwise rotations of the molecule by 90° around the z axes. In an analogous way, one can obtain the functions $H_i(\omega)$, with the only difference that now $\psi'=37.761\,25°$. If written in the "standard" coordinate frame with the Cartesian axes along the cube sides, these functions have the following explicit form:

$$P_1(\omega) = \alpha_P K_1(\omega) + \beta_P[K_8(\omega) + K_9(\omega) + K_{10}(\omega)] + \gamma_P[K_{11}(\omega) + K_{12}(\omega) + K_{13}(\omega)], \qquad (3)$$

$$H_1(\omega) = \alpha_H K_1(\omega) + \beta_H[K_8(\omega) + K_9(\omega) + K_{10}(\omega)] + \gamma_H[K_{11}(\omega) + K_{12}(\omega) + K_{13}(\omega)]. \qquad (4)$$

Using the values of a_0, a_5, and the elements of the matrices of the rotations mentioned above, we obtain $\alpha_P=-0.388\,66$, $\beta_P=0.314\,86$, $\gamma_P=-0.428\,77$, $\alpha_H=0.465\,88$, $\beta_H=0.377\,40$, and $\gamma_H=0.344\,32$. The functions P and H are normalized to unity. We use here the notations for cubic harmonics from Ref. 21.

Now let us investigate the orientational ordering (at $T_c \approx 260$ K) using the bifurcation approach.[14] The large number of nearest neighbor bonds allows for the mean-field description of the problem. From the first equation of the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy for the equilibrium orientational distribution functions or by minimizing the orientational free energy, one can obtain the following nonlinear integral equation:[29]

$$g_i(\omega_i) + \frac{1}{kT}\sum_{i\neq j} G_j \int d\omega_i \Phi_{ij}(\omega_i,\omega_j) e^{g_i(\omega_j)} = 0, \qquad (5)$$

where ω_i are the angles describing the orientation of the molecule, $g_i(\omega_i)=\ln\left[\frac{f_i(\omega_i)}{G_i}\right]$, $f_i(\omega_i)$ is the one-particle orientational distribution function for the molecule on the site i, and G_i are the normalization constants. We consider the molecules fixed on the rigid lattice sites. In the neighborhood of the bifurcation point T_b, we have a linearized over $\mu=1/T-1/T_b$ system containing the equation

$$h_1(\omega) + \frac{1}{4\pi T}\int d\omega'[B(\omega,\omega')h_2(\omega') + A(\omega,\omega')h_3(\omega') + D(\omega,\omega')h_4(\omega')] = 0, \qquad (6)$$

and analogous for the other three sublattices, where $g_i(\omega) = \mu h_i(\omega) + \cdots$.

Here, $A(\omega,\omega')$, $B(\omega,\omega')$, and $D(\omega,\omega')$ are the sums of interactions over the nearest neighbors in the sublattices. For example, the sum in the plane perpendicular to the x axis can be written explicitly in the form

$$\begin{aligned}D(\omega,\omega') = 2(&\{[P_1(\omega)+P_4(\omega)]J_P+[H_1(\omega)+H_4(\omega)]J_H\}[P_2(\omega')+P_3(\omega')+H_2(\omega')+H_3(\omega')] \\ &+[P_2(\omega)+P_3(\omega)+H_2(\omega)+H_3(\omega)]\{[P_1(\omega')+P_4(\omega')]J_P+[H_1(\omega')+H_4(\omega')]J_H\}+\{[P_2(\omega)+P_3(\omega)]J_P \\ &+[H_2(\omega)+H_3(\omega)]J_H\}[P_1(\omega')+P_4(\omega')+H_1(\omega')+H_4(\omega')]+[P_1(\omega)+P_4(\omega)+H_1(\omega)+H_4(\omega)]\{[P_2(\omega') \\ &+P_3(\omega')]J_P+[H_2(\omega')+H_3(\omega')]J_H\}). \qquad (7)\end{aligned}$$

