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NONRIGID LATTICE MODEL OF HYDROGEN DIFFUSION IN A TRANSITION METAL: A STATISTICAL MECHANICAL APPROACH*

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ABSTRACT

The isotopes of hydrogen diffuse through transition metals such as Pd with different rates. The observed rates show a complicated temperature dependence including a reversed isotope effect. The diffusion generally behaves nonclassically. Also at moderate densities of hydrogen in Pd, the embedded hydrogen can undergo second-order (mean-field type) phase transition. The transition of this kind implies that there exist long-range attractive forces between H atoms mediated by the Pd lattice. These forces are expected to play a fundamental role in the quantum diffusion of a hydrogen-dense Pd system. To provide a first-principles description of hydrogen diffusion in Pd, we have constructed a physical model based on two ideas: (i) H atoms occupy the interstitial sites of the Pd lattice. (ii) The Pd lattice is nonrigid. To calculate the time correlation function (from which the diffusion coefficient may be deduced), we must for technical reasons remove the nonrigidity from the model via a unitary transformation. The transformation, however, introduces into the model some equivalent interactions. If the transformation is appropriately chosen, the transformed model can be expressed in terms of certain quasiparticles called diffusons. Our resultant model predicts that the diffusion process itself depends on the isotope mass as expected but that the phase transition temperature does not depend on the isotope mass. Our results seem to have experimental support. Also, under some appropriate limits, our model yields exact analytic expressions for the time correlation function.

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I. INTRODUCTORY REMARKS

Transition metals such as Pd, V, Nb, and Tb have the remarkable property of selectively diffusing light gases, e.g., hydrogen and helium isotopes.[1] If used in the form of a membrane, these metals thus can act as, for example, isotope separation devices in nuclear fusion reactors. Here, a metal membrane may be used to extract tritium (T) from a coolant in the design of a fusion reactor in which T's are a by-product of a nuclear fusion reaction. Extracted T's may then be recycled as fuel for the DT reaction cycle. There may be other far-reaching applications.

A key to such an application evidently lies in understanding the nature of diffusion of light gases in these metals, hydrogen diffusion in Pd being a prototype example. At present, the nature of the hydrogen diffusion is only poorly understood. H atoms in an open metal such as Pd undergo rather complex transitions owing to mutual interaction (i.e., H-H interaction) effective over long distances, mediated by the Pd lattice. These long-range forces are brought about by phonons created by H atoms themselves through their occupation in the interstices of the Pd lattice and not by normal Debye-type phonons. It is necessary, therefore, to construct a quantum theory of diffusion. There are a number of experimental facts now known which provide us with clues as to how to approach this problem. These facts are described here as they form a basis for constructing our theory of quantum diffusion for a high-density H-Pd system.

II. THE PHYSICS OF THE PdH SYSTEM

A. Diffusion and Isotope Effect

Palladium can dissolve hydrogen to high concentrations in a nonstoichiometric manner. Neutron diffraction measurements show that the hydrogen atoms occupy the interstices of palladium, in which these interstitial sites themselves form an octahederal sublattice within the regular fcc palladium lattice.[2] The hydrogen occupying the interstices causes the volume of the palladium to expand. The static distortion of the lattice may be detected through the increase in the lattice parameters, the increase reflecting a measure of the interaction between the hydrogen and the lattice. Evidently there exists a favorable binding energy for the hydrogen at these sites through electron overlap (see C). The hydrogen atoms in fact vibrate about their interstitial sites. Owing to the lightness of the mass, the hydrogen (H) vibrational modes are of very high frequencies $\sim 10^{13}$ sec^{-1}, well above the lattice Debye (D) vibrational frequencies (cf., $\hbar\omega_H/k \simeq 1{,}000K$ vs. $\hbar\omega_D/k \simeq 200K$, where $\hbar$ and k are the Planck and Boltzmann constants, respectively, and ω_H and ω_D denote vibrational hydrogen and Debye frequencies, respectively). Thus, the hydrogen modes may be considered localized, independent of the lattice motions.[3]

