

## Pressure-induced orientational glass phase in molecular para-hydrogen

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We propose a theoretical description of a possible orientational glass transition in solid molecular para-hydrogen and ortho-deuterium under pressure supposing that they are mixtures of  $J=0$  and  $J=2$  states of molecules. The theory uses the basic concepts and methods of standard spin-glass theory. We expect our orientational glass to correspond to the II' phase of the high-pressure hydrogen phase diagram.

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### I. INTRODUCTION

The high-pressure phase diagram of solid hydrogen and its isotopes has been a fascinating subject of investigation during recent decades. Although the  $p$ - $T$  phase diagrams of ortho- $H_2$  and para- $D_2$  under not too high pressures are well understood, the same cannot be said for para- $H_2$  and ortho- $D_2$  and about extremely high pressures (see, e.g., the reviews in Refs. [1–3]).

At low temperature and ambient pressure, pure solid o- $H_2$  and p- $D_2$  consisting of molecules with orbital angular momentum  $J=1$  crystallize in hcp lattices with rotating molecules on the lattice sites. At lower temperature a transition takes place to the phase with the orientational long-range order (LRO) of antiferroquadrupolar type. This transition is accompanied by a structural transition to the fcc lattice. The transition temperature increases with pressure depending on the intermolecular distance  $R$  as  $R^{-5}$ , thus indicating that it is due to the anisotropic electric quadrupole-quadrupole (EQQ) interaction. This picture remains valid up to  $c \sim 0.55$ , where  $c$  is the concentration of moment bearing molecules. At intermediate concentrations ( $c \geq 0.12$ ) NMR experiments have been interpreted in terms of the freezing of the orientational degrees of freedom and the transition to the quadrupolar glass phase [1,4,5]. At the lower  $c$  concentration, there is no orientational ordering.

Molecular p- $H_2$  and o- $D_2$  also crystallize in hcp structure. However, at low pressure (LP) they remain in this structure up to 0 K. This phase has no orientational order ( $J=0$ ), and it is called phase I (or LP phase). At higher pressures ( $\sim 110$  GPa in p- $H_2$  and  $\sim 28$  GPa in o- $D_2$ ) solids transform to orientationally ordered broken-symmetry phases (phase II or BSP) [1–3]. The possibility of orientational order in systems of initially spherically symmetric molecule states is due to the involving of higher-order orbital moments  $J=2, 4, \dots$  in the physics under pressure. The crystal field of the neighbors perturbs the molecular wave functions, and one can gain in overall energy if the anisotropic the EQQ interaction between nonzero quadrupole moments is included. One has to keep in mind that the EQQ interaction rapidly increases with increasing pressure. The long-range orientational order appears abruptly at a fixed value of pressure through the first-

order phase transition just as it takes place in ortho-para mixtures when the concentration of moment-bearing molecules achieves a certain fixed value.

Goncharov *et al.* [6] investigated the high-resolution Raman spectra of almost pure o- $D_2$ . The authors indicate that in the intermediate-pressure range between the phases I and II the ordering is incomplete and orientational frustration takes place. They further speculate that this intermediate II' phase exhibits glassy behavior. Phase II' persists for a narrow pressure range ( $\sim 2$  GPa) and has abrupt boundaries.

It seems obvious that the  $T$ - $p$  phase diagram containing I, II', and II phases can be considered in close analogy to the  $T$ - $c$  phase diagram of ortho-para mixtures. For simplicity, we imagine that  $p$  maps  $c_2(p)$ —the concentration of molecules with  $J=2$ —although one should take into account other anisotropic interactions to understand the results of the precise experiments (e.g., Raman scattering [7]). The first attempts to describe in such a way the long-range order and the orientational glass phase in o- $D_2$  and p- $H_2$  on a microscopic theory level were done in Refs. [8–10].

### II. $J=2$ QUADRUPOLE GLASS MODEL

The purpose of this paper is to give a theoretical description of the possible orientational glass transition in solid molecular para-hydrogen and ortho-deuterium under pressure supposing that they are mixtures of  $J=0$  and  $J=2$  states of molecules. The theory uses the basic concepts and methods of standard spin-glass theory. We expect our orientational glass to correspond to the II' phase of the high-pressure hydrogen phase diagram.

It is well known that the number of  $J=0 \rightarrow J=2$  transitions increases rapidly with increasing pressure (see, e.g., Refs. [1–3,6,7,11–14]). The anisotropic interaction potential and the crystal field grow rapidly with increasing density. The energy of the many-body system can be lowered by taking advantage of the anisotropic interactions. So the single-molecule wave functions are no longer spherically symmetric, but are rather admixtures including higher-order excitations. This admixture is probably responsible for the decrease of the critical concentration of  $J=1$  molecules for

the LRO transition in ortho-para samples at high pressure, the deficit of momentum-bearing molecules being compensated by  $J=2$  molecules. It seems that the weak dependence of the transition to the III (or A) phase on the ortho-para composition can be described in an analogous way.

