PHYSICAL REVIEW B VOLUME 36, NUMBER 16 1 DECEMBER 1987

Mean-field theory of the proton glass

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(Received 15 January 1987)

The mixed ferroelectric-antiferroelectric compound $(Rb)_x(NH_4)_{1-x}H_2PO_4$ (RADP) exhibits a glassy phase which can be modeled as a spin glass. However, the protons whose order and disorder are being observed tunnel to a significant degree, making the spin glass an explicitly quantum-mechanical one. We solve the mean-field theory of a model for such a system, the Ising spin glass in a transverse field, by a novel combination of discretized-path-integral methods and replica techniques. The results provide an unambiguous microscopic picture of the effect of tunneling on a glass transition.

I. INTRODUCTION

From a theoretical standpoint, the glass transition[1] has proven equally resistant to the traditional methods of the solid state and the liquid state. Since glasses are, in general, topologically disordered (that is, the constituent molecules are disordered with respect to arrangement in space), lattice-based treatments of solids would seem to be of little relevance.[2] The integral equations and diagrammatic approaches of liquid theory are of course, undaunted by topological disorder.[3] However, they, too, seem inappropriate when confronted by the quenched (frozen-in) disorder characteristic of glasses.

An increasingly popular way to sidestep these difficulties, and one that we will pursue in this paper, is to consider a class of materials that might be called *glassy crystals*.[4-8] In many of these systems, typified by $K(Br)_{1-x}(CN)_x$,[5] $(Ar)_{1-x}(N_2)_x$,[6] and $(\text{para-}H_2)_{1-x}(\text{ortho-}H_2)_x$,[7] a crystalline solid is randomly doped with an impurity which fits neatly into the crystal lattice, but which possesses a rotational degree of freedom not present in the original material. At high enough temperatures the impurities (CN, N_2, and ortho-H_2, respectively) are orientationally disordered, regardless of concentration. However, when the concentration is high enough, there is a critical temperature below which the systems form an equilibrium orientationally ordered phase, whereas at lower concentrations, one finds a glass-transition temperature (T_g). Below this T_g, an orientationally disordered phase in formed (a so-called orientational glass) with the disorder frozen in rather than being thermal.

Even apart from the ill-posed question of whether such phases are "true" glasses, there are a number of reasons for looking at glassy crystals yet beyond these orientational glasses. To begin with, the orientational glass systems are complex. They inevitably go through crystal-structure changes in the relevant portions of their phase diagram, necessitating a coupled treatment of elastic, quadrupolar, and (sometimes) dipolar forces.[9] Moreover, even the simplest model which seems to capture the universal features of these systems attributes the glassiness to frustration imposed by the difficulties in ordering quadrupoles in three dimensions.[4] Since there is evidence that glassy behavior may be special in quadrupolar cases,[10] one should at least look at other examples for comparison purposes.

These comments should certainly not be construed as a claim that such materials are not relevant to the understanding of glasses. Indeed, among the many experimental attributes that these substances share with topological glasses is the presence of two-level systems—low-temperature behavior consistent with a finite density of zero-energy excitations and with a dynamics controlled by tunneling.[11,12] If one ever hopes to understand the ubiquity of these two-level systems it would clearly be helpful to understand tunneling in glassy crystals.

Accordingly, in this paper we will be considering a rather different kind of glassy crystal—one in which tunneling is manifestly important but in which the ordering is not quadrupolar and the crystal structure does not undergo dramatic changes. The *proton glass*,[13-15] RADP, as it is sometimes referred to, is the solid $Rb_{1-x}(NH_4)_xH_2PO_4$. One can think of it as a solid solution of the ferroelectric material RbH_2PO_4 (RDP) and the antiferroelectric material $(NH_4)H_2PO_4$ (ADP). Both of these materials are in the KH_2PO_4 (KDP) class of ferroelectric-antiferroelectrics.[16] Above a certain temperature (146 K for RDP and 148 K for ADP),[14] the acid (H_2) protons are thermally disordered, leading to a thermally random arrangement of dipoles—a paraelectric phase. Below this temperature, however, the protons (and hence the dipoles) spontaneously order. For RDP this order produces a macroscopic electrical polarization—a ferroelectric phase—but for ADP both the acid protons and the NH_4 ions hydrogen bond to the PO_4's. The resulting perturbed ordered dipolar pattern has nonzero polarization only on individual sublattices, so the crystal as a whole has no net moment—an antiferroelectric phase.

When RDP and ADP are mixed as $Rb_{1-x}(NH_4)_xH_2PO_4$, one finds a behavior reminiscent of orientational glasses. At concentrations close enough to the pure materials ($x < 0.22$ and $x > 0.74$),[14] one continues to observe an order-disorder transition from the paraelectric to the ferroelectric and antiferroelectric states, respectively. However, at intermediate concentrations, the transition is replaced by one to a proton glass state in which the disorder in proton positions becomes frozen in. The experimental evidence for there being such a glass transition is quite impressive;[13–15,17–19] in particular, we note the changes in Raman spectra,[14] the history dependence of the x-ray-diffraction studies,[17] and especially the observation of the same kind of Volgel-Fulcher frequency dependence[12] of thermal measurements that is found in topological glasses (and is found here over 16 decades in frequency).[15,18,19]

The presence of discrete proton positions and a well-characterized ferroelectric-antiferroelectric competition at each lattice site makes this material conceptually a little more straightforward than the orientational glass systems are. Nonetheless, one still has the same kind of fundamental questions to answer: (1) What is it that causes there to be a glassy phase instead of a paraelectric phase? For topological glass the equivalent question concerns how the solid glass differs from the supercooled liquid. (2) Is there a thermodynamic transition underlying the glass transition?[1] If there is, then perhaps the characteristic dependence of T_g on the measuring time scale, as dramatic as it is, can be viewed as simply a perturbation.

A third issue, which will particularly occupy our attention in this paper, deals with the significance of quantum fluctuation in glasses. The special relevance of this question lies in the two facts that one cannot have two-level tunneling dynamics without quantum tunneling and that the proton ordering in RADP, as evidenced by the large shifts in transition temperature upon deuteration of the pure components (146 → 223 K for RDP and 148 → 235 K for ADP),[16] is dominated by tunneling. We therefore suggest that the proton glass will eventually be an excellent candidate for a theoretical study of the origin of two-level systems (possibly even with some of the methodology presented here). However, the present paper will not be pursuing two-level systems, as such. The more obvious preliminary question (which we will pursue) is simply what quantum fluctuations do to the *stability* of the glassy phase—to T_g and to the range of glass-forming concentrations.

To try to answer these questions we will be performing a mean-field calculation on a quantum-mechanical spin-glass model for the RADP system. *Classical* spin-glass models, i.e., models with classical spins situated on lattice sites interacting with each other via quenched random bonds, have been discussed extensively in the literature,[12,20,21] so we will limit our discussion of them to the appropriate places in the text. We do note, though, that the use of such models instead of random vertex models[22] renders our study somewhat less applicable to details of RADP than one might like. The reason we have chosen our kind of model is largely because it makes possible a systematic generalization to a *quantal* spin-glass model. While there is considerably less known about quantum spin glasses than about their classical counterparts, there is practically nothing known about quantal vertex models for pure systems[23] (much less for disordered ones). Besides, our overall goal is less to mimic the special features of RADP than it is to understand the glass transition in a well-characterized system.

The quantal spin-glass studies that have been performed are mostly for the quantal Heisenberg spin glass.[24–28] These studies do raise interesting questions about the nature of the quantum coherence in the glassy region,[25] but the proper model for our purposes is really the *transverse Ising spin glass*.[29,30] Here, somewhat less work has been done. Chakrabarti[29] presented an outline of a mean-field theory but gave no explicit results for the phase diagram or transition temperature. Moreover, as pointed out by dos Santos, dos Santos, and Kischinhevsky[29] in their renormalization-group study of the zero-temperature behavior in one and two dimensions, Chakrabarti's use of the relationship between the d-dimensional quantal model and a $(d+1)$-dimensional classical model may not be quite correct. We shall return to this point later.

