

# Quadrupolar glass state in para-hydrogen and ortho-deuterium under pressure

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The main features of the possible quadrupolar glass state in ortho-deuterium and para-hydrogen under high pressure are predicted and considered in replica-symmetric approximation in analogy with glassy behavior of diluted ortho-hydrogen at low pressures. The quadrupolar model with  $J = 2$  is suggested. The orientational order and glass regime grow continuously on cooling just as it is in the case of ortho-para hydrogen mixtures at zero pressure.

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The structure of high pressure phases of solid hydrogen has been widely investigated recently (e.g. [1, 2]). At low pressures, the centers of para-hydrogen and ortho-deuterium molecules occupy the lattice sites of the hcp structure. The molecules are in spherically symmetric phase (I or SP). Between 28 Gpa for *o*-D<sub>2</sub> and 110 Gpa for *p*-H<sub>2</sub> and  $\sim 150$  Gpa the molecules become orientationally ordered in broken-symmetry phase II (BS).

High pressure breaks the rotational symmetry of the  $J = 0$  solids. The ordering occurs even in the systems of para-hydrogen and ortho-deuterium molecules because of mixing of higher order  $J$  levels with the ground state  $J = 0$  as a result of the increase of the intermolecular interactions at high pressures [1, 2]. The anisotropic interaction between two molecules is dominated at low pressures [3] by electrostatic quadrupole-quadrupole (EQQ) interaction, which plays a major role below 100 Gpa [1, 4]. However it is necessary to take into account other anisotropic interactions to understand the results of precise experiments (e.g. Raman scattering [1]).

The purpose of this article is to show the possibility of orientational glass state in solid *p*-H<sub>2</sub> and *o*-D<sub>2</sub> under pressure. Only the main features of this phenomenon will be taken into account. The  $J = 0 \rightarrow J = 2$  transitions take place as a result of the pressure increasing. In this case the  $J = 2$  molecules may be randomly distributed on a close packed lattice. It has been indicated in [2, 5] that rotational disorder under pressure may be frozen. The molecules with  $J = 0$  are spherically symmetric, have no electric quadrupole moment and play the role of dilutant.

So we can consider the quadrupolar glass state in analogy with glassy behavior of diluted *o*-H<sub>2</sub> and *p*-D<sub>2</sub> at low temperatures and pressures. In this case only the

ortho-hydrogen and para-deuterium molecular species are orientable. They have orbital angular momentum  $J = 1$ . The ordered state is characterized by a long-range orientational order at high ortho-H<sub>2</sub> and para-D<sub>2</sub> concentrations [3]. However, for concentrations less than approximately 55 %, measurements show no evidence of orientational phase transition. Instead, NMR experiments have been interpreted in terms of freezing of the the orientational degrees of freedom [3, 6]. This state is so called quadrupolar glass.

The EQQ interaction can bring about orientational glass state at high pressure in *p*-H<sub>2</sub> and *o*-D<sub>2</sub>. The rough estimation of  $0 \rightarrow 2$  transition probability  $\alpha$  can be done [4, 5] using quantum mechanical perturbation theory because the main anisotropic part (EQQ) of the intermolecular interaction is small [3]. We have  $\alpha = 4 \cdot 10^{-4}$  for D<sub>2</sub> and  $\alpha = 6 \cdot 10^{-5}$  for H<sub>2</sub> at zero pressure. The probability to find a  $J = 2$  molecule increases strongly with pressure;  $\alpha = 0.1$  at 40 Gpa for D<sub>2</sub> and 150 Gpa for H<sub>2</sub> and  $\alpha = 0.4$  for D<sub>2</sub> at 150 Gpa. It is possible that an intermediate range of  $\alpha$  exists where a quadrupolar glass occurs.

Let us consider the system of particles on lattice sites  $i, j$  with the truncated EQQ Hamiltonian

$$H = -\frac{1}{2} \sum_{i \neq j} J_{ij} Q_i Q_j, \quad (1)$$

where the quadrupole component  $Q = \frac{1}{2} [3(z/r)^2 - 1]$  can be replaced by equivalent operator with the same matrix elements  $\hat{Q} \sim [3J_z^2 - J(J+1)]$  in the space  $J = \text{const}$ .  $\text{Tr} \hat{Q} = 0$ .