The rough estimation of  $J=0 \rightarrow J=2$  transition probability  $\xi$  can be done using quantum-mechanical perturbation theory considering the field of the nearest neighbors as the perturbation [8]:

$$\xi = \frac{\eta}{(1+\eta)}, \quad \eta = 3.8 \left( \frac{25}{26} \frac{\Gamma}{12B} \right) \left( \frac{R_0}{R} \right)^{10}, \quad (1)$$

where  $B$  is the rotational constant,  $R$  is the intermolecular distance, and  $\Gamma/B=0.011$  in  $H_2$  and  $0.028$  in  $D_2$  [1]. The factor of 3.8 has a geometrical nature, and it corresponds to the hcp lattice. Using the compressibility data, we obtain the pressure dependence of  $\xi$ . This dependence is very strong. If we attribute to the probability  $\xi$  the meaning of the concentration of moment-bearing molecules, we see that the position and the width of the  $\Pi'$  phase qualitatively coincide with that of quadrupolar glass in ortho-para mixtures. For example,  $\xi=0.1$  at 40 GPa for o- $D_2$ . The isotope dependence is also roughly correct.

The admixture of  $J=2$  states causes the frustration in the case of hcp lattice. As to disorder, it is not obvious that one can think of  $J=2$  impurities as of the quenched disorder even at low temperature. Nevertheless, it seems possible to consider the whole ensemble of physically achievable realizations of mixed states as a convenient background (see, e.g., Ref. [15]) for the formulation of an orientational glass model in the spirit of the spin-glass theory [16].

Here we present two theoretical models of possible quadrupolar glass with  $J=2$ . The first one is a generalization of the well-known Sherrington-Kirkpatrick [17] spin glass, and it is analogous to the model [18] which describes well the quadrupolar glass in ortho-para mixtures [4,5]. The second model is a generalization of the so-called “ $p$ -spin glass,” and it is probably more adequate for high pressures when many particle interactions can play an important role. We consider the case  $p=3$  in detail. The results obtained for the models differ: in the three-site model discontinuities in the specific heat and in the glass order parameter as the functions of the temperature do appear. We hope that future experiments will discriminate between these models. The essential feature of the obtained intermediate phase in both models is the coexistence of the orientational glass with the long-range orientational order as is seen in the experiment [6].

### III. QUADRUPOLE GLASS WITH TWO-PARTICLE INTERACTION

As the first model of the quadrupole glass, we will consider a system of particles on lattice sites  $i$  and  $j$  with random truncated EQQ Hamiltonian

$$\hat{H} = -\frac{1}{2} \sum_{i \neq j} J_{ij} \hat{Q}_i \hat{Q}_j. \quad (2)$$

Here  $J_{ij}$  are random interactions distributed with Gaussian probability

$$P(J_{ij}) = \frac{\sqrt{N}}{\sqrt{2\pi\tilde{J}}} \exp\left[-\frac{(J_{ij})^2 N}{2\tilde{J}^2}\right], \quad (3)$$

where the factor  $N$  insures the sensible thermodynamic limit.

The operator  $\hat{Q} \sim [3J_z^2 - J(J+1)]$  is the axial quadrupole moment of the hydrogen molecule in the space  $J=\text{const}$ ;  $\text{Tr} \hat{Q}=0$ . In Ref. [18] quadrupole glass freezing in ortho-para mixtures has been considered on the basis of the Hamiltonian (2) in the subspace  $J=1$  with  $J_z=0, \pm 1$  and  $\hat{Q}=3J_z^2-2$ , so that

$$\hat{Q}_{(1)}^2 = 2 - \hat{Q}_{(1)}. \quad (4)$$

Now the Hamiltonian (2) will be considered in the subspace  $J=2$  with  $J_z=0, \pm 1, \pm 2$  and

$$\hat{Q} = \frac{1}{3} [3J_z^2 - 6]. \quad (5)$$

Let us emphasize that the model with  $J=2$  differs essentially from that with  $J=1$  because of the different operator algebras. For example, now the operators  $\hat{Q}$  are  $5 \times 5$  diagonal matrices, and instead of (4) we have

$$\hat{Q}^3 = 4 + 4\hat{Q} - \hat{Q}^2. \quad (6)$$

Following the standard methods of spin-glass theory (see, e.g., Ref. [19]) and using the replica technique, we can express the disorder-averaged free energy of the system in the form (see also Refs. [10,20])

$$\langle F \rangle_{J/NT} = \lim_{n \rightarrow 0} \frac{1}{n} \max \left\{ \frac{t^2}{4} \sum_{\alpha} (p^\alpha)^2 + \frac{t^2}{2} \sum_{\alpha > \beta} (q^{\alpha\beta})^2 - \ln \text{Tr}_{\{Q^\alpha\}} \exp \hat{\theta} \right\}, \quad (7)$$

where

$$\hat{\theta} = t^2 \sum_{\alpha > \beta} q^{\alpha\beta} \hat{Q}^\alpha \hat{Q}^\beta + \frac{t^2}{2} \sum_{\alpha} p^\alpha (\hat{Q}^\alpha)^2. \quad (8)$$

Here  $t=\tilde{J}/T$  and the numbers  $\alpha$  and  $\beta$  label replicas.

