Effect of the zero-point rotational motions on the quadrupolar glass order parameter in solid hydrogen

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With the help of thermodynamic perturbation theory the quantum effects on the quadrupolar glass order parameter of solid hydrogen are studied. It is shown that due to the quantum nature of the system, in the zero temperature limit the quadrupolar glass order parameter is reduced 50% in comparision with the case when quantum effects are not taken into account implicitly.

In the past 15 years there has been considerable experimental[1-10] and theoretical[11-23] studies, including Monte Carlo simulations[24,25] on the orientational ordering of randomly distributed quadrupole-bearing molecules of orthohydrogen (o-H_2) in a matrix of spherical parahydrogen species ($p-H_2$) for concentrations X of o-H_2 molecules smaller than 0.55. For such concentrations, no long-range order exists, and it is now believed that solid ortho-para hydrogen mixtures for $X < 0.55$ form a quadrupolar glass (QG), in which the local average orientation of o-H_2 molecule vary randomly from site to site without any long-range spatial correlation. In the previous paper by the author and a collaborator[23] (hereafter cited as I) the exact orientational Hamiltonian[26,27] for electrical quadrupole-quadrupole (EQQ) interaction has been reduced to some simplified one, which contains only two commuting components of the quadrupolar momentum operator, i.e.,

$$Q_{0,i} = 1 - \frac{3}{2}(J_i^z)^2 \tag{1a}$$

and

$$Q_{2,i} = \frac{\sqrt{3}}{2}\left[(J_i^x)^2 - (J_i^y)^2\right] \tag{1b}$$

related to the o-H_2 molecule at the ith site, where the operators J_i^x, J_i^y and J_i^z denote the components of the angular momentum operator $\mathbf{J}_i$ and act in the manifold of rotational states with the quantum number $J = 1$.[26,27] Moreover, the orientation of each o-H_2 molecule is specified to the local coordinate system chosen so as to coincide with the principal axes of the molecular quadrupolar momentum tensor.[1,8,26] The contribution due to the noncommuting part of the full EQQ Hamiltonian has been taken into account implicitly by the appropriate renormalization of the EQQ couplings (cf. I). In the local coordinate system only two intrinsic quadrupolar parameters remain (cf. Ref. 7), i.e.,

$$\sigma_i = \langle Q_{0,i}\rangle_T, \tag{2a}$$

$$\eta_i = \langle Q_{2,i}\rangle_T, \tag{2b}$$

where $\langle\cdots\rangle_T$ denotes a thermal average.

The local quadrupolar parameters σ_i (2a) and η_i (2b) measure, respectively, the alignment of orthomolecule along the local z_i axis and eccentricity.[7]

The temperature dependence of the quadrupolar glass order parameter $q = \left[\sigma_i^2 + \eta_i^2\right]_{av}$,[7,8,18] where $[\cdots]_{av}$ denotes an averaging over disorder, calculated in I is in fairly good agreement with experimental data[8] except for the range of very small temperatures where the value of q calculated theoretically is approximately twice larger than that obtained from an NMR experiment.[8]

In the present article we will show that such a discrepancy is caused by the zero-point rotational motions of o-H_2, which cannot be taken into account in the frame of the model formulated in I. Specifically, we will show that including, even by means of the thermodynamic perturbation theory, the noncommuting part of the full EQQ Hamiltonian gives considerable improving of the results in the low-temperature limit.

Similarly, as in I, we decompose the exact EQQ Hamiltonian into two parts: the diagonal part H_0 and nondiagonal (in the eigenstates of H_0) H_1 defined as

$$H_0 = -\frac{1}{2}\sum_{i\neq j}\left[\hat{x}_i\hat{x}_j\left(4J_{ij}^{00}Q_{0,i}Q_{0,j} - 4\sqrt{\frac{2}{3}}J_{ij}^{02}Q_{0,i}Q_{2,j} - 4\sqrt{\frac{2}{3}}J_{ij}^{20}Q_{2,i}Q_{0,j} + \frac{8}{3}J_{ij}^{22}Q_{2,i}Q_{2,j}\right)\right] \tag{3}$$