Quadrupolar glass freezing in mixtures of ortho- and para-hydrogen has been considered [7] with

$$Q = 3J_z^2 - 2, \quad (2)$$

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where  $J_z = 1, 0, -1$  and  $J = 1$ .

This model describes well the zero pressure experiments on ortho-para mixtures even in replica-symmetric approach.

Now the Hamiltonian (1) will be examined on the condition  $J = 2$  and  $J_z = 0, 1, -1, 2, -2$ :

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

where  $J_{ij}$  are random exchange interactions with Gaussian probability distribution

$$P(J_{ij}) = \frac{1}{\sqrt{2\pi J}} \exp \left[ -\frac{(J_{ij} - J_0)^2}{2J^2} \right].$$

The scaling  $J = \tilde{J}/\sqrt{N}$ ,  $J_0 = \tilde{J}_0/N$  ensures as usual sensible thermodynamic limit. The multiplier 1/3 in (3) is used for simplicity.

Using replica method the free energy is obtained in the form:

$$\begin{aligned} \langle F \rangle_J / NkT = & - \lim_{n \rightarrow 0} \frac{1}{n} \max \left\{ - \sum_{\alpha} \frac{(x^{\alpha})^2}{2} - \sum_{\alpha} \frac{(w^{\alpha})^2}{2} - \right. \\ & - \sum_{\alpha > \beta} \frac{(y^{\alpha, \beta})^2}{2} + \ln \text{Tr}_{\{Q^{\alpha}\}} \exp \left[ \sum_{\alpha} x^{\alpha} \sqrt{\frac{\tilde{J}_0}{kT}} Q^{\alpha} + \right. \\ & \left. \left. + \sum_{\alpha} w^{\alpha} \frac{1}{\sqrt{2}} t (Q^{\alpha})^2 + \sum_{\alpha > \beta} y^{\alpha, \beta} t Q^{\alpha} Q^{\beta} \right] \right\}, \end{aligned}$$

where  $t = \tilde{J}/kT$ .

Extreme conditions for the free energy give the equations for order parameters

$$m^{\alpha} = (x^{\alpha})^{\text{extr}} / \sqrt{\frac{\tilde{J}_0}{kT}} = \langle Q^{\alpha} \rangle_{\text{eff}}; \quad (4)$$

$$q^{\alpha, \beta} = (y^{\alpha, \beta})^{\text{extr}} / t = \langle Q^{\alpha} Q^{\beta} \rangle_{\text{eff}};$$

$$p^{\alpha} = (w^{\alpha})^{\text{extr}} \sqrt{2} / t = \langle (Q^{\alpha})^2 \rangle_{\text{eff}};$$

where averaging is performed with the effective Hamiltonian

$$\begin{aligned} -H_{\text{eff}} = & \sum_{\alpha} \frac{\tilde{J}_0}{kT} m^{\alpha} Q^{\alpha} + \sum_{\alpha} \frac{t^2}{2} p^{\alpha} (Q^{\alpha})^2 + \\ & + \sum_{\alpha > \beta} t^2 q^{\alpha, \beta} Q^{\alpha} Q^{\beta}. \end{aligned}$$

Free energy and order parameters in the replica-symmetric [8] case become

$$\begin{aligned} F = & -NkT \left\{ - \left( \frac{\tilde{J}_0}{kT} \right) \frac{m^2}{2} + t^2 \frac{q^2}{4} - t^2 \frac{p^2}{4} + \right. \\ & \left. + \int_{-\infty}^{\infty} \frac{dz}{\sqrt{2\pi}} \exp \left( -\frac{z^2}{2} \right) \ln \text{Tr} [\exp (\theta_2 Q + \theta_1 Q^2)] \right\}. \end{aligned} \quad (5)$$

Here

$$\theta_1 = t^2 \frac{p - q}{2} \text{ and } \theta_2 = zt\sqrt{q} + m \left( \frac{\tilde{J}_0}{kT} \right).$$