The standard conditions for the free-energy saddle point determine the glass order parameter  $q$  and the regular order parameter  $x$  (average quadrupole moment),

$$q^{\alpha\beta} = \langle \hat{Q}^\alpha \hat{Q}^\beta \rangle_\theta, \quad (9)$$

$$x^\alpha = \langle \hat{Q}^\alpha \rangle_\theta, \quad (10)$$

and also the auxiliary order parameter

$$p^\alpha = \langle (\hat{Q}^\alpha)^2 \rangle_\theta, \quad (11)$$

where

$$\langle \dots \rangle_\theta = \frac{\text{Tr}[(\dots) \exp(\hat{\theta})]}{\text{Tr}[\exp(\hat{\theta})]}. \quad (12)$$

In the replica-symmetric (RS) approximation, when all  $q_{\alpha\beta}$  are equal, expression (7) for the free energy becomes

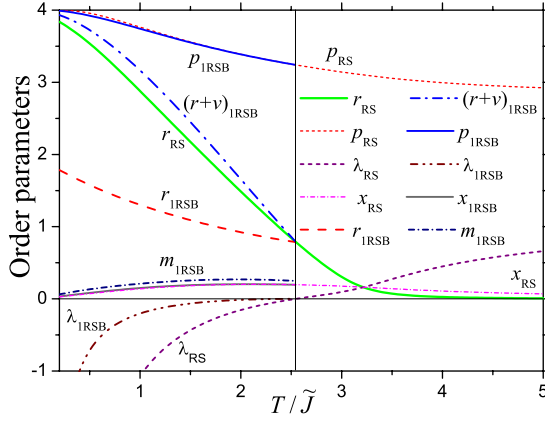


FIG. 1. (Color online) The temperature dependence of the order parameters for the quadrupole glass with the two-particle interaction. The replica symmetry breaking occurs at the temperature corresponding to  $\lambda_{(\text{RS})\text{repl}}=0$ .

$$F_{\text{RS}} = -NT \left\{ t^2 \frac{q^2}{4} - t^2 \frac{p^2}{4} + \ln \text{Tr}(\exp \hat{\theta}_{\text{RS}}) \right\}. \quad (13)$$

Here

$$\hat{\theta}_{\text{RS}} = zt\sqrt{q}\hat{Q} + t^2 \frac{p-q}{2} \hat{Q}^2, \quad (14)$$

$$\overline{(\cdots)} = \int \frac{dz}{\sqrt{2\pi}} (\cdots) \exp\left(-\frac{z^2}{2}\right) \equiv \int dz^G (\cdots). \quad (15)$$

Using the extremum conditions for the free energy, Eq. (13), we obtain the equations for the order parameters:

$$q = \overline{\langle \hat{Q} \rangle_{\theta_{\text{RS}}^2}}, \quad (16)$$

$$x = \overline{\langle \hat{Q} \rangle_{\theta_{\text{RS}}}}, \quad (17)$$

$$p = \overline{\langle \hat{Q}^2 \rangle_{\theta_{\text{RS}}}}. \quad (18)$$

The results of the numerical solution of Eqs. (16)–(18) are illustrated in Fig. 1. One can see that there is the coexistence of glass and LRO. The RS glass order parameter and the RS average quadrupole moment grow continuously on cooling and are nonzero even at arbitrary high temperature. The absence of a zero solution of Eqs. (16)–(18) follows from the fact that  $\text{Tr} \hat{Q}^{2k+1} \neq 0$ ,  $k=1, 2, \dots$  (see Ref. [20] for details). The orientational contribution to the heat capacity,

$$\frac{C_{v(\text{RS})}}{N} = \frac{d}{d(1/t)} \left[ t \frac{q^2 - p^2}{2} \right], \quad (19)$$

has a broad maximum at the temperature slightly lower than that of the instability of the RS solution. All these features are common for the quadrupole glass with  $J=2$  and  $J=1$  (see Refs. [4,5,18]).

The RS solution is stable unless the replicon-mode energy  $\lambda$  is nonzero [21]. For our model we have

$$\lambda_{(\text{RS})\text{repl}} = 1 - t^2 [\overline{\langle \hat{Q}^2 \rangle_{\theta_{\text{RS}}} - (\langle \hat{Q} \rangle_{\theta_{\text{RS}}})^2}]^2. \quad (20)$$