The functions $h_i(\omega)$ transform one into another under the action of the cubic group rotation elements which leave the fcc lattice invariant. At the bifurcation point, $T_b>0$, a nontrivial solution with the broken symmetry appears; it corresponds to the orientationally ordered phase. With the given above coefficients, J_P, J_H, α, β, and γ, we obtain $T_b=275$ K ($T_c^{(\exp)}\approx 260$ K) and the coefficients a, b, and c in

$$h_1(\omega)=aP_1(\omega)+bH_1(\omega)+cK_1(\omega), \qquad (8)$$

$$h_2(\omega)=aP_3(\omega)+bH_3(\omega)+cK_1(\omega), \qquad (9)$$

$$h_3(\omega)=aP_4(\omega)+bH_4(\omega)+cK_1(\omega), \qquad (10)$$

$$h_4(\omega)=aP_2(\omega)+bH_2(\omega)+cK_1(\omega), \qquad (11)$$

$$a\alpha_P+b\alpha_H+c=0. \qquad (12)$$

The solution has the turning point T_t which is some Kelvins higher than T_b. The actual first order phase transition obtained from the free energy behavior takes place between these two points. So, we obtain the bifurcation temperature, the first order phase transition, the symmetry of the ordered phase, and the part ρ_P (ρ_H) of the number of molecules with pentagon (hexagon) facing neighbor double bond near the phase transition in good agreement with the experimental data (see, e.g., Refs. 1 and 2):

$$\rho_P=\frac{a}{a+b}=0.608, \qquad (13)$$

$$\rho_H=\frac{b}{a+b}=0.392. \qquad (14)$$

To pass to the description of the orientational glass state in spin-glass-like theory manner, we need to make two comments on the exploiting of our model interaction: mathematical and physical ones.

First, we can rewrite our results in more compact way. In the orientational ordered phase, all the sublattices are physically equivalent: they convert to each other when we rotate the crystal by 90° along the z axis. The expressions for h_2, h_3, and h_4 formally coincide with $h_1(\tilde{\omega})$ in their "own" system of coordinates that we label by tilde. Then, we can write Eq. (6) as a single equation as follows:

$$h_1(\tilde{\omega})+\frac{1}{4\pi T}\int d\tilde{\omega}' E(\tilde{\omega},\tilde{\omega}')h_1(\tilde{\omega}')=0, \qquad (15)$$

where

$$\int d\omega'[B(\omega,\omega')h_2(\omega')+A(\omega,\omega')h_3(\omega')+D(\omega,\omega')h_4(\omega')] \equiv \int d\tilde{\omega}' E(\tilde{\omega},\tilde{\omega}')h_1(\tilde{\omega}'). \qquad (16)$$

The matrix elements of E are symmetrical. The E matrix can be diagonalized:

$$\begin{aligned}E(\tilde{\omega},\tilde{\omega}')=\frac{1}{4\pi T_b}&\{E_r[K_8(\tilde{\omega})+K_9(\tilde{\omega})+K_{10}(\tilde{\omega})]+E_S[K_{11}(\tilde{\omega}) \\ &+K_{12}(\tilde{\omega})+K_{13}(\tilde{\omega})]\}\{E_r[K_8(\tilde{\omega}')+K_9(\tilde{\omega}') \\ &+K_{10}(\tilde{\omega}')]+E_S[K_{11}(\tilde{\omega}')+K_{12}(\tilde{\omega}')+K_{13}(\tilde{\omega}')]\}. \qquad (17)\end{aligned}$$

The coefficients E_r and E_S depend on J_P, J_H, and the coefficients $\alpha_{P(H)}$, $\beta_{P(H)}$, and $\gamma_{P(H)}$.

The solution of Eq. (15) has the following form:

$$\begin{aligned}h(\tilde{\omega})=r&[K_8(\tilde{\omega})+K_9(\tilde{\omega})+K_{10}(\tilde{\omega})] \\ &+s[K_{11}(\tilde{\omega})+K_{12}(\tilde{\omega})+K_{13}(\tilde{\omega})], \qquad (18)\end{aligned}$$

where $r=a\beta_P+b\beta_H$ and $s=a\gamma_P+b\gamma_H$.