and

$$H_1 = -\frac{1}{2}\sum_{i\neq j}\sum_{\mu,\nu=\pm1,-2}J_{ij}^{\mu\nu}\hat{x}_iS_i^\mu\hat{x}_jS_j^\nu, \tag{4}$$

where $\hat{x}_i$ denotes the occupation number equal to 1 and 0 for ortho and parahydrogen molecule, respectively,

$$S_i^{+1} = \frac{1}{\sqrt{2}}\left(J_i^+J_i^z + J_i^zJ_i^+ + J_i^-J_i^z + J_i^zJ_i^-\right), \tag{5a}$$

$$S_i^{-1} = \frac{-i}{\sqrt{2}}\left(J_i^+J_i^z + J_i^zJ_i^+ - J_i^-J_i^z - J_i^zJ_i^-\right), \tag{5b}$$

and

$$S_i^{-2} = \frac{-i}{\sqrt{2}}\left[\left(J_i^+\right)^2 - \left(J_i^-\right)^2\right] \tag{5c}$$

with

$$J_i^{\pm} = J_i^x \pm iJ_i^y .$$

The 25 parameters $J_{ij}^{\mu\nu}$ entering Eqs (3) and (4) are simple linear combinations of EQQ couplings $\gamma_{ij}^{\mu,\nu}$ defined in Ref. 26 (cf. also I). Similarly as in Refs. 22 and I we decompose the averaging over the disorder $[\cdots]_{av}$ into a sequence of two stages: first one averages over directions of the local coordinate system (the orientational averaging) and next over configurations of o-H_2 species. The orientational averaging gives

$$\overline{J_{ij}^{\mu\nu}} = 0 \tag{6}$$

and

$$\overline{J_{ij}^{\mu\nu}J_{i'j'}^{\mu'\mu'}} = \left(\delta_{ii'}\delta_{jj'}\delta_{\mu\mu'}\delta_{\nu\nu'} + \delta_{ij'}\delta_{i'j}\delta_{\mu\nu'}\delta_{\mu'\nu}\right)A_\mu^2 A_\nu^2 J_{ij}^2 , \tag{7}$$

where the coefficients A_μ and parameter J_{ij} are defined in I.

With the help of the replica method taking into account Eqs. (6) and (7) we obtain:

$$-\beta F = \lim_{n \to 0}\frac{1}{n}\ln Z_n , \tag{8}$$

where n denotes the replicas number and

$$Z_n = \text{Tr}T_\tau \exp\left[\int_0^\beta d\tau d\tau' H(\tau,\tau')\right] \tag{9}$$

with

$$H(\tau,\tau') = \frac{1}{4}\sum_{i,j}\sum_{\alpha,\alpha'}J_{ij}^2 \hat{x}_i \hat{q}_i^{\alpha\alpha'}(\tau,\tau')\hat{x}_j \hat{q}_j^{\alpha\alpha'}(\tau,\tau') , \tag{10}$$

where $0 < \tau,\tau' < \beta$ denote the imaginary times, T_τ is the time-ordering operator, and the replica indices α,α' run from 1 to n. The parameter J_{ij} in Eq. (10) differs from that entering Eq. (6) by the factor $4/25$, i.e., the change $J_{ij} \to 4/25 J_{ij}$ has been made. The operator $\hat{q}_i^{\alpha\alpha'}$ in Eq. (10) is defined as

$$\hat{q}_i^{\alpha\alpha'} = \sum_{\mu=0,2}Q_{\mu,i}^\alpha(\tau)Q_{\mu,i}^{\alpha'}(\tau')$$
$$+ \frac{3}{8}\sum_{\mu=\pm1,-2}S_{i,\alpha}^\mu(\tau)S_{i,\alpha'}^\mu(\tau') . \tag{11}$$