At the temperature  $T_0$  defined by the condition  $\lambda_{(\text{RS})\text{repl}}=0$  the RS solution becomes unstable and one needs to look for the solutions with replica symmetry breaking (RSB). Using the standard procedure (see, e.g., Ref. [19]), we perform the first stage of the replica symmetry breaking (1RSB) according to Parisi ( $n$  replicas are divided into  $n/m$  groups with  $m$  replicas in each) and obtain the free energy in the form (with  $q^{\alpha\beta}=r_1$  if  $\alpha$  and  $\beta$  are from the different groups and  $q^{\alpha\beta}=r_1+v$  if  $\alpha$  and  $\beta$  belong to the same group)

$$F_{1\text{RSB}} = -NT \left\{ t^2 \left( m \frac{r_1^2}{4} + (1-m) \frac{(r_1+v)^2}{4} - \frac{p^2}{4} \right) + \frac{1}{m} \int dz^G \ln \int ds^G [\text{Tr} e^{\hat{\theta}_{1\text{RSB}}}]^m \right\}, \quad (21)$$

where

$$\hat{\theta}_{1\text{RSB}} = zt\sqrt{r_1}\hat{Q} + st\sqrt{v}\hat{Q} + t^2 \frac{p-r_1-v}{2} \hat{Q}^2. \quad (22)$$

The extremum conditions for  $F_{1\text{RSB}}$  yield the equations for the glass order parameters  $r_1$  and  $v$ , the regular order parameter  $x$ , the additional order parameter  $p$ , and the parameter  $m$  [see Appendix A, where  $\hat{\theta}_{1\text{RSB}}$  is given by Eq. (22) for  $l=2$ ].

To estimate the form of the 1RSB solution near the bifurcation point  $T_0$  at which it ceases to coincide with the RS solution (i.e., in the neighborhood of  $T_0$ ), we expand the expression for the free energy, Eq. (7), up to the third order inclusively, assuming that the deviations  $\delta q^{\alpha\beta}$  from  $q_{\text{RS}}$  are small. In fact, we expand the argument of the exponent:

$$\hat{\theta} = t^2 \sum_{\alpha>\beta} \delta q^{\alpha\beta} \hat{Q}^\alpha \hat{Q}^\beta + \frac{t^2}{2} p \sum_{\alpha} (\hat{Q}^\alpha)^2 + t^2 q_{\text{RS}} \sum_{\alpha>\beta} \hat{Q}^\alpha \hat{Q}^\beta, \quad (23)$$

with  $t=t_0+\Delta t$ . Using the formulas of Appendix B, we obtain

$$\begin{aligned} \frac{\Delta F}{NT} &= \frac{t^2}{4} (1-t^2 W) \{ -[r - (m-1)v]^2 + v^2 m(m-1) \} \\ &+ \frac{t^4}{2} L [r - (m-1)v]^2 - t^6 \{ C [r - (m-1)v]^3 \\ &+ D [r - (m-1)v] v^2 m(m-1) - B_3 v^3 m^2(m-1) \\ &+ B_4 v^3 m(m-1)(2m-1) \} + \cdots, \end{aligned} \quad (24)$$

where  $t=t_0+\Delta t$ ,  $r=r_1-q_{\text{RS}}$ , and the expressions for the parameters  $W$ ,  $L$ ,  $C$ ,  $D$ ,  $B_3$ , and  $B_4$  are given in Appendix C.

Using the extremum conditions for the free energy, Eq. (24), and the fact that  $L|_{t=t_0} \neq 0$ , we obtain the branching condition  $r - (m-1)v = 0 + o(\Delta t)^2$ —i.e., the condition that there be no linear term in the glass order parameters. There is no other linear term because  $(1-t^2 W)|_{t=t_0} = \lambda_{(\text{RS})\text{repl}}|_{t=t_0} = 0$  at the bifurcation point. Finally, we obtain

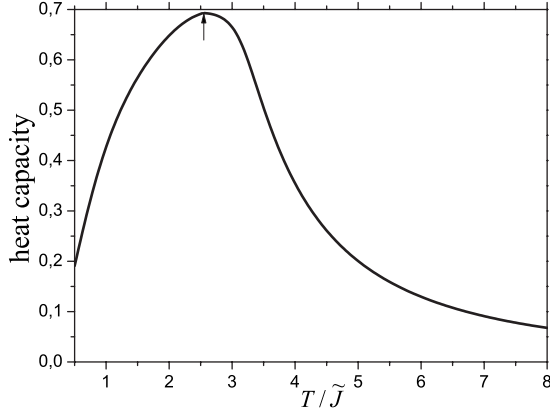


FIG. 2. The heat capacity of the quadrupole glass with two-particle interactions as a function of temperature. The arrow marks the temperature corresponding to the boundary between RS and more stable 1RSB solution.

$$2 \left[ -\frac{t_0}{2} - \frac{t_0^4}{4} \frac{dW}{dt} \Big|_{t=t_0} \right] \Delta t = t_0^6 [-B_4 + m(-B_3 + 2B_4)]v,$$

$$(2m-1) \left[ -\frac{t_0}{2} - \frac{t_0^4}{4} \frac{dW}{dt} \Big|_{t=t_0} \right] \Delta t = t_0^6 \{ (2m-1)[-B_4 + m(-B_3 + 2B_4)] + m(m-1)(-B_3 + 2B_4) \} v, \quad (25)$$

where  $B_3$  and  $B_4$  are taken at  $T=T_0$ . So

$$v \sim \Delta t, \quad r = (m-1)v, \quad (26)$$

in the neighborhood of  $T_0$ , where the 1RSB solution appears and

$$m = \frac{B_4}{B_3} \quad (27)$$

at the branch point  $T_0$ .