More recent mean-field studies have actually succeeded in calculating the critical condition for the *symmetric* transverse Ising spin glass (i.e., the model corresponding to $x=\frac{1}{2}$ in RADP).[30] Unfortunately, the authors either fail to report a finite-temperature phase diagram or have been forced to make additional approximations involving the (imaginary-) time dependence of their quantal formalism. Usadel,[30] for example, uses what he terms the "static approximation," whereas Walasek and Lukierska-Walasek[30] use the Bray and Moore approach[26] of completely ignoring the imaginary time dependence of the glassy order parameter. In any case, none of the work is for other than the symmetric model, so it is impossible to compare it with the experimental phase diagram for RADP—which gives the transition temperature as a function of *composition (x)*.

A more detailed study on the transverse Ising spin glass was, in fact, aimed at precisely the proton glass. Pirc, Tadić, and Blinc[31] used replica methods on a variant of the Sherrington-Kirkpatrick Ising model[32] to calculate a complete phase diagram. As useful as their work was, though, it should be emphasized that it was not intended to be any more than a phenomenological treatment of the quantum mechanics. Quantum fluctuations were explicitly excluded from their computation. One consequence of this exclusion is that they were not able to identify the way in which quantum mechanics modifies the order parameter which signals the glass transition. This feature, too, will be discussed later.

What we set out to do in this paper is to calculate a complete diagram for our model of the proton glass and to do so *without* making any approximations beyond those necessary to treat the classical model in mean-field theory. In particular, we will present a method that allows us to handle the quantum mechanics exactly. To this end, the remainder of the paper will be organized as follows: Section II will present our formulation of the model, discussing in that context our new approach of combining replica methods[20] for dealing with the quenched disorder with discretized path integrals[33] for representing the quantum mechanics. Section III will then give our mean-field solution and Sec. IV will conclude the paper with some specific comments on the proton glass and some more general remarks about quantum effects on the glass transition.

II. FORMULATION OF THE MODEL

A. Hamiltonian and the form of the disorder

In the *classical* limit it is possible to make a reasonably faithful model of KDP-like solids.[16] Each acidic (mobile) proton is simultaneously hydrogen-bonded to two phosphates. The proton is thus in a double-well potential, since it can choose to be near either phosphate. However, experience with hydrogen-bonded solids indicates that the proton positions are correlated not only by long-range dipolar forces, but also by the fact that such systems invariably obey the so-called ice rules[22]—which enforce a local correlation by governing the number of protons near any one phosphate. Indeed, one way of understanding why ADP is antiferroelectric when RDP is ferroelectric is to note that the hydrogen bonding from the ammoniums in ADP make it difficult to have a ferroelectric proton pattern which still satisfies the ice rules.[14,34] Perhaps it is not surprising then, that these considerations were explicitly included in the first theoretical treatments of RADP.[35-37] After it became clear that it was important to treat the disorder at a higher level than effective-medium theory, Matsushita and Matsubara[37] were able to include the ice rules in a random six-vertex model, given them a phase diagram with the experimentally correct topology.

An alternative theoretical approach, which turns out to be not only far more useful for making a *quantal* model, but qualitatively correct, as well, is simply to ignore the ice rules. Akhiezer and Spol'nik[38] pointed out that if one does so, a mixture of hydrogen-bonding ferroelectric and antiferroelectric materials could be considered as an Ising spin glass. The Ising variable corresponds to the two possible proton positions and the proton positions interact with each other through forces which are randomly ferromagnetic or antiferromagnetic, the proportion depending on the relative concentration of ferroelectric- and antiferroelectric-inducing cations (Rb and NH_4). While such a model is no better at including proton tunneling than the vertex model is, it can easily be generalized. In precisely the same way that one often includes the quantum mechanics in pure KDP-like ferroelectrics,[16] one just adds a transverse field to the Ising spin glass to make it appropriate to the proton glass.

Our model, then, is the following. The Hamiltonian is taken to be

$$\mathcal{H}(\{J_{jk}\}) = -\sum_{\langle j,k\rangle} J_{jk}\sigma_j^z\sigma_k^z - K\sum_j \sigma_j^x \;, \tag{2.1}$$

where $\{J_{jk}\}$ refers to the set of quenched random-coupling constants between all the neighboring sites (j,k) on our lattice, K is the single-site tunneling integral, and

$$\sigma^z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad \sigma^x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

are Pauli spin matrices.[39] In any given realization of the set $\{J_{jk}\}$, the partition function is

$$Q(\{J_{jk}\}) = \mathrm{Tr}\, e^{-\beta\mathcal{H}(\{J_{jk}\})} \;. \tag{2.2}$$

However, to calculate the ensemble average of any quantity the whole thermal average must be averaged over the quenched disorder (including the normalization).[20] Hence the relevant free energy for our purposes is the quenched average of the logarithm of Q,

$$-\beta F = \overline{\ln Q} \;. \tag{2.3}$$

Here and henceforth, the overbar refers to an average over a quenched distribution of J_{jk}'s.

This probability distribution should, strictly speaking, be correlated in accordance with the ice rules,[37] but consistent with our whole philosophy of using an Ising representation, we shall assume each bond is governed by an independent probability distribution $P(J_{jk})$. Following Akhiezer and Spol'nik,[38] and Pirc, Tadić, and Blinc,[31] we further take this distribution to be Gaussian with a mean J_0 and variance Δ chosen to reflect the relative concentrations $1-x$ and x of ferroelectric and antiferroelectric cations (respectively),

$$-\beta F = \int \cdots \int \ln Q(\{J_{jk}\}) \prod_{\langle j,k\rangle} [P(J_{jk})dJ_{jk}] \;, \tag{2.4a}$$

$$P(J_{jk}) = (2\pi\Delta^2)^{-1/2}\exp[-(J_{jk}-J_0)^2/(2\Delta^2)] \;. \tag{2.4b}$$

In a slight departure from the previous papers, though, we make the specific connection to the proton glass by associating ferroelectric and antiferroelectric bonds (respectively) with $+J$ and $-J$ coupling constants and by letting $1-x$ and x be the concentrations of these *bonds*. Equating the means and variances of our Gaussian distribution, Eq. (2.4b), with that of the $\pm J$ binary distribution then requires

$$-J_0 = (2x-1)J, \quad \Delta^2 = 4x(1-x)J^2 \;. \tag{2.5}$$

As an aside, we note that the previous work,[38] which had a site rather than bond-based mapping, ends up with almost the same expressions (the only difference being a factor of 2 in Δ^2). Nonetheless, the site mapping sets the bonds between ferroelectric and antiferroelectric sites to zero—which means that it is *not* a frustrated model.[40] Although neither the level of treatment discussed here nor that in the literature is sufficient to see the consequences of this fact,[41] one would not expect a realistic nonfrustrated model to even produce a glassy phase.

To this point, the only difference between our model and the one considered previously is that we choose not to assume an infinitely weak, infinitely-long-ranged interaction between spins. That is, we will be developing a mean-field theory for the short-ranged Hamiltonian, Eq. (2.1), rather than taking the Sherrington-Kirkpatrick approach[32] and assuming that an infinite-ranged model automatically generates mean-field behavior. Still, neither this feature nor the bond mapping are all that novel. What our main methodological contribution is is the introduction of discretized path integrals to the problem.