The dissolved hydrogen atoms are also extremely mobile. The transition rate is $\sim 10^{12}$ sec^{-1} and the self-diffusion coefficient is $\sim 10^{-6}$ cm^2/sec, both of which are comparable to those of protons in water. The hydrogen atoms, on the average, remain about their sites for some 10 oscillations before moving to their nearest-neighbor sites. With respect to these fast moving interstitial hydrogen atoms, the lattice palladium atoms may be thought of as essentially unmoving or very slowly moving, undergoing only coherent lattice vibrations (i.e., low-energy phonons).[3]

The vibrational and transitional motions of the dissolved hydrogen atoms are determined to a large extent by their zero-point energies and discrete energy levels.[4] At normal temperatures, the protons diffuse by hopping from site to site and do not propagate like conduction electrons (i.e., no coherence between the initial and final states). The hopping transitions are very sensitive to the slow motions of the palladium lattice since the path of the octahedral-site transition for the hydrogen lies directly between two fcc lattice palladium atoms which can therefore interfere. The transition can be brought about by symmetric lattice modes, producing a lattice activation or distortion energy of 0.1 to 0.5 eV (for the tetrahedral-site transition or in a bcc lattice metal, the situation is quite different). Hence, the interaction between the local modes and phonons is the important rate-determining factor for the transition. At low concentrations, the hydrogen atoms can appear to diffuse as if by a random walk with jump length equal to the distance between nearest-neighbor octahedral sites (~2.85Å). At higher concentrations, the diffusion becomes more complex owing to greater distortions of the lattice resulting in a more complex interaction between the local modes and the lattice. It indicates therefore that there may be different diffusion mechanisms operating in different physical regimes. The observed nonclassical behavior of the isotope effect confirms the complexity of diffusion.[5]

Classical rate theory[6] predicts that, for a family of isotopes, the lighter members diffused faster than the heavier ones. This prediction is quite generally observed for families of heavy isotopes. Also, for families of light isotopes, e.g., H and D, this prediction in metals such as V, Nb, Ta is valid although classical rate theory cannot otherwise explain the experimental data. In contrast, the diffusion of H and D in palladium shows the reversed isotope dependence[5] for the temperature range of 100 to 500K. But the diffusion is "normal" outside this range, i.e., above 600K and below 50K. Although there are few measurements of the tritium diffusion in palladium, the available information adds further confusion. Above 600K, the diffusion rate follows the sequence of T, H, and D. In the range of 100 to 500K, it is D, H and T. Below 50K, there are no measurements for T. Evidently, one can learn from the observed isotope dependence the mechanisms of the hydrogen diffusion in palladium. The classical rate theory is wholly inadequate to deal with the quantum diffusion processes. The existing nonclassical theories are largely phenomenological and they differ considerably from one another in the details of the hydrogen-lattice coupling, about which still too little is known. These theories more or less predict the Arrhenius behavior for the proton diffusion at high temperatures and suggest a considerable departure from it at temperatures below the Debye temperature. The first-principles (quantum) theories of diffusion are, however, not yet sufficiently developed to be in a position to provide an interpretation of these experimental results.

B. Critical Point Behavior

The pressure-concentration isotherms for hydrogen in palladium show an appealing similarity to the well known pressure-density isotherms for simple fluids.[1] In fact, the isotherms of the lattice hydrogen display a critical point below which a low concentration A-phase is separated from a high concentration B-phase by a mixed or coexisting phase region. By analogy, the A phase region may be regarded as corresponding to a vapor-like phase and the B phase to a liquid-like phase (even though in both the A and B phases the hydrogen occupies the octahedral interstitial positions of the fcc palladium lattice). The crystalline structural features of the hydrogen in the PdH system and the vapor-liquid interpretation are not incompatible. The PdH system is a realization of the lattice gas model, the palladium providing the lattice cells or interstitial sites which the hydrogen can occupy as a lattice gas.[7] The measured critical values of the lattice hydrogen[8] are approximately $T_c = 566\text{K}$, $P_c = 20$ atm., $\rho_c = 0.021$ atoms/Å^3, which may be compared with those of the "free" hydrogen, $T_c = 33\text{K}$, $P_c = 13$ atms., $\rho_c = 0.009$ molecules/Å^3. Here, T_c, P_c, and ρ_c denote the critical temperature, pressure and density, respectively.