Let us notice that all the obtained expressions hold for Hamiltonian (2), where  $\hat{Q}$  is the arbitrary diagonal operator such that  $\text{Tr} \hat{Q}=0$ ,  $\text{Tr} \hat{Q}^3$ , and  $L|_{t=t_0}$  are nonzero.

For our model with  $\hat{Q}$  defined by Eq. (5), it follows from above formulas that  $m=0.25$  and there is no jump in the order parameters at the point where the 1RSB solution appears (as usually when  $m < 1$ ). The solutions of the equations giving the extremum conditions of (21) are presented in Fig. 1. The orientational order and the glass regime coexist and grow smoothly on cooling even through the RS-1RSB transition. In addition, the curve for the heat capacity changes a little in passing from the RS to 1RSB solution (Fig. 2).

The 1RSB solution is stable above the temperature determined by the solution of the condition,  $\lambda_{(1RSB)\text{repl}}=0$  (see Fig. 1),

$$\lambda_{(1RSB)\text{repl}} = 1 - t^2 \int dz^G \times \frac{\int ds^G [\text{Tr} e^{\hat{\theta}_{1RSB}}]^m [\langle \hat{Q}^2 \rangle_{\theta_{1RSB}} - (\langle \hat{Q} \rangle_{\theta_{1RSB}})^2]^2}{\int ds^G [\text{Tr} e^{\hat{\theta}_{1RSB}}]^m}. \quad (28)$$

At  $T < T_0$  we have the nonergodic state. At  $T \rightarrow 0$  one expects the full replica symmetry breaking (FRSB).

#### IV. $p$ -SPIN-GLASS-LIKE QUADRUPOLE MODEL

In this section we consider a generalized  $p$ -spin interaction spin glass model—the  $p$ -quadrupole model. The three-quadrupole case will be considered in detail (see below). The model of Sec. III is a two-quadrupole model. The  $p$ -spin-glass model with random interaction of  $p$  Ising spins was considered in a large number of papers (see, e.g., Refs. [22–26]) and serves as a generic model for investigation of glasses without reflection symmetry.

Now we consider  $l$ -quadrupole model described by the Hamiltonian

$$\hat{H} = - \sum_{i_1 \leq i_2 \leq \dots \leq i_l} J_{i_1 \dots i_l} \hat{Q}_{i_1} \hat{Q}_{i_2} \dots \hat{Q}_{i_l}, \quad (29)$$

where  $i = 1, 2, \dots, N$  and  $\hat{Q}$  is defined in Sec. III. The coupling strengths are independent random variables with a Gaussian distribution

$$P(J_{i_1 \dots i_l}) = \frac{\sqrt{N^{l(l-1)}}}{\sqrt{l! \pi \tilde{J}}} \exp \left[ - \frac{(J_{i_1 \dots i_l})^2 N^{l(l-1)}}{l! \tilde{J}^2} \right]. \quad (30)$$

Using the replica approach, we can write the free energy averaged over the disorder (see for details Ref. [22]) in the form

$$\langle F \rangle_J / NT = \lim_{n \rightarrow 0} \frac{1}{n} \max \left\{ -\frac{t^2}{4} \sum_{\alpha} (p^{\alpha})^l + \sum_{\alpha} \mu^{\alpha} (p^{\alpha}) - \frac{t^2}{4} \sum_{\alpha \neq \beta} (q^{\alpha\beta})^l + \sum_{\alpha \neq \beta} \lambda^{\alpha\beta} q^{\alpha\beta} - \ln \text{Tr}_{\{Q^{\alpha}\}} \exp \hat{\theta} \right\}, \quad (31)$$

where

$$\hat{\theta} = \sum_{\alpha \neq \beta} \lambda^{\alpha\beta} \hat{Q}^{\alpha} \hat{Q}^{\beta} + \sum_{\alpha} \mu^{\alpha} (\hat{Q}^{\alpha})^2. \quad (32)$$

The extremum in Eq. (31) is taken over the physical order parameters and over the corresponding Lagrange multipliers  $\lambda^{\alpha\beta}$  and  $\mu^{\alpha}$ . So the saddle-point conditions give the glass order parameter

$$q^{\alpha\beta} = \langle \hat{Q}^{\alpha} \hat{Q}^{\beta} \rangle_{\theta}, \quad (33)$$

the regular order parameter (average quadrupole moment)