B. Discretized-path-integral representation

The presence of tunneling, and the requisite noncommutativity of operators in the Hamiltonian, creates a potentially difficult technical problem. Fortunately, it is straightforward to treat transverse Ising systems rigorously by the simple expedient of writing the problem in a discretized-path-integral language. How this can be done has been reviewed extensively in the literature,[33] so we will not belabor it here. Briefly, however, one takes the partition function, Eq. (2.2), and repeatedly inserts complete sets of states. The net result is that the position of any one proton, which we can represent as a (scalar) Ising variable μ at each of the N sites,

$$\begin{bmatrix}1\\0\end{bmatrix},\quad \mu=+1;\qquad \begin{bmatrix}0\\1\end{bmatrix},\quad \mu=-1$$

now can take on many different values $\mu(1),\ldots,\mu(P)$ at each site. In effect it becomes a P-dimensional vector $\boldsymbol{\mu}$ whose components are all ± 1. The partition function for the Hamiltonian of Eq. (2.1) is then reduced to a trace over these vector μ's of a (now) classical effective Hamiltonian

$$Q(\{J_{jk}\})=\sum_{\mu_1}\cdots\sum_{\mu_N}\exp\left[\sum_{\langle j,k\rangle}(\beta J_{jk}/P)\boldsymbol{\mu}_j\cdot\boldsymbol{\mu}_k+\sum_j\boldsymbol{\mu}_j\cdot\overleftrightarrow{a}\cdot\boldsymbol{\mu}_j+NPc\right], \qquad (2.6)$$

$$(\overleftrightarrow{a})_{t,t'}\equiv a\,\delta_{t,t'-1},\quad a\equiv\tfrac{1}{2}\ln\coth(\beta K/P),$$

$$c\equiv\tfrac{1}{2}\ln[\cosh(\beta K/P)\sinh(\beta K/P)],\quad \mu(P+1)\equiv\mu(1).$$

This mapping is *exact* in the limit $P\to\infty$, but a useful physical interpretation obtains[33] if we consider any finite P. In a sense, the physical reason for introducing multiple copies of each μ is to represent the quantal fluctuations (uncertainty) by a statistical average over the values at different t's. Hence the relative magnitude of the quantal fluctuations ought to be described by the correlation function

$$C(t_1,t_2)=\langle\mu(t_1)\mu(t_2)\rangle \qquad (2.7)$$

and the appropriate susceptibility

$$\begin{aligned}\chi&=P^{-2}\sum_{t_1,t_2=1}^{P}C(t_1,t_2)\\&=\int_0^1 d\tau_1\int_0^1 d\tau_2\,C(\tau_1,\tau_2),\end{aligned} \qquad (2.8)$$

where we have defined

$$\tau\equiv\lim_{P\to\infty}(t/P)$$

(rewriting C accordingly) and the angular brackets represent the thermal average subject to the Hamiltonian of Eq. (2.6). Clearly, as the uncertainty decreases, the correlation between the t components must increase; in the classical limit all the components have identical values, making C and χ both 1. Conversely, as quantum fluctuations increase, the different t copies ought to become progressively less correlated.

A somewhat more familiar interpretation of Eq. (2.6) is derived by explicitly writing out the sums over t

$$\begin{aligned}\boldsymbol{\mu}_j\cdot\boldsymbol{\mu}_k&=\sum_{t=1}^{P}\mu_j(t)\mu_k(t),\\\boldsymbol{\mu}_j\cdot\overleftrightarrow{a}\cdot\boldsymbol{\mu}_j&=a\sum_{t=1}^{P}\mu_j(t)\mu_j(t+1).\end{aligned} \qquad (2.9)$$

In this light one recognizes that the t index can be construed as labeling another direction in space beyond those of the physical lattice. As long as one is at zero temperature (so that the coupling constant a is finite $P\to\infty$), this perspective affords us an easy way to see that a d-dimensional quantal system is equivalent to a $(d+1)$-dimensional classical system.[42] However, there is another restriction on this interpretation besides the limitation to zero temperature. In a quenched *disordered* model, such as ours, the disorder is present only in the physical directions—and there is no reason why the resulting "striped disorder" model should be in the same universality class as an isotropically disordered model.[29,30] In fact, in our application, and we suspect in other quantal glass problems, the t index will end up coming into the glass order parameter in a way fundamentally different from that of the space indices.

C. Replica approach and definition of the order parameters

Even without quantum mechanics, treating quenched disorder requires coming to grips with the average of a logarithm, as shown in Eqs. (2.3) and (2.4). The standard technique[20] that we shall use for doing so is to use the formal identity[43]

$$\ln Q=\lim_{n\to 0}\left[\frac{\partial Q^n}{\partial n}\right], \qquad (2.10)$$

which turns the free energy into a manageable average over a *product* of n partition functions,

$$-\beta F=\lim_{n\to 0}\left[\frac{\partial}{\partial n}\right]\overline{Q^n}.$$

If we represent this product by defining n independent *replicas* of each spin μ_j^α $(\alpha=1,\ldots,n)$, we obtain a trace over all the spin replicas of a product of Boltzmann factors, one for each set of replicated spins α. From Eq. (2.6),

$$Q^n=\sum_{\mu_1^1}\sum_{\mu_1^2}\cdots\sum_{\mu_N^n}\exp\left[-\beta\sum_{\alpha=1}^{n}\mathcal{H}(\{\mu^\alpha\})\right]$$

$$-\beta\sum_{\alpha=1}^{n}\mathcal{H}(\{\mu^\alpha\})\equiv\sum_{\langle j,k\rangle}\sum_{\alpha=1}^{n}(\beta J_{jk}/P)\boldsymbol{\mu}_j^\alpha\cdot\boldsymbol{\mu}_k^\alpha+\sum_{j}\sum_{\alpha=1}^{n}\boldsymbol{\mu}_j^\alpha\cdot\overleftrightarrow{\mathrm{a}}\cdot\boldsymbol{\mu}_j^\alpha+nNPc\ . \tag{2.11}$$

The quenched average can now be performed using Eqs. (2.4) and (2.10), leaving us with the desired free energy

$$-\beta F=\lim_{n\to 0}\frac{\partial}{\partial n}\left[\sum_{\mu_1^1}\cdots\sum_{\mu_N^n}\exp(-\beta\mathcal{H}^{\text{eff}})\right]\ , \tag{2.12}$$

where the effective Hamiltonian is given by

$$-\beta\mathcal{H}^{\text{eff}}=\sum_{\langle j,k\rangle}\left[(\beta J_0/P)\sum_{\alpha}\boldsymbol{\mu}_j^\alpha\cdot\boldsymbol{\mu}_k^\alpha+\tfrac{1}{2}(\beta\Delta/P)^2\left[\sum_{\alpha}\boldsymbol{\mu}_j^\alpha\cdot\boldsymbol{\mu}_k^\alpha\right]^2\right]+\sum_{j}\sum_{\alpha}\boldsymbol{\mu}_j^\alpha\cdot\overleftrightarrow{\mathrm{a}}\cdot\boldsymbol{\mu}_j^\alpha+nNPc\ . \tag{2.13}$$

Thus, the proton-glass problem has been turned, without approximation, into an ordinary classical spin problem, but each spin variable μ_j that we started with now appears as nP copies—n for the disorder and P for the quantum mechanics.

Of course, the end result of the calculation will not be the free energy *per se*. What we really want are the order parameters. For the purposes of distinguishing the ferroelectric from the paraelectric phase, it suffices to look at the magnetization

$$m=N^{-1}\sum_{j=1}^{N}\langle\sigma_j^z\rangle=(nNP)^{-1}\sum_{j,\alpha,t}\langle\mu_j^\alpha(t)\rangle\ . \tag{2.14}$$

[Technically, we also need an order parameter for *sublattice* magnetization if we wish to look at the onset of antiferroelectric order, but it is easy to show from Eq. (2.5) that our Hamiltonian is symmetric about $x=\frac{1}{2}$ except for the replacement of J by $-J$. Hence, the paraelectric-antiferroelectric boundary is precisely that of the paraelectric-ferroelectric boundary with x replaced by $1-x$.]