Second, the solution for $h(\tilde{\omega})$ was obtained for the vicinity of the bifurcation point. It is not difficult to find the solution of the basic nonlinear integral equations, Eq. (5), for the distribution functions at lower temperatures. The shape of $h(\tilde{\omega})$ preserves with the temperature dependent coefficients $a(T)$, $b(T)$, and $c(T)$ [$r(T)$ and $s(T)$]. However, the ratios ρ_P and ρ_H obtained in such a way at fixed J_P and J_H weakly depend on the temperature that does not correspond to the experimental data. It is obvious that this is the consequence of the fact that J_P and J_H do not depend on the temperature. The cause is that the two minima in the potential energy (corresponding to P and H orientations) are separated by the height energy barrier that is not directly taken into account in our model. Molecules are able to jump between the two minima due to the process of a thermal activation at high enough temperatures. So, we introduce $J_P=J_P(T)$ and $J_H=J_H(T)$ to correct it (compare with Ref. 22). It is obvious that the pair interactions between molecules become less sensible to their mutual orientations when the temperature increases because the libration increases. The theoretical estimate[17] shows that the libration amplitude about the [111] direction increases nearly twice when the temperature changes from T_g to T_c. Our approach permits us to obtain the dependences $J_P=J_P(T)$ and $J_H=J_H(T)$ by solving a kind of inverse problem. We tried to fit experimental data to our solution [Eq. (18)]. Changing J_P and J_H and solving Eqs. (15) and (5) for each pair of values, we fit $J_P(T)$ and $J_H(T)$ as to describe the experimental dependence of $\rho_P(T)$ and $\rho_H(T)$. This dependence is nonlinear, and it follows that when $\rho_P \to 0.7$ from below, then $T_b \to 150$ K from above and $J_H \to 0$ (J_H changes sign at this value of ρ_P, but $J_P < 0$). So the two types of mutual molecular orientations are profitable above this temperature: (a) the pentagon of one molecule versus the double bond of the neighbor molecule or (b) the hexagon of one molecule versus the double bond of the neighbor molecule. Above this concentration, $\rho_P = 0.7$, the frustration appears: (a) interaction is profitable and (b) interaction is not.

Let us note that in our model, the presence of the barriers between the energy levels is taken into account indirectly through the effective parameters J_P and J_H. An orientational disorder at low temperatures leads to the nonhomogeneous lattice deformation (see Ref. 9 and references therein). The neutron scattering data show that at low enough temperatures, a relatively large fraction of the intermolecular contacts was with double bonds pointing to pentagonal or hexagonal faces. Only a small fraction of molecules was oriented at random. However, this picture does not lead to the low temperature glass phase, but only to partly frustrated structures.[30] It follows from the experimental data[1,9] that there is small anomaly at $T \approx 150$ K, but it is still unclear whether this temperature corresponds to the arrest of the free uniaxial rotation or to a glass transition similar to that observed near 90 K. Note that the discrete description of the orientational ordering, Eqs. (8)–(12), includes as the answer the equiprobable distribution of the molecule orientations in the cubic lattice, $K_1(\omega)$, that corresponds to the rotations in the cubic lattice [see, e.g., Ref. 23] in addition to H and P states.

Now, we can formulate the physical reasons of the glass formation. At high temperatures, the molecules travel slightly between different types of mutual orientations. When the temperature decreases, the possibility of changing the orientation of the molecule decreases, because of the large potential barrier between the lowest orientational states. Then, the unfavorable H state of the molecule is a rather rare phenomenon at low temperatures. The glassy state is obtained when the thermal energy is not sufficient to overcome the potential barrier that separates the two orientational configurations. The H state of the molecule (six hexagons and six double bonds) is then profitable from the double bond side and is not from the hexagon side. The double bonds of a molecule in the H state can be energy beneficial if they face the pentagon of the neighboring molecule. The P state of the molecule (six pentagons and six double bonds) is then profitable from the double bond side and from the pentagon side. We see that the behavior of our system at low temperatures is similar to the behavior of the "dilute" molecular crystals. If we compare the behavior with that of ortho-para hydrogen, we see that it is the hexagon part of H states here that plays the role of p-H_2 molecules in ortho-para mixture. The solution, Eq. (18) [and Eqs. (8)–(12)], correctly describes long-range orientational order at all temperatures. However, the coefficients r and s (a, b, and c) should be determined indirectly from the experimental data for ρ_P and ρ_H. On this basis, we suggest the following model for the description of the orientational glass transition in C_{60}. The large number of the nearest neighbor bonds allows for the spin-glass theory description of the problem.