A formal dependence of the quadrupolar operators on imaginary time has been introduced in order to treat them as c numbers.[28] Taking into account the complexity of the problem, we will calculate the QG order parameter within the replica symmetric mean-field approach. After a Sherrington-Kirkpatrick type of procedure (cf. Ref. 29) generalized to the quantum spin,[28,30] one obtains in the limit $n \to 0$ the following result:

$$\beta F = -\frac{\beta^2}{4}NzX^2J^2q + \frac{1}{4}NzX^2J^2\int_0^\beta d\tau d\tau' p^2(\tau - \tau') - \lim_{n \to 0}\frac{1}{n}\ln \text{Tr}T_\tau$$
$$\times \exp\left\{NzX^2J^2\left[q\sum_{\alpha \neq \alpha'}\int_0^\beta d\tau d\tau' \hat{q}_i^{\alpha\alpha'}(\tau,\tau') + \sum_\alpha \int_0^\beta d\tau d\tau' p(\tau - \tau')\hat{q}^{\alpha\alpha}(\tau,\tau')\right]\right\} , \tag{12}$$

where N, $z = 12$, X and J denote, respectively, the total number of molecules, the coordination number for hcp lattice, concentration of o-H_2 species, and the parameter J_{ij} for the nearest neighbors (cf. I). Furthermore, in Eq. (12) q is the QG order parameter and $p(\tau - \tau')$ denotes the parameter diagonal in the replica indices, which is equal to

$$\sum_{\mu=0,2}\left[\langle T_\tau Q_{\mu,i}^\alpha(\tau)Q_{\mu,i}^{\alpha'}(\tau')\rangle_T\right]_{av} + \frac{3}{8}\sum_{\mu=\pm1,-2}\left[\langle T_\tau S_{i,\alpha}^\mu(\tau)S_{i,\alpha'}^\mu(\tau')\rangle_T\right]_{av} .$$

Note that for the simplicity in Eq. (12) the sums like $\sum_{i,j}\cdots$ has been replaced by $NzX^2\cdots$.

In the static approximation, which will be used, $p(\tau - \tau') = p$. Thus we get finally for the free energy the following formula:

$$\frac{\beta F}{NX} = -\frac{\beta^2}{4}zXJ^2q^2 + \frac{\beta^2}{4}zXJ^2p^2$$
$$- \frac{1}{(2\pi)^{5/2}}\int_{-\infty}^\infty \prod_\mu^5 dx_\mu \exp\left(-\frac{1}{2}\sum_\mu x_\mu^2\right)\ln\left[\frac{1}{(2\pi)^{5/2}}\int_{-\infty}^\infty \prod_\mu^5 dy_\mu \exp\left(-\frac{1}{2}\sum_\mu y_\mu^2\right)\text{Tr}\exp(\beta JzX\mathcal{H})\right] \tag{13}$$

with

$$\mathcal{H} = \sum_\mu (x_\mu\sqrt{q} + y_\mu\sqrt{p - q})R_\mu , \tag{14}$$

where R_μ is Q_μ and S^μ for $\mu = 0,2$ and $\mu = \pm1. - 2$, respectively, and the operator R_μ refers to an arbitrary site

occupied by the o-H_2 molecule. The parameters q and p can be calculated from the stationary conditions:

$$\frac{\partial F}{\partial q} = 0 \tag{15a}$$

and

$$\frac{\partial F}{\partial p} = 0 . \tag{15b}$$

The solution of Eqs. (15a) and (15b) is an extremely tremendous numerical problem, and we will not perform it there. Our aim is to show with the help of simple analytical method, i.e., the thermodynamic perturbation theory that the treating the non-diagonal part H_1 (4) of the full EQQ Hamiltonian as a perturbation leads to the significant decreasing of the QG order parameter q at $T \to 0$ in accordance with experimental data.[8]

Thus we decompose $\mathcal{H}$ (14) into two parts:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 , \tag{16}$$

where

$$\mathcal{H}_0 = \sum_{\mu=0,2} (x_\mu \sqrt{q} + y_\mu \sqrt{p-q}) Q_\mu \tag{17}$$

and

$$\mathcal{H}_1 = \sum_{\mu=\pm 1,-2} (x_\mu \sqrt{q} + y_\mu \sqrt{p-q}) S^\mu , \tag{18}$$

which is generated by H_1 (4). The free energy (13) is approximated as follows:

$$\frac{\beta F}{NX} \approx \frac{\beta F_0}{NX} + \frac{\beta F_1}{NX} , \tag{19}$$

where F_1 is the second-order correction with the respect of $\mathcal{H}_1$ (18). After tedious but straighforward calculations one obtains