A more interesting question is what we have to look at to observe the glass transition. In classical spin glasses, one commonly looks at the Edwards-Anderson order parameter[44,45] for an arbitrary site j,

$$q=\overline{\langle\mu_j\rangle^2}\ ,$$

which, via replica methods, can be rewritten as[20,46]

$$q\equiv q^{\alpha\beta}=\langle\mu_j^\alpha\mu_j^\beta\rangle\quad(\alpha\neq\beta)\ ,$$

where the last average is performed with respect to the (classical limit of the) effective Hamiltonian, Eq. (2.13). This quantity certainly satisfies the minimum requirements for a glass order parameter: In the paraelectric phase (above T_g), q vanishes because the thermal average of any spin is zero *for any realization* of the random couplings J_{jk}. There is no *net* magnetization in the glassy phase (below T_g) either, but then q is finite since the magnetization of any given spin does not vanish until the quenched average is performed.

Still, to be an experimentally interpretable order parameter, the quantity q would have to specify on what time scale the experiments were to be conducted. Unfortunately, there is no unanimity as to how one should make such a specification. Some aspects of the relationship between the various definitions of q and the multiple time scales characteristic of glasses have been discussed in the literature,[45] but even these aspects are largely concerned with q within the glassy phase—which we cannot study in mean-field theory without breaking replica symmetry.[46] Since we lack a scheme which tells us how to break replica symmetry quantum mechanically, we will have to be content here with simply locating a T_g without commenting on the detailed dynamics of the glass. Our results should probably be taken to mean as much (or as little) as those of the rest of the spin-glass literature in this regard. We do note, however, that for RADP itself, Courtens, Huard, and Vacher[19] suggest that they have actually measured q at Brillouin scattering frequencies ($\sim 3\times 10^{10}$ Hz).

Our *quantum mechanical* equivalent of the classical Edwards-Anderson order parameter is clearly[29]

$$q=\overline{\langle\sigma_j^z\rangle^2}\ . \tag{2.15}$$

As with the classical version, we can use also replica techniques to rewrite this q as a thermal average under an effective Hamiltonian. The quantity which is to be subjected to the quenched average is

$$\langle\sigma_j^z\rangle^2=\mathrm{Tr}(\sigma_j^z e^{-\beta\mathcal{H}})\,\mathrm{Tr}(\sigma_j^z e^{-\beta\mathcal{H}})Q^{-2}(\{J_{jk}\})\ ,$$

but the partition function for a given realization, Eq. (2.2), obeys the relation

$$Q^{-2}(\{J_{jk}\})=\lim_{n\to 0}Q^{n-2}(\{J_{jk}\})=\lim_{n\to 0}\sum_{\mu_1^1}\cdots\sum_{\mu_N^{n-2}}\exp\left[-\beta\sum_{\alpha=1}^{n-2}\mathcal{H}(\{\mu^\alpha\})\right]$$

with the argument of the exponent defined by Eq. (2.11). Moreover, by first inserting the appropriate generating field into the Hamiltonian, Eq. (2.1), then converting it to path-integral form[33]

$$\beta h_j\sigma_j^z\to(\beta h_j/P)\sum_{t=1}^{P}\mu_j(t)\ ,$$

and finally differentiating with respect to the field, it is easy to confirm that

$$\mathrm{Tr}(\sigma_j^z e^{-\beta\mathcal{H}}) = \lim_{h_j \to 0} \left[\frac{\partial Q(\{J_{jk}\})}{\partial(\beta h_j)} \right] = P^{-1} \sum_{t=1}^{P} \sum_{\mu_1^{n-1}} \cdots \sum_{\mu_N^{n-1}} \mu_j^{n-1}(t) \exp[-\beta\mathcal{H}(\{\mu^{n-1}\})] ,$$

since we can arbitrarily assign the replica label $(n-1)$ to this set of spins. Thus, combining these expressions,

$$\langle \sigma_j^z \rangle^2 = \lim_{n \to 0} P^{-2} \sum_{t,t'=1}^{P} \sum_{\mu_1^1} \cdots \sum_{\mu_N^n} \mu_j^{n-1}(t) \mu_j^n(t') \times \exp\left[-\beta \sum_{\alpha=1}^{n} \mathcal{H}(\{\mu^\alpha\}) \right] ,$$

and taking the quenched averaged required by Eq. (2.15) enables us to write the desired form for the quantal Edwards-Anderson order parameter

$$\begin{aligned} q &= \left\langle P^{-2} \sum_{t,t'=1}^{P} \mu_j^\alpha(t) \mu_j^\beta(t') \right\rangle \quad (\alpha \neq \beta) \\ &= [Nn(n-1)]^{-1} \sum_{j=1}^{N} \sum_{\substack{\alpha,\beta \\ (\alpha\neq\beta)}} \left\langle P^{-2} \sum_{t,t'=1}^{P} \mu_j^\alpha(t) \mu_j^\beta(t') \right\rangle . \end{aligned} \tag{2.16}$$

Here, the average is understood to be taken with respect to the effective Hamiltonian given in Eq. (2.13). In writing Eq. (2.16), we used both the fact that we could relabel replicas $(n-1)$ and (n) as some α and β, and the restriction to unbroken replica symmetry in order to note that all $n(n-1)$ pairs of $\alpha \neq \beta$ give identical answers. To take care of the normalization of the average, we also used the special feature that replica-derived effective Hamiltonians have of vanishing in the $n \to 0$ limit.

The special form of the order parameter constitutes one of the principal results of this paper. In particular, it is hard to miss the fact that our expression has a structure similar to that of the literature order parameters for both the quantal Heisenberg model and the transverse Ising model.[26,30] In path-integral terms one can understand this structure fairly easily. Classically, one often interprets the correlation between replicas α and β to be a measure of the "overlap" between any two of the many local free-energy minima present in a glass.[45] In light of our interpretation of the quantal susceptibility, Eq. (2.8),[33] what we are seeing is how quantum fluctuations diminish that overlap. Hence, even in advance of doing a calculation, we can immediately predict that tunneling ought to decrease the extent of a glassy phase.

III. MEAN-FIELD THEORY

A. Derivation

One can approach the statistical mechanics of the classical effective Hamiltonian, Eq. (2.13), by any number of routes. We choose to do so here via a version of mean-field theory that has already been proven useful in the pure (transverse Ising) limit of our problem.[33] The general strategy is to consider the spin-spin interaction terms,

$$-\beta V \equiv -\beta V_1 - \beta V_2 , \tag{3.1a}$$

$$-\beta V_1 = \sum_{\langle j,k \rangle} (\beta J_0/P) \sum_{\alpha} \boldsymbol{\mu}_j^\alpha \cdot \boldsymbol{\mu}_k^\alpha , \tag{3.1b}$$

$$-\beta V_2 = \sum_{\langle j,k \rangle} \tfrac{1}{2}(\beta\Delta/P)^2 \left[\sum_{\alpha} \boldsymbol{\mu}_j^\alpha \cdot \boldsymbol{\mu}_k^\alpha \right]^2 , \tag{3.1c}$$

as a perturbation on the single-site Hamiltonian,

$$-\beta\mathcal{H}_0 = \sum_j \sum_\alpha \boldsymbol{\mu}_j^\alpha \cdot \overleftrightarrow{\mathrm{a}} \cdot \boldsymbol{\mu}_j^\alpha + nNPc .$$