Order parameters are:  $m$  – quadrupolar order parameter (analog of magnetic moment in spin glasses),  $q$  – glass order parameter and  $p$  – auxiliary order parameter:

$$\begin{aligned} m = & \int_{-\infty}^{\infty} \frac{dz}{\sqrt{2\pi}} \exp \left( -\frac{z^2}{2} \right) \frac{\text{Tr} [Q \exp (\theta_2 Q + \theta_1 Q^2)]}{\text{Tr} [\exp (\theta_2 Q + \theta_1 Q^2)]} = \\ = & \int_{-\infty}^{\infty} \frac{dz}{\sqrt{2\pi}} \exp \left( -\frac{z^2}{2} \right) 2 \times \end{aligned} \quad (6)$$

$$\times \left\{ \frac{\exp(4\theta_1) [-\exp(-2\theta_2) + \exp(2\theta_2)] - \exp(-\theta_2\theta_1)}{\exp(4\theta_1) [\exp(-2\theta_2) + 2\exp(2\theta_2)] + 2\exp(-\theta_2\theta_1)} \right\},$$

$$\begin{aligned} q = & \int_{-\infty}^{\infty} \frac{dz}{\sqrt{2\pi}} e^{-z^2/2} \left\{ \frac{\text{Tr} [Q \exp (\theta_2 Q + \theta_1 Q^2)]}{\text{Tr} [\exp (\theta_2 Q + \theta_1 Q^2)]} \right\}^2 = \\ = & \int_{-\infty}^{\infty} \frac{dz}{\sqrt{2\pi}} \exp \left( -\frac{z^2}{2} \right) 4 \times \end{aligned} \quad (7)$$

$$\times \left\{ \frac{\exp(4\theta_1) [-\exp(-2\theta_2) + \exp(2\theta_2)] - \exp(-\theta_2\theta_1)}{\exp(4\theta_1) [\exp(-2\theta_2) + 2\exp(2\theta_2)] + 2\exp(-\theta_2\theta_1)} \right\}^2,$$

$$\begin{aligned} p = & \int_{-\infty}^{\infty} \frac{dz}{\sqrt{2\pi}} e^{-z^2/2} \frac{\text{Tr} [Q^2 \exp (\theta_2 Q + \theta_1 Q^2)]}{\text{Tr} [\exp (\theta_2 Q + \theta_1 Q^2)]} = \\ = & \int_{-\infty}^{\infty} \frac{dz}{\sqrt{2\pi}} \exp \left( -\frac{z^2}{2} \right) 2 \times \end{aligned} \quad (8)$$

$$\times \left\{ \frac{2\exp(4\theta_1) [-\exp(-2\theta_2) + 2\exp(2\theta_2)] - \exp(-\theta_2\theta_1)}{\exp(4\theta_1) [\exp(-2\theta_2) + 2\exp(2\theta_2)] + 2\exp(-\theta_2\theta_1)} \right\}.$$

The temperature dependence of order parameters obtained from (6)–(8) is represented in Fig.1. There is no trivial solution  $m = 0$ ,  $q = 0$  at finite temperature because  $\text{Tr} Q^3 \neq 0$ . The orientational order and glass regime grow continuously on cooling just as it is in the case of the Hamiltonian (1)–(2) describing the ortho-para hydrogen mixtures at zero pressure [7]. The quadrupolar long range order is present for  $T > 0$  even if  $\tilde{J}_0 = 0$ . In the pure case ( $\tilde{J} = 0$ ,  $\tilde{J}_0 \neq 0$ ) we have from (6)–(7)  $q^{1/2} = m$ .

