

Does Coupling to a Condensed Phase Increase or Decrease Tunneling?

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This Letter presents a model for tunneling-induced disorder in solids which encompasses both hindered rotors (such as H_2 and CH_4) and hydrogen-bonded ferroelectrics (such as KH_2PO_4). The model indicates that while the interaction between tunneling systems decreases tunneling, coupling to phonons actually increases tunneling.

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A cursory reading of the recent literature on tunneling in condensed phases suggests that the answer to the title question will almost always be *decreases*.¹⁻³ While there are a few interesting models which suggest the opposite, theoretical studies of single tunneling systems (whether they be double-well systems or single-well, metastable systems) usually find that the *dissipation* caused by the environment reduces tunneling frequency—a fact confirmed by experiment.⁴ However, this generalization clearly does not tell the entire story. Not only are there instances of “anomalous dissipation”⁵ reversing the direction of the effect, but there are intriguing examples of increased tunneling formulated and analyzed without any discussion of dissipation at all.

What distinguishes these examples⁶ is that the form of the *coupling* to the bath is special. In particular, these studies of hydrogen diffusion on surfaces, unlike most of the prior models, have significant coupling at the top of the tunneling barrier. More generally, however, such examples prompt one to wonder if it is possible to predict what features of the many-body Hamiltonian are most influential in modifying the tunneling (independently of the extent to which the features produce dissipation). This question turns out to be an experimentally accessible one. As will be discussed in this Letter, some solids displaying *tunneling-induced disorder*⁷⁻⁹ have their tunneling decreased with applied pressure, whereas others show marked increases in tunneling. To the extent that the full range of tunneling-induced disorder can be described by a single model, we therefore have the opportunity to study which parts of the coupling enhance tunneling and which parts suppress it. The remainder of the article will be devoted to constructing and analyzing a model for just this purpose.

The experimental motivation for the model is that in cases involving hindered rotation in crystals⁷ (such as H_2 and CH_4), and in cases involving hydrogen-bonded ferroelectrics^{8,9} [such as KH_2PO_4 (KDP)], one finds that there can be disorder at zero temperature. In both kinds of cases the disorder arises from the tunneling of protons between a small number of discrete sites, the energies of interaction between any two tunneling

centers depending on the relative positions of the two tunneling protons. Because the interaction is maximized when quantum fluctuations are at their smallest,¹⁰ the existence of a condensed phase (as manifested by the interaction) *decreases* the extent of tunneling. In practice, there is often a critical pressure at which zero-temperature disordering occurs,⁷⁻⁹ so that this statement is equivalent to saying that the larger the interaction, the larger the range of pressures over which tunneling is weak enough to allow ordering.

Yet, the very existence of a pressure dependence means that the underlying lattice is compressible, which raises the possibility that coupling to phonons is relevant. It is not inconceivable that the compressibility merely defines a phenomenological dependence of interaction strength on pressure (as assumed by some standard models⁷), nor is it impossible for coupling to phonon dynamics simply to modulate the interaction¹¹ (as in the generic tunneling models referred to earlier¹⁻³). Either effect would be consistent with the idea of the condensed phase decreasing tunneling. However, in the hindered rotation and ferroelectric examples, an alternative consequence of a variation in lattice spacing might be a change in the single-particle tunneling integral. With hindered rotation, decreasing the lattice spacing increases the height of the barrier to rotation, whereas, with hydrogen-bonded systems, the same decrease in lattice constant decreases the distance over which tunneling occurs (and thus decreases the barrier width). Since the tunneling integral depends exponentially on the barrier,⁶ there is a chance for a significant effect on the tunneling—perhaps even an increase in tunneling.

To study this possibility, a simple model for tunneling-induced disorder in solids was constructed: A transverse Ising model on a compressible lattice, with phonon coupling through the tunneling integral,

$$\hat{\mathcal{H}} = \sum_{\langle j,k \rangle} [-J \sigma_j^z \sigma_k^z - K(\mathbf{r}_j, \mathbf{r}_k) \sigma_j^x] + \mathcal{H}_L(\mathbf{r}). \quad (1)$$

As is commonplace in transverse Ising representations of tunneling,⁹ the use of the Pauli spin matrices σ^z and σ^x in our Hamiltonian puts a double-well tunneling system on each lattice site. The quantity K is then the

single-particle tunneling integral and J is the interaction energy between tunneling systems on near-neighbor lattice sites j and k . For the limited purposes of this calculation, the lattice Hamiltonian, \mathcal{H}_L , as a function of lattice-site coordinates $\mathbf{r} = (\mathbf{r}_1, \dots, \mathbf{r}_N)$ was chosen to be the one used by Gunther, Bergman, and Imry,¹²

$$\mathcal{H}_L = \sum_{(j,k)} [\phi(\hat{\mathbf{e}}_{jk} \cdot \mathbf{r}_{jk}) + \lambda \hat{\mathbf{e}}_{jk} \cdot \mathbf{r}_{jk}], \quad (2)$$

$$\phi(x) \equiv \frac{1}{2}k(x - a_0)^2, \quad \mathbf{r}_{jk} \equiv \mathbf{r}_j - \mathbf{r}_k,$$

and the phonon coupling $K(\mathbf{r}_j, \mathbf{r}_k)$ was chosen to be linear and adiabatic,¹³

$$K(\mathbf{r}_j, \mathbf{r}_k) = K_0 + K_1 \hat{\mathbf{e}}_{jk} \cdot \mathbf{r}_{jk}. \quad (3)$$

Here, λ is the Lagrange multiplier corresponding to (and roughly proportional to) the applied pressure,¹² a_0 is the original equilibrium lattice spacing, and $\hat{\mathbf{e}}_{jk}$ is the unit vector between the original equilibrium positions of lattice sites j and k .