More specifically, we define an "optimum" reference system by using two Lagrange multipliers, γ and ζ, to enforce the constraint that order parameters m and q (respectively) take on their self-consistently determined values *in the reference system itself.*[47] From Eqs. (2.9), (2.14), and (2.16), this requirement is seen to suggest that we revise $\mathcal{H}_0$ into the reference Hamiltonian by writing

$$\begin{aligned} -\beta\mathcal{H}_0 = a \sum_{j,\alpha,t} \mu_j^\alpha(t) \mu_j^\alpha(t+1) + nNPc \\ -\gamma \left[Nnm - P^{-1} \sum_{j,\alpha,t} \mu_j^\alpha(t) \right] \\ -\zeta \left[Nn(n-1)q - P^{-2} \sum_j \sum_{\substack{\alpha,\beta \\ (\alpha\neq\beta)}} \sum_{t,t'} \mu_j^\alpha(t) \mu_j^\beta(t') \right], \end{aligned} \tag{3.2a}$$

and defining the reference-system partition function

$$Q_0 = \mathrm{Tr}(e^{-\beta\mathcal{H}_0}) . \tag{3.2b}$$

To first order in a cumulant expansion, the partition function for the full effective Hamiltonian Q may then by written in terms of Q_0 and the interaction averaged in the reference system, $\langle V \rangle_0$:

$$Q = \mathrm{Tr} e^{-\beta\mathcal{H}^{\mathrm{eff}}} = Q_0 e^{-\langle \beta V \rangle_0} .$$

Provided we do enforce the order-parameter constraint, it has been shown that this level of approximation is precisely equivalent to ordinary Curie-Weiss mean-field theory.[33,47] However, our application differs from previous ones in two ways. First, we obtain the desired free energy not by taking a logarithm, but by taking the derivative prescribed by Eq. (2.12). Since each term of $\mathcal{H}_{\mathrm{eff}}$ vanishes as $n \to 0$,

$$-\beta F = \lim_{n \to 0} \left[\frac{\partial}{\partial n} \right] Q_0 + \lim_{n \to 0} \left[\frac{\partial}{\partial n} \right] \langle -\beta V \rangle_0 . \tag{3.3}$$

Secondly, because we have spin-spin interactions (in replica space) even in the reference system, we cannot treat the reference system exactly. Fortunately, for our rather limited purposes of simply ascertaining the phase boundaries, it suffices to derive a Landau expansion through second order in the order parameters. In what follows we will calculate each of the two terms in Eq. (3.3) through second order in γ and ζ—confirming along the way that this order is all that is necessary.

1. Reference free energy and the constraint conditions

It is convenient to perform an expansion for Q_0 with the trivially transformed Hamiltonian

$$-\beta\mathcal{H}'_0 = -\beta\mathcal{H}_0 + \gamma(Nnm) + \zeta[Nn(n-1)q] , \tag{3.4}$$

so that the reference free energy becomes

$$\begin{aligned} -\beta F_0 &\equiv \lim_{n\to 0}\left[\frac{\partial}{\partial n}\right] Q_0 \\ &= -N\gamma m + N\zeta q + \lim_{n\to 0}\left[\frac{\partial}{\partial n}\right] Q'_0 \end{aligned} \tag{3.5}$$

with

$$\begin{aligned} Q'_0 = (Q'_0)_{00} &+ \gamma\left[\frac{\partial Q'_0}{\partial\gamma}\right]_{00} + \zeta\left[\frac{\partial Q'_0}{\partial\zeta}\right]_{00} \\ &+ \tfrac{1}{2}\gamma^2\left[\frac{\partial^2 Q'_0}{\partial\gamma^2}\right]_{00} + \gamma\zeta\left[\frac{\partial^2 Q'_0}{\partial\gamma\partial\zeta}\right]_{00} \\ &+ \tfrac{1}{2}\zeta^2\left[\frac{\partial^2 Q'_0}{\partial\zeta^2}\right]_{00} + \cdots . \end{aligned} \tag{3.6}$$

Here the subscript 00 means $\gamma=\zeta=0$.

From Eqs. (3.2) and (3.4),

$$(Q'_0)_{00} = (\mathrm{Tr}\, e^{-\beta\mathcal{H}'_0})_{00} = \left[\sum_{\mu(1)}\cdots\sum_{\mu(P)} \exp\left[a\sum_{t=1}^{P}\mu(t)\mu(t+1) + Pc\right]\right]^{Nn} ,$$

$$\left[\frac{\partial Q'_0}{\partial\gamma}\right]_{00} = N\left\langle P^{-1}\sum_{\alpha,t}\mu^{\alpha}(t)\right\rangle'_{00} ,$$

$$\left[\frac{\partial Q'_0}{\partial\zeta}\right]_{00} = N\left\langle P^{-2}\sum_{\substack{\alpha,\beta\\(\alpha\neq\beta)}}\ \sum_{t,t'}\mu^{\alpha}(t)\mu^{\beta}(t')\right\rangle'_{00} ,$$

$$\left[\frac{\partial^2 Q'_0}{\partial\gamma^2}\right]_{00} = N\left\langle P^{-2}\sum_{\alpha,\beta}\ \sum_{t,t'}\mu^{\alpha}(t)\mu^{\beta}(t')\right\rangle'_{00} ,$$

$$\left[\frac{\partial^2 Q'_0}{\partial\zeta^2}\right]_{00} = N\left\langle P^{-4}\sum_{\substack{\alpha,\beta,\delta,\nu\\(\alpha\neq\beta)\\(\delta\neq\nu)}}\ \sum_{\substack{t_1,t_2\\t_3,t_4}}\mu^{\alpha}(t_1)\mu^{\beta}(t_2)\mu^{\delta}(t_3)\mu^{\nu}(t_4)\right\rangle'_{00} ,$$

$$\left[\frac{\partial^2 Q'_0}{\partial\gamma\partial\zeta}\right]_{00} = N\left\langle P^{-2}\sum_{\alpha}\ \sum_{\substack{\beta,\delta\\(\beta\neq\delta)}}\ \sum_{t_1,t_2,t_3}\mu^{\alpha}(t_1)\mu^{\beta}(t_2)\mu^{\gamma}(t_3)\right\rangle'_{00} ,$$

where for any quantity X we define its average in the $\gamma=\zeta=0$ reference system by

$$\langle X\rangle'_{00} \equiv \mathrm{Tr}(X e^{-\beta\mathcal{H}'_0})_{00} ,$$

and we have made explicit use of the fact that $\mathcal{H}'_{00}$ is diagonal in the site index j.

As we note in the Appendix, it is possible to take the (exact quantal) $P\to\infty$ limit of these expressions analytically. If we do so, we can take advantage of two features of the 00 reference: different replicas factor and, for any given replica, only averages with an even power of μ survive. The end result is that most of the derivatives of Q'_0 vanish, and of the remainder, only certain terms contribute. In particular, only

$$\begin{aligned} (Q'_0)_{00} &= [2\cosh(\beta K)]^{Nn} , \\ \left[\frac{\partial^2 Q'_0}{\partial\gamma^2}\right]_{00} &= Nn\chi_{(0)} , \\ \left[\frac{\partial^2 Q'_0}{\partial\zeta^2}\right]_{00} &= 2Nn(n-1)\chi^2_{(0)} \end{aligned} \tag{3.7}$$

survive. Note that the coefficients involving n come from the replica sums and the quantity

$$\begin{aligned} \chi_{(0)} &\equiv \int_0^1 d\tau \int_0^1 d\tau' C_{(0)}(\tau,\tau') \\ &= \tanh(\beta K)/\beta K \end{aligned} \tag{3.8}$$

is the reference system equivalent of the susceptibility of

Eq. (2.8). That is, it requires the isolated spin-(imaginary-time) correlation function

$$C_{(0)}(\tau,\tau')=\langle\mu(\tau)\mu(\tau')\rangle_{(0)} \tag{3.9}$$

calculated with the single-site, single-replica Hamiltonian

$$-\beta H_{(0)}=a\sum_{t=1}^{P}\mu(t)\mu(t+1)+Pc\ . \tag{3.10}$$

Combining Eqs. (3.5)–(3.7) now gives us the final form for the reference free energy (through second order),

$$\begin{aligned}-\beta F_0/N={}&-m\gamma+q\zeta+\ln[2\cosh(\beta K)]\\&+\tfrac{1}{2}\gamma^2\chi_{(0)}-\zeta^2\chi^2_{(0)}\ .\end{aligned} \tag{3.11}$$

We must still calculate what γ and ζ have to be in order to satisfy the order-parameter constraints, but it is easy to verify from Eqs. (3.2) and (3.5) that the conditions

$$\frac{\partial(-\beta F_0)}{\partial\gamma}=0,\quad \frac{\partial(-\beta F_0)}{\partial\zeta}=0$$

will serve to fix the magnetization and glass order parameters, respectively. Hence by direct differentiation of Eq. (3.11) we find the constraint conditions to be

$$m=\gamma\chi_{(0)},\quad q=2\zeta\chi^2_{(0)}\ , \tag{3.12}$$

at least through leading order. As promised, Eq. (3.12) confirms that an expansion second order in γ and ζ is also second order in m and q.