III. ORIENTATIONAL GLASS

After we have shown that frustration and disorder (two main ingredients of spin glasses) are presented in our system, it is rightful to construct the spin-glass-like Hamiltonian for the model. This can be done in close analogy with the approach of the pioneering papers on spin-glass theory,[31,32] where the usual Ising model was transformed in the Sherrington-Kirkpatrick (SK) model using physical assumptions and mathematics of limit theorems. In Refs. 12 and 13, basing on the analogous arguments, a model for orientational glass transition in ortho-para hydrogen that described the experiments successfully was developed. Formally, the model changes the spin of Ref. 32 for quadrupole moment. As this model is a ψ^3 model in contrast to SK case, the partial orientational long-range order coexists with quadrupole glass order. Now we propose to change the spin of SK model for the combination Eq. (18). We apply then the standard methods of spin glass theory, including replica approach and the concept of replica symmetry breaking (see, e.g., Ref. 33). As some of the integrals,

$$\langle k,m,n\rangle = \int d\omega K_k(\omega) K_m(\omega) K_n(\omega), \tag{19}$$

are nonzero, we obtain the coexistence of the long-range and glass orders. Technically, the consideration below is close to that of Ref. 34.

So, we consider a system of particles on lattice sites i,j with Hamiltonian

$$H = -\frac{1}{2}\sum_{i\neq j} J_{ij}\hat{U}_i\hat{U}_j, \tag{20}$$

where J_{ij} are quenched Gaussian interactions with zero mean,

$$P(J_{ij}) = \frac{1}{\sqrt{2\pi}J}\exp\left[-\frac{(J_{ij})^2}{2J^2}\right], \tag{21}$$

with $J = \tilde{J}/\sqrt{N}$, and

$$\hat{U} = c[K_8^i(\omega) + K_9^i(\omega) + K_{10}^i(\omega)] + d[K_{11}^i(\omega) + K_{12}^i(\omega) + K_{13}^i(\omega)], \tag{22}$$

In principle, c and d depend on the ratio of the P and H states, and one has to take this dependence into account to describe the whole phase disgram. However, it is known that in the glass phase, this ratio is constant, so it is possible to put $d/c = -0.914$ and $\rho_P = 0.83$, as it is at the pressure $P = 0$, $T = T_g$.

Using replica approach, we can write the free energy averaged over disorder in the form

$$\frac{\langle F\rangle_J}{NkT} = \lim_{n\to 0}\frac{1}{n}\max\left\{\frac{t^2}{4}\sum_{\alpha}(p^{\alpha})^2 + \frac{t^2}{2}\sum_{\alpha>\beta}(q^{\alpha\beta})^2 - \ln \mathrm{Tr}_{\{U^{\alpha}\}}\exp\left[\frac{t^2}{2}\sum_{\alpha}p^{\alpha}(\hat{U}^{\alpha})^2 + t^2\sum_{\alpha>\beta}q^{\alpha\beta}\hat{U}^{\alpha}\hat{U}^{\beta}\right]\right\}. \tag{23}$$

Here, $t=\tilde{J}/kT$ and $Tr(\cdots)\equiv\int_0^{2\pi}d\varphi\int_0^{\pi}d\cos(\theta)(\cdots)$.

The saddle point conditions for the free energy give the glass and regular order parameters

$$q^{\alpha\beta} = \frac{\mathrm{Tr}[\hat{U}^{\alpha}\hat{U}^{\beta}\exp(\hat{\theta})]}{\mathrm{Tr}[\exp(\hat{\theta})]}, \tag{24}$$

$$m^{\alpha} = \frac{\mathrm{Tr}[\hat{U}^{\alpha}\exp(\hat{\theta})]}{\mathrm{Tr}[\exp(\hat{\theta})]} \tag{25}$$

and the auxiliary order parameter

$$p^{\alpha} = \frac{\mathrm{Tr}[(\hat{U}^{\alpha})^2\exp(\hat{\theta})]}{\mathrm{Tr}[\exp(\hat{\theta})]}. \tag{26}$$

Here,

$$\hat{\theta} = \frac{t^2}{2}\sum_{\alpha}p^{\alpha}(\hat{U}^{\alpha})^2 + t^2\sum_{\alpha>\beta}q^{\alpha\beta}\hat{U}^{\alpha}\hat{U}^{\beta}. \tag{27}$$

In the replica symmetric (RS) approximation,[32] the free energy, Eq. (23), has the form

$$F = -NkT\left\{t^2\frac{q^2}{4} - t^2\frac{p^2}{4} + \int_{-\infty}^{\infty}\frac{dz}{\sqrt{2\pi}}\times\exp\left(-\frac{z^2}{2}\right)\ln \mathrm{Tr}[\exp(\hat{\theta})]\right\}. \tag{28}$$