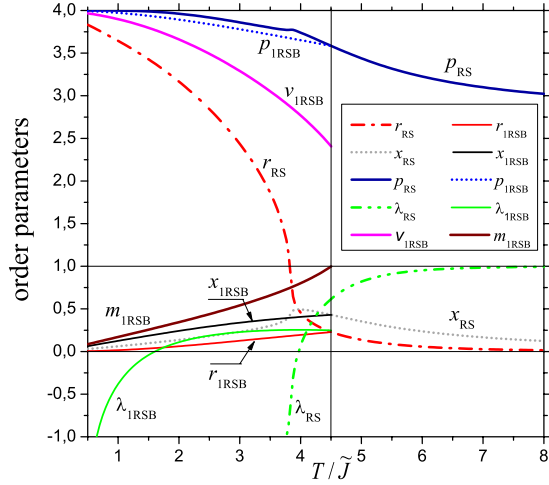


FIG. 3. (Color online) Order parameters evolution with the temperature for 3-quadrupole model. The transition RS-1RSB takes place at the point defined by the condition  $m=1$ . Glass order parameter  $v$  has a jump at this point.

$$x^\alpha = \langle \hat{Q}^\alpha \rangle_\theta, \quad (34)$$

the auxiliary order parameter

$$p^\alpha = \langle (\hat{Q}^\alpha)^2 \rangle_\theta, \quad (35)$$

and the parameters

$$\lambda^{\alpha\beta} = \frac{t^2}{4} l(q^{\alpha\beta})^{(l-1)}, \quad \mu^\alpha = \frac{t^2}{4} l(p^\alpha)^{(l-1)}. \quad (36)$$

Using the standard procedure (see, e.g., Ref. [19]), we can obtain RS and 1RSB expressions for the free energy. Let us write  $F_{1RSB}$  for the case  $l=3$ . The free energy  $F_{RS}$  can be obtained if one put  $v=0$ :

$$F_{1RSB} = -NT \left\{ m t^2 \frac{r_1^3}{2} + (1-m) t^2 \frac{(r_1+v)^3}{2} - t^2 \frac{p^3}{2} + \frac{1}{m} \int dz^G \ln \int ds^G [\text{Tr} \exp(\hat{\theta}_{1RSB})]^m \right\}. \quad (37)$$

Here

$$\hat{\theta}_{1RSB} = zt \sqrt{\frac{3r_1^2}{2}} \hat{Q} + st \sqrt{\frac{3[(r_1+v)^2 - r_1^2]}{2}} \hat{Q} + t^2 \frac{3[p^2 - (r_1+v)^2]}{4} \hat{Q}^2. \quad (38)$$

The extremum conditions for  $F_{1RSB}$  yield the equations for the glass order parameters  $r_1$  and  $v$ , the regular order parameter  $x$ , the additional order parameter  $p$ , and the parameter  $m$  [see Appendix A, where  $\hat{\theta}_{1RSB}$  is given by Eq. (38) for  $l=3$ ].

It is easy to show that the corresponding condition  $\lambda_{(RS)\text{repl}}=0$  does not determine a physical solution in the vicinity of the bifurcation point  $T_0$ : one passes to the unphysical free-energy branch. In fact, the transition RS-1RSB takes place at the point  $T_1 > T_0$  defined by the condition  $m=1$ . At

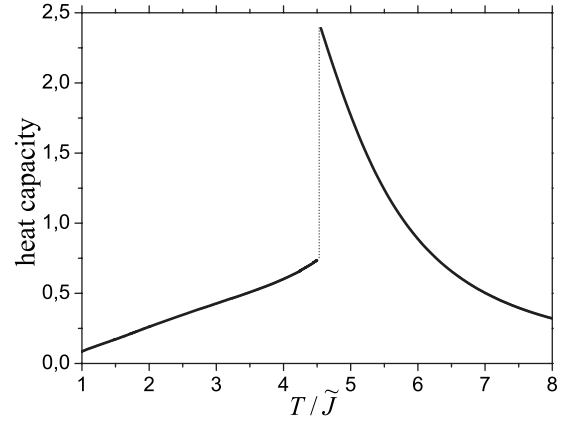


FIG. 4. The heat capacity of the quadrupole glass with three-particle interactions as a function of temperature. There is a jump at the RS-1RSB transition.

this point,  $F_{RS}=F_{1RSB}$ . There are no discontinuities in free energy. The order parameters  $r$ ,  $x$ , and  $p$  are continuous and  $v$  has a jump (see Fig. 3). When the temperature is decreased,  $m$  becomes smaller than 1 and the 1RSB solution leads to a larger free energy than the RS solution. The transition obtained by static approach is a thermodynamic one. Let us remark that the temperature of the dynamical transition can be obtained in the frame of static approach using the marginality condition. Usually the dynamic transition temperature is higher than the thermodynamic one (for details see Refs. [27–33]).

The corresponding discontinuity occurs also in the heat capacity

$$\frac{C_{v(1RSB)}}{N} = \frac{d}{d\left(\frac{1}{t}\right)} \left[ t \frac{m r_1^3 + (1-m)(r_1+v)^3 - p^3}{2} \right]. \quad (39)$$

The form of the curve for the heat capacity, Fig. 4, is analogous to obtained in Ref. [23] for the spherical  $p$ -spin model.