2. *Average potential energy*

The remaining term in the full free energy, Eq. (3.3), is the interaction term, which is given by Eq. (3.1). With the aid of Eq. (2.9) we can express the necessary averages as

$$\begin{aligned}\langle -\beta V_1\rangle_0/N&=\tfrac{1}{2}z(\beta J_0/P)\sum_{\alpha,t}\langle\mu^\alpha(t)\rangle_0^2\ ,\\ \langle -\beta V_2\rangle_0&=\tfrac{1}{4}z(\beta\Delta/P)^2\sum_{\alpha,\beta}\sum_{t,t'}\langle\mu^\alpha(t)\mu^\beta(t')\rangle_0^2\ ,\end{aligned} \tag{3.13}$$

for any lattice of coordination number z. These reference system averages, as with Q_0, have to be expanded in powers of the Langrange multipliers. However, since the calculation proceeds similarly to that of the reference system, we simply report that, to lowest order,

$$P^{-1}\sum_{t=1}^{P}\langle\mu^\alpha(t)\rangle_0^2=\gamma^2\chi^2_{(0)}\ ,$$

whereas, to lowest order,

$$P^{-2}\sum_{t_1,t_2=1}^{P}\langle\mu^\alpha(t_1)\mu^\beta(t_2)\rangle_0^2=\begin{cases}4\zeta^2\chi^4_{(0)} & (\alpha\neq\beta)\ ,\\ \eta_{(0)}+\gamma^2\psi_{(0)}+4(n-1)\zeta^2\chi_{(0)}\psi_{(0)} & (\alpha=\beta)\ ,\end{cases}$$

with the relevant isolated spin-correlation functions and susceptibilities

$$\begin{aligned}\eta_{(0)}&=\int_0^1 d\tau\int_0^1 d\tau' C^2_{(0)}(\tau,\tau')=\tfrac{1}{2}\operatorname{sech}^2\beta K+\tfrac{1}{2}\tanh(\beta K)/\beta K\ ,\\ \psi_{(0)}&=\int_0^1 d\tau_1\int_0^1 d\tau_2\int_0^1 d\tau_3\int_0^1 d\tau_4 C_{(0)}(\tau_1,\tau_2)[C_{(0)}(\tau_1,\tau_2,\tau_3,\tau_4)-C_{(0)}(\tau_1,\tau_2)C_{(0)}(\tau_3,\tau_4)]\\ &=-[3\operatorname{sech}^2(\beta K)/4(\beta K)^2]+[3\tanh(\beta K)/4(\beta K)^3]-[\tanh(\beta K)\operatorname{sech}(\beta K)/(2\beta K)]\ ,\\ C_{(0)}(\tau_1,\tau_2,\tau_3,\tau_4)&=\langle\mu(\tau_1)\mu(\tau_2)\mu(\tau_3)\mu(\tau_4)\rangle_{(0)}\ ,\end{aligned} \tag{3.14}$$

described and calculated in the Appendix.

Substituting these results into Eqs. (3.13) and (3.1a) yields the final form for the interaction term in the free energy,

$$\begin{aligned}\lim_{n\to 0}\left[\frac{\partial}{\partial n}\right]\langle -\beta V\rangle_0/N={}&\tfrac{1}{2}(\beta J_0)z\gamma^2\chi^2_{(0)}+\tfrac{1}{4}(\beta\Delta)^2 z\\&\times[\eta_{(0)}+\gamma^2\psi_{(0)}\\&\quad+4\zeta^2\chi_{(0)}(\psi_{(0)}+\chi^3_{(0)})]\ .\end{aligned} \tag{3.15}$$

Through second order, the entire mean-field free energy, Eq. (3.3), is determined by Eqs. (3.11), (3.12), and (3.15).

B. Results

In classical Landau-theory fashion, our phase boundaries are prescribed by the condition that if we look at the sum of Eqs. (3.11) and (3.15) the coefficients of the order parameters squared must vanish. Thus, for the paraelectric-ferroelectric phase boundary, we require that the coefficient of m^2 (or equivalently of γ^2) vanishes,

$$\chi_{(0)}=(\beta J_0)z\chi^2_{(0)}+\tfrac{1}{2}(\beta\Delta)^2 z\psi_{(0)}\ , \tag{3.16}$$

and for the paraelectric-glass phase boundary, the *glass transition*, we require that the coefficient of q^2 (or ζ^2) vanishes,

$$\chi_{(0)}=(\beta\Delta)^2 z(\chi^3_{(0)}+\psi_{(0)})\ . \tag{3.17}$$

Along with the order-parameter definition, Eq. (2.16), these two equations are the major results of this paper; they describe the dependence of the critical and glass-transition temperatures on the average bond strength, J_0, and the width of the bond distribution, Δ.

The physical content of the equations is somewhat obscured by their dependence on the two functions of the tunneling integral, $\chi_{(0)}(\beta K)$ and $\psi_{(0)}(\beta K)$, which are defined by Eqs. (3.8) and (3.14). However, looking at some limiting cases immediately reveals most of the physics. In the *classical limit* $(K/J_0 \rightarrow 0)$

$$\chi_{(0)} \rightarrow 1, \quad \psi_{(0)} \rightarrow 0 \ ,$$

so the two equations reduce to

$$1 = (\beta J_0) z, \quad 1 = (\beta \Delta)^2 z \ , \tag{3.18}$$

the standard, mean-field result for a classical Ising spin glass.[20] We have plotted the predictions of these equations in Fig. 1 using Eq. (2.5) to relate J_0 and Δ to the proton glass, or more correctly (since $K=0$ here) to the 100% deuterated proton glass.

Several features of this figure stand out. To begin with, our (rather simplistic) original model built in the fact that the phase diagram has to be symmetric about $x=\frac{1}{2}$. Somewhat surprisingly, not only in this regard, but in a variety of other attributes our phase diagram ends up being in reasonably good agreement with experimental results. For example, our glass-forming concentration range (assuming $z=4$ for a diamond lattice of phosphates) is $0.2764 \leq x \leq 0.7236$, whereas real RADP (Ref. 14) seems to have $0.22 \leq x \leq 0.74$. The general topology of the diagram is also correct,[13] although it should be pointed out that the methods of this paper, by themselves, cannot be used to predict the ferroelectric-glass (and antiferroelectric-glass) boundaries. In order to draw the vertical dashed lines, we had to appeal to an argument by Toulouse[48] to the effect that Parisi's replica-breaking scheme[46] requires that equations governing such boundaries cannot involve temperature.