Here,

$$\hat{\theta} = zt\sqrt{q}\hat{U} + t^2\frac{p-q}{2}\hat{U}^2. \tag{29}$$

The extremum conditions for the free energy [Eq. (28)] give the following equations for the glass and regular order parameters:

$$q = \int dz^G\left\{\frac{\mathrm{Tr}[\hat{U}\exp(\hat{\theta})]}{\mathrm{Tr}[\exp(\hat{\theta})]}\right\}^2, \tag{30}$$

$$m = \int dz^G\left\{\frac{\mathrm{Tr}[\hat{U}\exp(\hat{\theta})]}{\mathrm{Tr}[\exp(\hat{\theta})]}\right\}, \tag{31}$$

and the auxiliary equation

$$p = \int dz^G\frac{\mathrm{Tr}[\hat{U}^2\exp(\hat{\theta})]}{\mathrm{Tr}[\exp(\hat{\theta})]}. \tag{32}$$

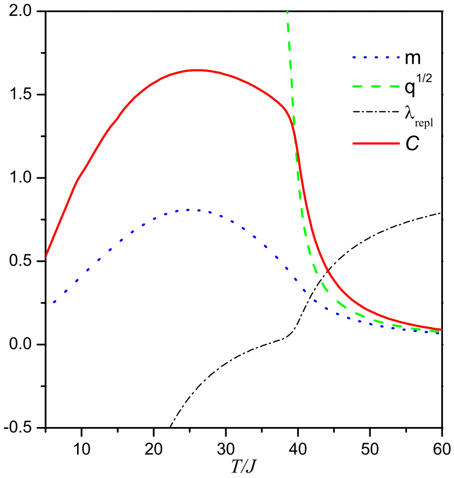

FIG. 1. (Color online) Order parameters and the heat capacity evolution with the temperature. Here, $d/c=-0.914$, red solid curve is the heat capacity, dotted blue and dashed green curves are the order parameters m and $\sqrt{q}$, respectively, and the black dashed-dotted curve is the replicon mode λ_{repl}. The replica symmetry breaking occurs at the temperature T_0 corresponding to $\lambda_{\mathrm{repl}}=0$; the glass transition temperature T_g is usually very close to T_0.

Here,

$$\int dz^G = \int_{-\infty}^{\infty}\frac{dz}{\sqrt{2\pi}}\exp\left(-\frac{z^2}{2}\right). \tag{33}$$

The specific heat is

$$\frac{C_v}{kN} = \frac{d}{d(kT/\tilde{J})}\left[\left(\frac{\tilde{J}}{kT}\right)\frac{q^2-p^2}{2}\right]. \tag{34}$$

The replica symmetric solution is stable unless the replicon mode energy λ is nonzero. For our model, we have

$$\lambda_{\mathrm{RS}} = 1 - t^2\int dz^G\left\{\frac{\mathrm{Tr}[\hat{U}^2\exp(\hat{\theta})]}{\mathrm{Tr}[\exp(\hat{\theta})]} - \left[\frac{\mathrm{Tr}[\hat{U}\exp(\hat{\theta})]}{\mathrm{Tr}[\exp(\hat{\theta})]}\right]^2\right\}^2. \tag{35}$$

The results of the calculations are illustrated in Fig. 1. The order parameters do not go to zero because $\int d\omega u^{2k+1}(\omega)\neq 0$, $k=1,2,\ldots$. The coexistence of the orientational ordered state (the order parameter $m\neq 0$) and the glass (the order parameter $q\neq m^2$) is in agreement with the experimental data.[1,2]

The replica symmetry breaking occurs at the temperature T_0 corresponding to $\lambda_{\mathrm{repl}}=0$; the glass transition temperature T_g is usually very close to T_0. The mildly sloping curve with the broad maximum for the heat capacity qualitatively corresponds (after subtraction of a subground) to the curve $C_p^{\exp}(T)$ obtained in Refs. 5, 9, 10, and 35–37.