The 1RSB solution can be stable above the temperature  $T=T_2$  determined by the second solution of the condition  $\lambda_{(1RSB)\text{repl}}=0$  (see Fig. 3):

$$\lambda_{(1RSB)\text{repl}} = 1 - t^2 \frac{l(l-1)(r_1+v)^{(l-2)}}{2} \int dz^G \times \frac{\int ds^G [\text{Tr} e^{\hat{\theta}_{1RSB}}]^m \{ \langle \hat{Q}^2 \rangle_{\theta_{1RSB}} - (\langle \hat{Q} \rangle_{\theta_{1RSB}})^2 \}^2}{\int ds^G [\text{Tr} e^{\hat{\theta}_{1RSB}}]^m}. \quad (40)$$

At the point  $T_2$  a transition to a FRSB state or to a stable 2RSB state may take place.

## V. CONCLUSIONS

In this paper we give a theoretical description of possible orientational glass transition in solid molecular para-



hydrogen and ortho-deuterium under pressure supposing that they are mixtures of  $J=0$  and  $J=2$  states of molecules. The theory uses the basic concepts and methods of the standard spin-glass theory. We expect that our orientational glass corresponds to the  $\text{II}'$  phase of the high-pressure hydrogen phase diagram.

We present two theoretical models of possible quadrupole glass with  $J=2$ . The first one is a generalization of the well known Sherrington-Kirkpatrick spin glass. The second model is a generalization of so-called “ $p$ -spin glass,” and it is probably more adequate for high pressures when many particle interactions can play an important role. We consider in detail the case  $p=3$ . The results obtained for two models differ: in the three-site model the discontinuities in the heat capacity and in the glass order parameter as functions of the temperature do appear. We hope that future experiments will discriminate between these models. The essential feature of the obtained intermediate phase in both models is the coexistence of the orientational glass with the long-range orientational order as is seen experimentally [6].

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#### APPENDIX A

The equations for 1RSB glass order parameters  $r_1$  and  $v$ , the regular order parameter  $x$ , the additional order parameter  $p$ , and the parameter  $m$  are

$$r_1 = \int_{z^G} \left\{ \frac{\int_{s^G} [\text{Tr} e^{\hat{\theta}_{1\text{RSB}}}]^{(m-1)} [\text{Tr} \hat{Q} e^{\hat{\theta}_{1\text{RSB}}}]^2}{\int_{s^G} [\text{Tr} e^{\hat{\theta}_{1\text{RSB}}}]^m} \right\}^2, \quad (\text{A1})$$

$$v + r_1 = \int_{z^G} \frac{\int_{s^G} [\text{Tr} e^{\hat{\theta}_{1\text{RSB}}}]^{(m-2)} [\text{Tr} \hat{Q} e^{\hat{\theta}_{1\text{RSB}}}]^2}{\int_{s^G} [\text{Tr} e^{\hat{\theta}_{1\text{RSB}}}]^m}, \quad (\text{A2})$$

$$x = \int_{z^G} \frac{\int_{s^G} [\text{Tr} e^{\hat{\theta}_{1\text{RSB}}}]^{(m-1)} [\text{Tr} \hat{Q} e^{\hat{\theta}_{1\text{RSB}}}]}{\int_{s^G} [\text{Tr} e^{\hat{\theta}_{1\text{RSB}}}]^m}, \quad (\text{A3})$$

$$p = \int_{z^G} \frac{\int_{s^G} [\text{Tr} e^{\hat{\theta}_{1\text{RSB}}}]^{(m-1)} [\text{Tr} \hat{Q}^2 e^{\hat{\theta}_{1\text{RSB}}}]}{\int_{s^G} [\text{Tr} e^{\hat{\theta}_{1\text{RSB}}}]^m}, \quad (\text{A4})$$

and

$$\begin{aligned} & m \frac{t^2}{4} (l-1) [(r_1 + v)^l - (r_1)^l] \\ &= -\frac{1}{m} \int_{z^G} \ln \int_{s^G} [\text{Tr} e^{\hat{\theta}_{1\text{RSB}}}]^m \\ &+ \int_{z^G} \frac{\int_{s^G} [\text{Tr} e^{\hat{\theta}_{1\text{RSB}}}]^m \ln [\text{Tr} e^{\hat{\theta}_{1\text{RSB}}}]}{\int_{s^G} [\text{Tr} e^{\hat{\theta}_{1\text{RSB}}}]^m}. \end{aligned} \quad (\text{A5})$$