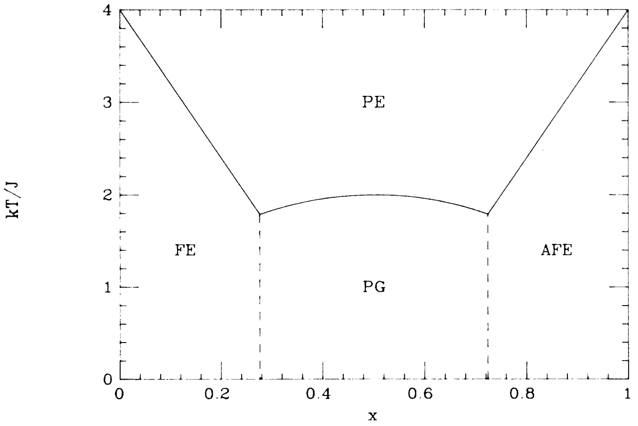

FIG. 1. The mean-field phase diagram predicted for $Rb_{1-x}(NH_4)_xH_2PO_4$ in the classical limit. The vertical axis is the temperature in units of the interaction energy, J, and the horizontal axis is the mole fraction, x, of antiferroelectric cation $NH_4{}^+$. PE refers to the paraelectric (thermally disordered) phase, AFE and FE refer to the antiferroelectric and ferroelectric (crystalline ordered) phases, and PG refers to the proton glass (frozen-in disordered) phase. To create solid lines in this diagram, Eq. (3.18) was solved with $z=4$ and $0 \leq x \leq \frac{1}{2}$. The right-hand side of the diagram then follows by symmetry. As explained in the text, the fact that the dashed lines must be vertical follows from replica-symmetry-breaking considerations not pursued in this paper.

Perhaps we should also point out that more realistic treatment of the disorder will yield the experimentally observed convex shape to the T_g-versus-x curve, in place of our concave shape.[37,49] Further, our (frequency-independent) predictions for the location of this curve can, at best, be in qualitative accord with experimental measurements that are explicit functions of frequency. Thus, we can do little more than note that our ratio of the glass-transition temperature, T_g, to the pure-system (RDP) critical temperature is $T_g/T_c = 0.48$ at $x=0.35$, whereas the real ratio ranges from the highest-frequency Raman result of $T_g/T_c = (110\ \text{K})/(146\ \text{K}) = 0.75$ to the lowest-frequency dielectric result of $(20\ \text{K})/(146\ \text{K}) = 0.14$ (at this same concentration).[15] Still, the original physical question that motivated this work—what it is that tunneling can do to such a phase diagram?—has finally come within our reach.

If we look at the *zero-temperature limit* $(kT/J \rightarrow 0)$

$$\chi_{(0)} \rightarrow (\beta K)^{-1}, \quad \psi_{(0)} \rightarrow \tfrac{3}{4}(\beta K)^{-3} \ ,$$

the two phase boundary equations become

$$1 = (J_0/K) z + \tfrac{3}{8}(\Delta/K)^2 z, \quad 1 = \tfrac{7}{4}(\Delta/K)^2 z \ . \tag{3.19}$$

These results, plotted in Fig. 2 show that not only the ordered phases, but also the glassy phase, can be suppressed by tunneling; for both kinds of phases there exists critical values of K/J beyond which only paraelectric behavior is possible—even at zero temperature. An equivalent way of seeing this effect is to solve Eq. (3.17) numerically for the glass-transition temperature as a function of the tunneling integral (as is shown in Fig. 3). The monotonic decrease of T_g with K/J looks much like the decrease of T_c with K/J observed in the pure transverse Ising model,[33] but rather than destroying ferroelectric order the way it does in the pure model, quantum fluctuations here are evidently suppressing glassy frustration.

Our overall phase diagram (Fig. 4) makes these points in somewhat more detail. Interestingly enough, this diagram disagrees with some of the speculation that has appeared in the literature. Before any quantum studies were done, it was expected that tunneling would substantially *increase* the glass-forming concentration range.[35] By way of contrast, our maximum glass-forming range, that at $T=0$, is $0.2695 < x < 0.7305$ for $z=4$, practically identical with our classical (0.2764–0.7236) range. Similarly, while Pirc, Tadić, and Blinc[31] successfully predicted that quantum effects ought to lower the glass-transition temperature, their phenomenological results are quantitatively, and even qualitatively, different from

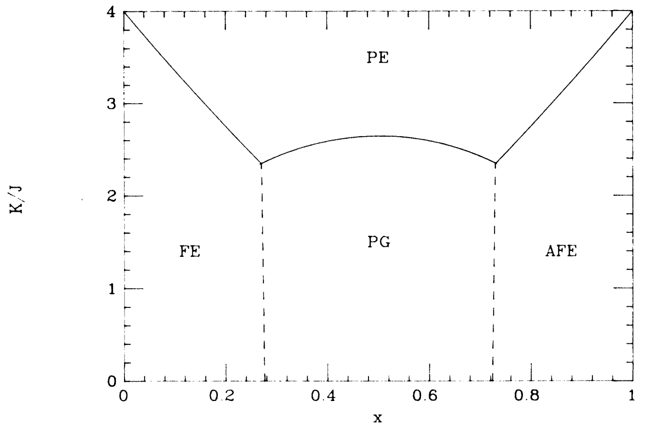

FIG. 2. The mean-field phase diagram for RADP at zero temperature. The vertical axis here is the tunneling integral, K, in units of the interaction energy, J, and the dashed lines are schematic (not precisely vertical) lines connecting the known points at the classical value of $K/J=0$ and at the critical value of K/J. Otherwise, the labeling of the figure is as discussed in the caption to Fig. 1. Note that the critical K/J for destroying the glassy phase is lower than that for destroying the ordered phases, but that the width (in x) of the glassy region is largely independent of K/J—largely unchanged by quantum effects.

ours. In particular, they arrive at the unphysical result that increasing the amount of frustration (increasing x from 0 or decreasing x from 1) ought to stabilize the ordered [ferroelectric (FE) and antiferroelectric (AFE)] phases with respect to quantum fluctuations—ought to increase the critical K/J. Moreover, they predict that there ought to exist some K/J high enough to destabilize the ordered phases while preserving the glassy phase. We find that the glassy phase is *more* susceptible to destruction by tunneling than the ordered phases.

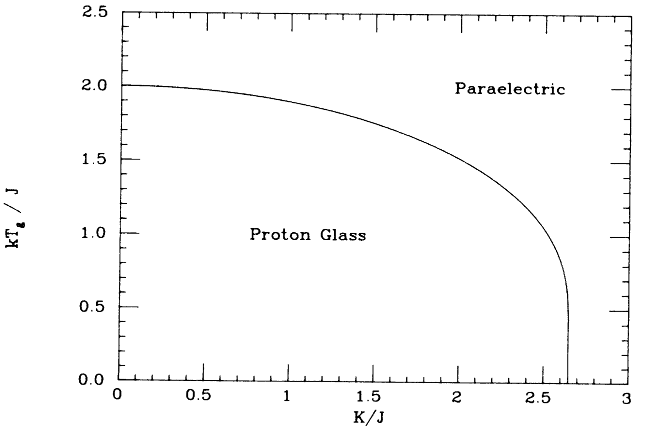

FIG. 3. The dependence of the glass-transition temperature T_g on the tunneling integral K for $x=\frac{1}{2}$ (the traditional spin-glass condition of equal fractions of ferroelectric and antiferroelectric bonds). For the $z=4$ curve shown, any increase in tunneling beyond the critical value of $K/J=7^{1/2}$ will forbid the existence of a glassy phase at any temperature.

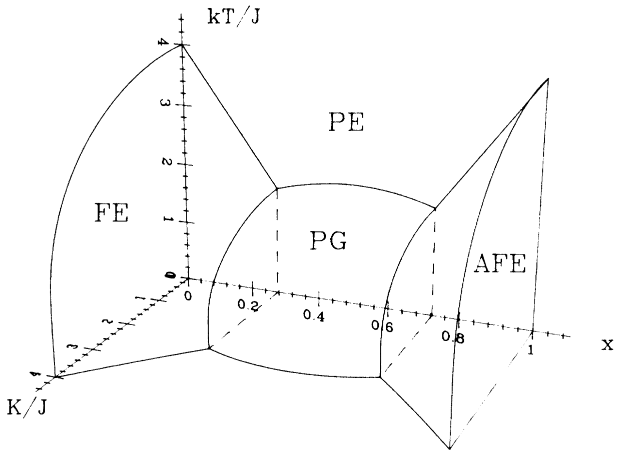

FIG. 4. The complete mean-field phase diagram for RADP. The labeling and the significance of the dashed lines are as discussed with Figs. 1 and 2. Note that there is no temperature which permits a glassy phase without also allowing an ordered phase.