$$\frac{\beta F_0}{NX} = -\frac{\beta^2}{4} zX J^2 q^2 + \frac{\beta^2}{4} zX J^2 p^2 - \frac{\beta^2}{2} zX J^2 (p-q)$$
$$- \frac{1}{(2\pi)} \int_{-\infty}^{\infty} d\xi d\eta \exp[-\tfrac{1}{2}(\xi^2 + \eta^2)] \ln[1 + 2\exp(-3\beta J zX \sqrt{q}\xi/2) \cosh(\sqrt{3}\beta J zX \eta)] \tag{20}$$

and

$$\frac{\beta F_1}{NX} = \frac{3\beta}{2} J^2 zX p e^{\frac{3}{8}\beta^2 J^2 zX} \int_{-\infty}^{\infty} \frac{d\xi d\eta}{2\pi} e^{-\frac{1}{2}(\xi^2+\eta^2)} \left\{ \exp\left(\frac{\beta J}{4}\sqrt{zXq}(\xi - \sqrt{3}\eta)\right) \right.$$
$$\times \int_{-\beta/2}^{\beta/2} d\tau \exp\left[\tfrac{3}{2}\tau^2 J^2 zX(p-q) - \tfrac{3}{2}\tau J\sqrt{zXq}(\xi + \eta/\sqrt{3})\right]$$
$$+ \exp^{\frac{\beta J}{2}\sqrt{zXq}\xi} \int_{-\beta/2}^{\beta/2} d\tau \exp\left[\tfrac{3}{2}\tau^2 J^2 zX(p-q) - \tau J\sqrt{3zXq}\eta\right]$$
$$+ \exp\left(\frac{\beta J}{4}\sqrt{zXq}(\xi + \sqrt{3}\eta)\right) \int_{-\beta/2}^{\beta/2} d\tau \exp\left[\tfrac{3}{2}\tau^2 J^2 zX(p-q) - \tfrac{3}{2}\tau J\sqrt{zXq}(\xi - \eta/\sqrt{3})\right] \right\}$$
$$\times \left[e^{\beta J\sqrt{zXq}\xi} + 2e^{-\frac{\beta J}{2}\sqrt{zXq}\xi} \cosh\left(\frac{\sqrt{3}}{2}\beta J\sqrt{zXq}\eta\right) \right]^{-1} . \tag{21}$$

The integration over τ can be reduced to the error function, for the imaginary argument, defined as[31] $\mathrm{erfi}(u) = 2/\sqrt{\pi} \int_0^u d\tau e^{\tau^2}$, where in our case the variable u is proportional to the inverse temperature β. In the limit $T \to 0$ we use this function in the asymptotic form[32] for large u. Taking into account the leading terms in the limit $T \to 0$ in Eq. (21) we obtain surprisingly simple result:

With the help of Eq. (22), Eqs. (15a) and (15b) take the form:

$$\frac{\beta F}{NX} = -\frac{\beta^2 J^2 zX}{4} q^2 + \frac{\beta^2 J^2 zX}{4} p^2$$
$$- \frac{\beta^2 J^2 zX}{2}(p-q) - \frac{2p}{p-q}. \tag{22}$$

$$q - 1 + \frac{4T^2}{J^2 zX} \frac{p}{(p-q)^2} = 0 \qquad (23a)$$

and

$$p - 1 - \frac{4T^2}{J^2 zX} \frac{1}{p-q} + \frac{4T^2}{J^2 zX} \frac{1}{p-q}$$

$$+ \frac{4T^2}{J^2 zX} \frac{p}{(p-q)^2} = 0 . \qquad (23b)$$

This gives

$$(q - p)^2 = \frac{4T^2}{J^2 zX} \qquad (24a)$$

and

$$q + p = 1 . \qquad (24b)$$

For the unperturbed case, i.e., $\mathcal{H} = \mathcal{H}_0$ it can be easily

shown that at $T = 0$ $q = p = 1$. There is no reason that taking into account $\mathcal{H}_1$ as the perturbation q differs from p. Moreover, from Eq. (24a) it follows that for $T = 0$ one of the solutions (23) satisfies the relation $q = p$. Taking this into account we obtain from (24b) $q = p = 1/2$. The extrapolation of q to $T = 0$ from NMR data measured by Meyer and Washburn[8] gives that $q \approx 0.40$, 0.55, and 0.64 for the orthohydrogen concentration $X = 0.25$, 0.39, and 0.45, respectively. Therefore, it is seen that the effect of the non-diagonal part, of the EQQ Hamiltonian responsible for the zero-point rotational motions gives even in the frame of the perturbation approach, the result towards experimental data[8] extrapolated to $T = 0$.