#### APPENDIX B

The only nonzero sums are

$$\lim_{n \rightarrow 0} \frac{1}{n} \sum'_{\alpha, \beta} (\delta q^{\alpha\beta})^3 = (m-1) \eta^3 - m \xi^3 \quad (\text{B1})$$

and

$$\begin{aligned} \lim_{n \rightarrow 0} \frac{1}{n} \sum'_{\alpha, \beta, \gamma} \delta q^{\alpha\beta} \delta q^{\beta\gamma} \delta q^{\gamma\alpha} &= (m-1)(m-2) \eta^3 \\ &- 3m(m-1) \eta \xi^2 + 2m^2 \xi^3, \end{aligned} \quad (\text{B2})$$

$$\begin{aligned} \lim_{n \rightarrow 0} \frac{1}{n} \sum'_{\alpha, \beta, \gamma} (\delta q^{\alpha\beta})^2 \delta q^{\alpha\gamma} &= (m-1)^2 \eta^3 - m(m-1)(\eta \xi^2 + \eta^2 \xi) \\ &+ m^2 \xi^3, \end{aligned} \quad (\text{B3})$$

$$\begin{aligned} \lim_{n \rightarrow 0} \frac{1}{n} \sum'_{\alpha, \beta, \gamma, \delta} \delta q^{\alpha\beta} \delta q^{\alpha\gamma} \delta q^{\beta\delta} &= (m-1)^3 \eta^3 + 3m^2(m-1) \eta \xi^2 \\ &- 3m(m-1)^2 \eta^2 \xi - m^3 \xi^3, \end{aligned} \quad (\text{B4})$$

where  $\eta = r + v$  and  $\xi = r$ . The prime on the sum means that only superscripts belonging to the same  $\delta q$  are necessarily different in  $\Sigma'$ . The sum in Eq. (B4) remains the same if we replace,  $\delta q^{\beta\delta}$  by  $\delta q^{\alpha\delta}$ .

#### APPENDIX C

The formulas used to calculate the parameters are

$$W = \langle \hat{Q}_1^2 \hat{Q}_2^2 \rangle - 2 \langle \hat{Q}_1^2 \hat{Q}_2 \hat{Q}_3 \rangle + \langle \hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \rangle, \quad (\text{C1})$$

$$L = -\langle \hat{Q}_1^2 \hat{Q}_2 \hat{Q}_3 \rangle + \langle \hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \rangle, \quad (\text{C2})$$

$$C = -(B_2 + B_2') + 2B_3 + B_3' - B_4, \quad (C3)$$

$$D = -3B_3 - B_3' + 3B_4, \quad (C4)$$

where

$$B_2 = \frac{1}{2} \langle \hat{Q}_1^2 \hat{Q}_2^2 \hat{Q}_3 \hat{Q}_4 \rangle + \frac{1}{2} \langle \hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \hat{Q}_5 \hat{Q}_6 \rangle - \langle \hat{Q}_1^2 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \hat{Q}_5 \rangle,$$

$$B_2' = \frac{1}{3} \langle \hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \hat{Q}_5 \hat{Q}_6 \rangle - \frac{1}{2} \langle \hat{Q}_1^2 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \hat{Q}_5 \rangle + \frac{1}{6} \langle \hat{Q}_1^3 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \rangle,$$

$$B_3 = \frac{1}{6} \langle \hat{Q}_1^2 \hat{Q}_2^2 \hat{Q}_3^2 \rangle - \frac{1}{2} \langle \hat{Q}_1^2 \hat{Q}_2^2 \hat{Q}_3 \hat{Q}_4 \rangle - \frac{1}{6} \langle \hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \hat{Q}_5 \hat{Q}_6 \rangle + \frac{1}{2} \langle \hat{Q}_1^2 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \hat{Q}_5 \rangle,$$

$$B_3' = - \langle \hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \hat{Q}_5 \hat{Q}_6 \rangle + \frac{5}{2} \langle \hat{Q}_1^2 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \hat{Q}_5 \rangle - \frac{1}{2} \langle \hat{Q}_1^3 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \rangle - \frac{3}{2} \langle \hat{Q}_1^2 \hat{Q}_2^2 \hat{Q}_3 \hat{Q}_4 \rangle + \frac{1}{2} \langle \hat{Q}_1^3 \hat{Q}_2^2 \hat{Q}_3 \rangle,$$

$$B_4 = \frac{1}{3} \langle \hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \hat{Q}_5 \hat{Q}_6 \rangle - \langle \hat{Q}_1^2 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \hat{Q}_5 \rangle + \frac{1}{3} \langle \hat{Q}_1^3 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \rangle + \frac{3}{4} \langle \hat{Q}_1^2 \hat{Q}_2^2 \hat{Q}_3 \hat{Q}_4 \rangle - \frac{1}{2} \langle \hat{Q}_1^3 \hat{Q}_2^2 \hat{Q}_3 \rangle + \frac{1}{12} \langle \hat{Q}_1^3 \hat{Q}_2^3 \rangle,$$

and

$$\langle \hat{Q}_\gamma^k \hat{Q}_\delta^n \dots \rangle = \frac{\text{Tr}[(\hat{Q}^\gamma)^\gamma (\hat{Q}^\delta)^\delta \dots \exp \Xi]}{\text{Tr}[\exp \Xi]}, \quad (C5)$$

$$\hat{\Xi} = \frac{t^2}{2} p \sum_\alpha (\hat{Q}^\alpha)^2 + t^2 q_{RS} \sum_{\alpha > \beta} \hat{Q}^\alpha \hat{Q}^\beta. \quad (C6)$$

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