IV. DISCUSSION

Although much of this paper was written with the compound RADP in mind, the paper is probably better regarded as having presented the mean-field theory for the asymmetric transverse Ising spin glass—perhaps the simplest microscopic model incorporating both tunneling and glassy behavior. We found that one could indeed set up and solve such a theory by combining replicas with discretized path integrals (and thereby avoid making any approximations for either the disorder or the quantum mechanics). For this model, at least, we were able to identify the onset of glassy disorder with a corresponding change in a quantum-mechanical Edwards-Anderson order parameter. The glassy region (so defined) was then shown to be even easier for tunneling to thermally disorder than the analogous crystalline ordered phases, though we also showed that the relative stability of the glassy and ordered phases was all but unaffected by the presence of tunneling.[50]

To the extent that one really can think of RADP in the terms presented here, there are a number of fairly specific experimental implications of our results. We note, first, that it is possible to increase the effective value of the tunneling integral, K, by subjecting the crystals to pressure.[51] Since Fig. 3 can thus be read as a plot of the glass-transition temperature versus pressure, we predict (as did Samara and Schmidt[52]) that it ought to be possible to totally destroy the glassy phase at high enough pressure. Moreover, contrary to what is implied by previous work,[31] we would predict that the critical pressure ought to be less than the 15 kbar required to disorder pure RDP (Ref. 53)—so there should be pressures which do allow ferroelectric or antiferroelectric ordering in the appropriate concentration ranges, but which fail to permit a glass to exist at *any* concentration.

Of course, one can decrease K experimentally, as well as increase it because substituting deuterium for hydrogen effectively sets K to zero.[16] So clearly, a comparison of the results obtained[52,54,55] for $\mathrm{Rb}_{1-x}(\mathrm{ND}_4)_x\mathrm{D}_2\mathrm{PO}_4$ with those of the fully protonated material ought to be equivalent to a direct check of the qualitative influence of tunneling (at least for temperatures much larger than the 1 K associated with seeing two-level–system behavior[11]). Consistent with our ideas, it has already been found that the glass-transition temperature is 2–3 times larger for deuterated compounds.[54] We can go further though, and use Fig. 4 to predict that the fully deuterated material ought to have a qualitatively similar phase diagram to that of the protiated version, with almost the same critical concentrations, but with a noticeably lower ratio of T_g $(x \approx \frac{1}{2})$ to T_c $(x=0,1)$.

From a somewhat broader perspective, it would also be useful if this paper could serve to point out some of the limits to our current knowledge of quantal behavior in glasses. We still have no model which predicts both two-level systems *and* macroscopic glassy behavior from a microscopic Hamiltonian. At a minimum, the work here would have to be extended so as to permit treatment of elementary excitations in the glassy region itself before either the model or the methods would be relevant. Similarly, we have no particular insight into the frequency dependence of any measurable quantities [although it might prove illuminating to examine the analytical continuation of the order parameter defined by Eq. (2.16)].

One direction in which there has been some progress, though, is in raising the question of what quantum mechanics does to frustration.[25,26] We have noted here that quantal fluctuations act against crystalline order in much the same way (albeit slightly less efficiently) than they act against glassy disorder. In a path-integral language[33] one might be able to think about such effects by remembering that quantum mechanics tends to tip the vectors $\boldsymbol{\mu}$ away from the classical $(1,1,\ldots,1)$ direction, making the $\boldsymbol{\mu}_j \cdot \boldsymbol{\mu}_k$ interaction terms weaker. The vectors could actually become perpendicular—setting the interaction and hence the frustration to zero—if we let $K \rightarrow \infty$. Certainly, in this limit both frustration and crystalline order are destroyed, but for less extreme cases we still notice that a quantal spin has more "degrees of freedom" (more components in this path-integral sense) than a classical spin. By analogy with comparisons of Ising and Heisenberg spins,[57] this fact alone may suggest why it is that quantum mechanics leads to a lessening of frustration.

Note added in proof. Since this paper was submitted, experimental studies by G. A. Samara and H. Terauchi [Phys. Rev. Lett. **54**, 347 (1987)] have confirmed our prediction that the glassy phase should be destroyed by pressures even less than those necessary to suppress the ordered phases.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant No. CHE-8420214 and by the Brown University Materials Research Laboratory. We thank Steven Adachi, Robert Harris, Anthony Houghton, and especially Eric Courtens for helpful discussions. One of us (R.M.S.) acknowledges additional support from the Alfred P. Sloan Foundation.

APPENDIX

This appendix summarizes some of the statistical mechanics of the isolated spin Hamiltonian, Eq. (3.10). Since each $\mu(t)$ is ± 1 and $\mu(P+1) \equiv \mu(1)$, the behavior of the isolated system is just that of a one-dimensional Ising model with periodic boundary conditions and coupling constant $a = \frac{1}{2}\ln\coth(\beta K/P)$. As such, the partition function and correlation functions can be evaluated exactly via transfer-matrix methods for any value of P.

In terms of the eigenvalues of the transfer matrix,

$$\lambda_{\pm} = e^{\pm\beta K/P} ,$$

the partition function is

$$Q_{(0)} = \lambda_+^P + \lambda_-^P = 2\cosh(\beta K) , \tag{A1}$$

and the general correlation functions can be written as

$$\begin{aligned} C_{(0)}(t_1,\ldots,t_k) &\equiv \langle \mu_{t_1}\mu_{t_2}\cdots\mu_{t_k}\rangle_{(0)} , \\ &= Q_{(0)}^{-1}(\lambda_+^{t_2-t_1}\lambda_-^{t_3-t_2}\lambda_+^{t_4-t_3}\cdots\lambda_+^{t_k-t_{k-1}}\lambda_-^{P-t_k+t_1} + \lambda_-^{t_2-t_1}\lambda_+^{t_3-t_2}\lambda_-^{t_4-t_3}\cdots\lambda_-^{t_k-t_{k-1}}\lambda_+^{P-t_k+t_1}) \\ &= \cosh(\beta K)[1+2(\tau_1-\tau_2+\tau_3-\cdots-\tau_k)]/\cosh(\beta K) \quad (0<\tau_1<\tau_2<\cdots<\tau_k<1) \end{aligned} \tag{A2}$$

for k even. For k odd, the analogous correlation functions vanish by symmetry.

Note that by defining

$$\tau_j \equiv t_j/P$$

we have arrived at expressions which are equally valid for finite or for infinite P. However, in actual use one often has to compute susceptibilities involving sums over t's,

$$P^{-m}\sum_{t_1=1}^{P}\cdots\sum_{t_m=1}^{P} .$$

When these kinds of sums are required it is obviously easiest to take the $P \rightarrow \infty$ limit and turn the sums into integrals,

$$\int_0^1 d\tau_1 \cdots \int_0^1 d\tau_m .$$

We also point out that while the correlation function in Eq. (A2) is manifestly independent of the ordering of the μ's,

$$\langle \mu_{t_1}\mu_{t_2}\rangle_{(0)} = \langle \mu_{t_2}\mu_{t_1}\rangle_{(0)} ,$$

the final formula requires that we first order the Ising sites $t_1, \cdots, t_k$ if we are going to plug into the formula. This feature no doubt arises because classical spins are naturally ordered on a one-dimensional lattice. Still, it is amusing to note the analogy with the time ordering that shows up in nondiscretized-path-integral versions of quantum mechanics.

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