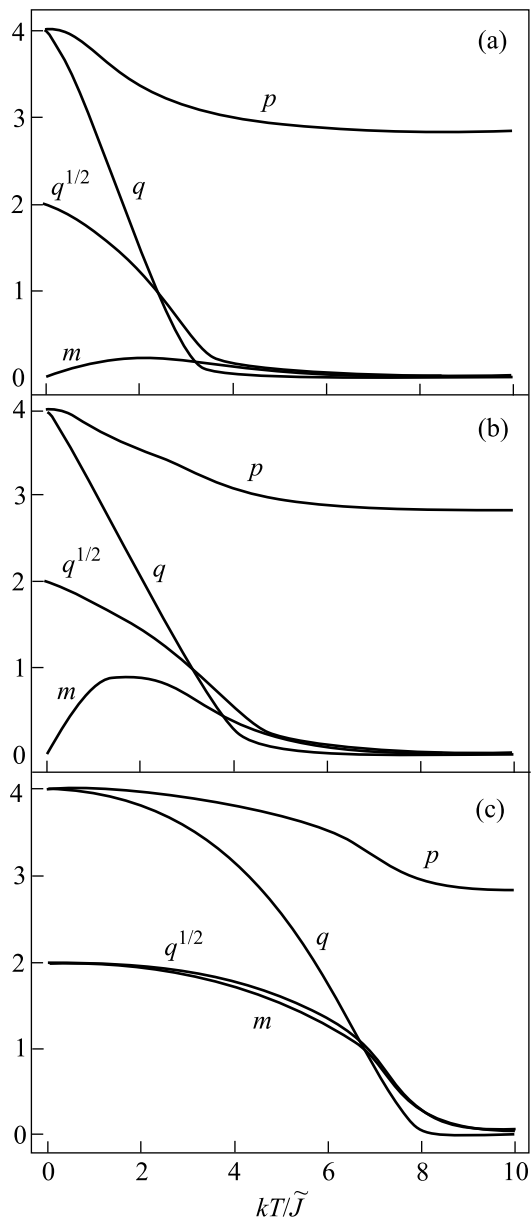


Fig.1. Order parameters for the cases: (a)  $\tilde{J}_0/\tilde{J} = 0$ , (b)  $\tilde{J}_0/\tilde{J} = 1$ , and (c)  $\tilde{J}_0/\tilde{J} = 2.5$

It is easy to see from (2) that  $Q^2 = 2 - Q$ . So the equation for  $p$  is not independent and  $p = 2 - m$ . There is no similar expression for  $Q^2$  from (3) and for order parameter  $p$  here.

Using the equation (5) for the free energy the heat capacity can be written in the form

$$\frac{C_v}{kN} = \frac{d}{d(kT/\tilde{J})} \left\{ \left( \frac{\tilde{J}}{kT} \right) \frac{q^2 - p^2}{2} \right\} - \left( \frac{\tilde{J}_0}{\tilde{J}} \right) m \frac{dm}{d(kT/\tilde{J})}. \quad (9)$$

Specific heat as a function of  $(kT/\tilde{J})$  calculated from (9) for the four cases of  $(\tilde{J}_0/\tilde{J})$  is shown in Fig.2. The

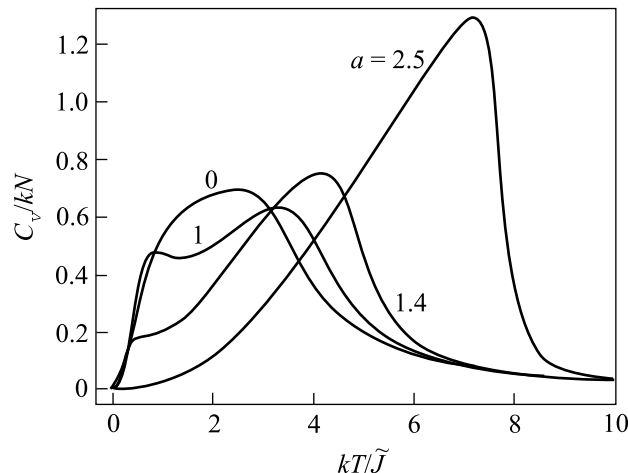


Fig.2. Specific heat as a function of  $(kT/\tilde{J})$  for the cases  $a = \tilde{J}_0/\tilde{J} = \{0; 1; 1.4; 2.5\}$

dependence of  $C_v$  on the temperature is smooth as in ortho-para mixtures at zero pressure.

In conclusion, the main features of the random quadrupolar system (1), (3) are considered in the replica-symmetric mean-field approximation. This system with  $J = 2$  was not been considered earlier. The possible realization of the quadrupolar glass state under high pressure in ortho-deuterium and para-hydrogen is predicted.

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