IV. PRESSURE EFFECTS

Now let us make some remarks about the situation under not very high pressures, that is, in the region where the dependence of J_P and J_H on pressure may be considered as

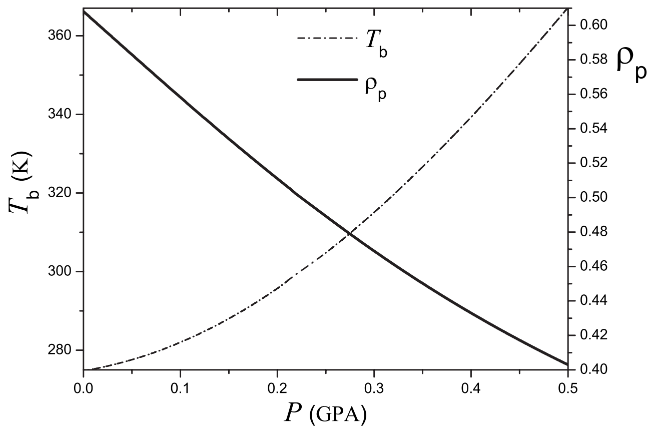

FIG. 2. The ratio of the number of molecules with pentagons facing neighbor double bonds, ρ_P, and the bifurcation temperature T_b as the functions of pressure.

linear, and speculate a little about the whole accessible orientational phase diagram of solid molecular C_{60}.

It is well known that the temperature of orientational transition increases with pressure. There is a spread of experimental values for dT_g/dp mainly because some pressure transmitting gases intercalate into C_{60}. The currently accepted value of dT_g/dp is about 165 K GPa^{-1}.[1,2] The H orientation is favored under pressure, and the energy difference between two orientations vanishes at a weakly temperature dependent pressure. It corresponds to $\rho_H = \rho_P = 0.5$ and $J_P = J_H = J_0$. We choose the value $J_0 = 300$ K at the pressure $p_0 = 0.225$ GPa.[1,2,38,39] Then we get from our model using the bifurcation condition for the transition temperature $J_0 = -242$ K. If we assume that J_P and J_H depend linearly on p at not very high pressures, then we get

$$J_P = -300(\mathrm{K}) + 256.8(\mathrm{K/GPa})P, \tag{36}$$

$$J_H = -110(\mathrm{K}) - 587.6(\mathrm{K/GPa})P. \tag{37}$$

In the Fig. 2 the dependence of the bifurcation temperature on the pressure is presented. Our curve is weakly nonlinear contrary to the experiment. The absolute values of $T_b(p)$ are close to the experimental values[1,2,39] (see also a theoretical paper, Ref. 40). Let us emphasize that the obtained values of $\rho_P(p)$, Fig. 2, weakly depend on the choice of J_0 and p_0, contrary to the value of $T_c(p)$. Our values of $\rho_P(p)$ agree well with the results of phenomenological description of the experimental data.[1,7,38] We use the model, Eqs. (20)–(22), as before, for the description of the glass phase under pressure with d and c chosen in a proper way, as described above. The results do not differ significantly from Fig. 1.

When $P \to 1.2$ GPa, it follows from Eqs. (36) and (37) that $J_P \to 0$ (it changes its sign here) and $J_H < 0$. So, our simple model for the orientational ordering becomes invalid. Experiments show[1,2,6–8] that at these pressures, the number of P states is very small.

The orientational glass transition is hardly experimentally seen at $P \sim 0.2$ GPa ($\rho_P \approx \rho_H$ at all temperatures[1]) and $P \gtrsim 1$ GPa ($\rho_P \ll 1$), which does not contradict the above description of the glass transition. When $\rho_P \approx \rho_H$, the P and H states are both profitable, and the analogy with diluted multipole systems becomes invalid. When the pressure is large enough, ρ_P becomes very small and there is no sense speaking about disorder and frustration.

V. CONCLUSIONS

To summarize, the model that was proposed previously for the orientational ordering transition is used now for the description of the low temperature orientational glass transition in solid molecular C_{60} using the basic concepts and methods of spin-glass and multipole-glass theory. The solution of this model gives, in agreement with experimental data, the low-temperature phase transition into an orientational glass phase with partly conserved orientational long-range order and a broad maximum on the specific heat (orientational contribution) curve. The model potential is now generalized to include the pressure effects. The orientational phase diagram of solid molecular C_{60} is discussed in terms of the proposed potential that gives the correct ratio ρ_P/ρ_H in certain region of p and T.

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