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[1] N. S. Sullivan, M. Devoret, B. P. Cowan, and C. Urbina, Phys. Rev. B **17**, 5016 (1978).

[2] N. S. Sullivan and D. Estève, Physica B+C **107**, 189 (1981).

[3] D. Estève and N. S. Sullivan, J. Phys. C **15**, 4481 (1982); N. S. Sullivan, D. Estève, and M. Devoret, ibid. **15**, 4985 (1982).

[4] S. Washburn, M. Calkins, H. Meyer, and A. B. Harris, J. Low Temp. Phys. **49**, 101 (1982).

[5] S. Washburn, M. Calkins, H. Meyer, and A. B. Harris, J. Low Temp. Phys. **53**, 585 (1983).

[6] D. J. Haase, L. R. Perrel, and A. M. Saleh, J. Low Temp. Phys. **55**, 283 (1984).

[7] N. S. Sullivan, M. Devoret, and D. Estève, Phys. Rev. B **30**, 4935 (1984).

[8] H. Meyer and S. Washburn, J. Low Temp. Phys. **57**, 31 (1984).

[9] M. Calkins and H. Meyer, J. Low Temp. Phys. **57**, 265 (1984).

[10] C. M. Edwards, D. Zhou, Y. Lin, and N. S. Sullivan, J. Low Temp. Phys. **72**, 1 (1988).

[11] V. B. Kokshenev, Solid State Commun. **55**, 143 (1985).

[12] A. B. Harris and H. Meyer, Can J. Phys. **63**, 3 (1985).

[13] Y. Lin and N. S. Sullivan, J. Low Temp. Phys. **65**, 1 (1986).

[14] Y. Lin and N. S. Sullivan, Mol. Liq. Cryst. **142**, 141 (1987).

[15] N. S. Sullivan, C. M. Edwards, Y. Lin, and D. Zhou, Can.

J. Phys. **65**, 1463 (1987)

[16] V. B. Kokshenev and A. A. Litvin, Sov. J. Low Temp. Phys. **13**, 195 (1987).

[17] N. S. Sullivan, Can. J. Chem. **66**, 908 (1988).

[18] X. Li, H. Meyer, and A. J. Berlinsky, Phys. Rev. B **37**, 3216 (1988).

[19] Y. Lin and N. S. Sullivan, Phys. Rev. B **38**, 5158 (1988).

[20] Y. Lin and N. S. Sullivan, J. Magn. Res. **86**, 319 (1990).

[21] V. B. Kokshenev, Phys. Status Solidi B **164**, 83 (1991).

[22] K. Walasek, Phys. Rev. B **46**, 14 480 (1992).

[23] K. Walasek and K. Lukierska-Walasek, Phys. Rev. B **49**, 9460 (1994).

[24] M. A. Klenin, Phys. Rev. B **23**, 5199 (1983).

[25] M. Devoret and D. Estève, J. Phys. C **16**, 1827 (1983).

[26] J. C. Raich and R. D. Etters, Phys. Rev. **168**, 425 (1968).

[27] A. B. Harris, Phys. Rev. B **1**, 1881 (1970).

[28] A. J. Bray and M. A. Moore, J. Phys. C **13**, L655 (1980).

[29] K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).

[30] K. Walasek and K. Lukierska-Walasek, Phys. Rev. B **34**, 4962 (1986).

[31] I. S. Gradstein and I. M. Ryzhik, *Tables of Integrals, Sums, Series, and Products* (Nauka, Moscow, 1971) (in Russian).

[32] H. Bateman and A. Erdélyi, *Higher Transcendental Functions* (McGraw-Hill, New York, 1953), Vol. 2.