It turns out that by using discretized path integrals to make the problem resemble a classical spin problem,¹⁰ one can analytically solve the mean-field theory for this model on a simple cubic lattice in any number of dimensions, d . (In fact, a systematic first correction can also be solved.) The details will be discussed in a future publication,¹⁴ but it is perhaps not surprising that the mean-field result for the phase boundary and disordered regions is

$$k_B T/Jz = \frac{\langle \sinh \beta K(x) / \beta K(x) \rangle}{\langle \cosh \beta K(x) \rangle}, \quad (4)$$

where $\beta = (k_B T)^{-1}$, $z = 2d$ is the coordination number of the lattice, $K(x) = K_0 + K_1 x$, and the angular brackets are phonon integrals,

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} dx f(x) \exp[-(\beta k/2d)x^2 - \beta \lambda x]. \quad (5)$$

The predicted phase diagrams for this model are shown in Fig. 1. Exactly as one would hope, simply changing the sign of the tunneling integral and phonon coupling, K_1 , allows an increase of the pressure to either order or disorder the system at zero temperature. Increasing the pressure always decreases the lattice constant, but for the hindered rotation case, $K_1 > 0$, since $K(x)$ must decrease as x decreases (and the barrier height increases), whereas for ferroelectrics, $K_1 < 0$, since $K(x)$ must increase as x (and the barrier width) decreases. Thus, in complete agreement with experimental results, increasing pressure orders hindered rotors⁷ but disorders hydrogen-bonding ferroelectrics.⁸

This result, of course, has some bearing on our analysis of condensed-phase effects on tunneling be-

cause it is tunneling that causes the zero-temperature disorder—so any statement about an increase or decrease in that disorder is simultaneously a comment about changes in the tunneling rate. This correspondence between the strength of tunneling and the value of the critical pressure means that we can make the implications of our results a bit more precise. It is not difficult to deduce the zero-temperature critical pressure, λ_c , from Eqs. (4) and (5). It is even easier to calculate what the critical pressure, λ_c (static), would be if the phonon dynamics were omitted, i.e., if the Hamiltonian, Eq. (1), had the term \mathcal{H}_L deleted [but \mathcal{H}_L were still used to determine the effect of pressure on the average lattice spacing (and thus the average tunneling integral)].¹⁵ A comparison of the two yields (as shown in Fig. 1)

$$\lambda_c = \lambda_c(\text{static}) + K_1. \quad (6)$$

Hence, regardless of the sign of K_1 , the effect of pho-

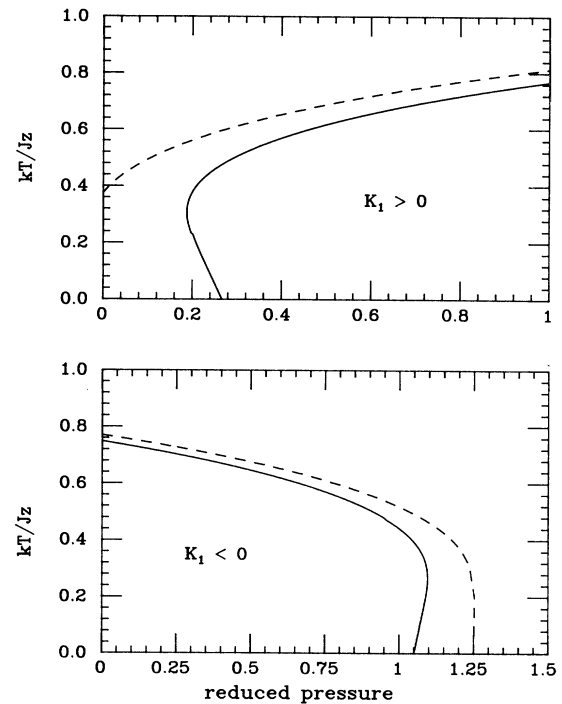


FIG. 1. Phase diagrams for the transverse Ising model on a compressible lattice, plotted as reduced temperature ($T^* = k_B T/Jz$) vs reduced pressure [$\lambda^* = \lambda/(kJz)^{1/2}$]. Solid lines are for the full model described in the text (including coupling to phonon dynamics) and dashed lines are for the uncoupled model (in which the lattice is rigid on the time scale of the tunneling). The upper curves are for reduced parameters $K_0^* = K_0/Jz = 0.99$, $K_1^* = K_1/(kJz)^{1/2} = 0.30$, and the lower ones are for $K_0^* = 0.75$, $K_1^* = -0.20$, but in all cases the ordered region is under the curves. Hence, phonon dynamics *increases* zero-temperature disorder.

nons is always to decrease the size of the ordered region. In other words, *phonons always increase the tunneling for our model*.¹⁶

It is important to note that what we have not shown is that any of the previous studies on tunneling are incorrect. Strictly speaking, what we have done is to note that there is a set of experimental phenomena which allow one to measure the importance of tunneling experimentally and, in the course of modeling those phenomena, we have shown that some aspects of the condensed phase decrease tunneling whereas others increase it. The model itself is rather simplistic, particularly with regard to its use of the adiabatic approximation and the Gunther-Bergman-Imry lattice, and its neglect of short-range-order effects⁹ in ferroelectrics. Nonetheless, it may be one of the simplest models showing a wide range of tunneling behavior, combining, as it does, the effects of many interacting tunneling systems with coupling to phonons. It is obviously dangerous to draw sweeping conclusions from this kind of model, but still, it is perhaps worth suggesting that some thought be given to coupling to barriers (σ^x) rather than wells (σ^z). While the effect of a condensed phase coupled to wells may always be to decrease tunneling, the effect of coupling to barriers may very well be the opposite.

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¹⁵Without coupling to phonon dynamics the model is simply a transverse Ising model.

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