Beyond the broad similarity between the hydrogen of PdH and the lattice gas model, there are some important differences which serve to bring out information about forces operating in PdH. The most significant of these is that, unlike the rigid lattice gas model, the palladium lattice is nonrigid. The phase transition in the lattice gas model is caused by the short-range, two-body attractive interaction. For the phase transition in the PdH system, the non-rigidity of the Pd lattice is the primary source of the attractive interaction.[7] The nature of this attractive interaction can best be observed through the critical behavior of the PdH system.

The recent experimental work[8] indicates that for a critical region greater than 10^{-3} the static critical exponents are all mean-field-like [i.e., within the experimental errors $\alpha = 0$ (discontinuous), $\beta = 1/2$, $\Delta = 1$, $\delta = 3$ and the dynamic exponents may also be mean-field-like (i.e., $\tau \sim |T-T_c|^{-\Delta}$ where $\Delta = 1$)]. Here, α, β, γ, δ and Δ are critical exponents for the specific heat, density, isotherm and higher-order free energy (gas exponent), respectively, and τ denotes the relaxation time and T the temperature.[14] Now most nonclassical systems (i.e., systems not behaving mean-field-like) display nonclassical behavior for a critical region already much greater than 10^{-3}. Hence, one believes that the critical behavior of the PdH system is classical entirely and suspects that it is classical because of the special nature of forces operating between the hydrogen atoms in the palladium lattice. These forces are recently recognized to be predominantly elastic arising from the hydrogen atoms acting as defects in the palladium lattice. Since each defect influences all other defects, the forces must operate over long distances in a body of finite size. The forces of this type are attractive, hence the system can condense. But the long-range forces, or a high number of interacting neighbors, give rise to the observed classical behavior of the phase transition in the PdH system.

C. Superconductivity

Pure palladium metal does not display superconductivity. But when hydrogen is dissolved in palladium, the PdH system begins to exhibit superconductivity when the concentration of the hydrogen reaches the value of $x \simeq 0.7$, where x denotes the number of H per Pd.[9] The superconducting transition temperature T_s begins to increase very sharply as x increases attaining its maximum value at $x \simeq 1$ and then it begins to decrease as x further increases, finally vanishing at $x \simeq 2$. The maximum transition temperature, 9K at $x \approx 1$, is high compared with the transition temperatures of standard superconducting metals [cf., 4.2K for Hg, 3.5K for Sn, 0.9 for Zr, etc.]. Essentially the same has been observed for deuterium in palladium (PdD). Nothing is yet known about tritium in palladium (PdT). Presumably it, too, becomes superconducting at about the same value of x.

Superconductivity pertains to the transport of electrons. At a first glance, one may think that it should bear no relationship to our transport of protons and deuterons. As mentioned before, the hydrogen occupying an interstitial site of the palladium experiences a favorable binding energy (of about 0.1 eV) through electron overlap. In this electronic structure one also finds the source of superconductivity. Hence, the superconductivity in PdH and PdD can reveal information about the coupling of H and D to the palladium lattice which also determines the diffusion of H and D. The connection becomes more apparent through the following observation: It is known that T_s is related to the isotopic mass M by the relation $T_s \cdot M^{\frac{1}{2}}$ = constant for a given element.[20] One finds that at x = 1, for example, $T_s(H) = 9K$ and $T_s(D) = 11K$, indicating again a reversed isotope dependence as in the diffusion of H and D.[5]

The electronic structure of Pd is as follows:[9] The Fermi energy of Pd lies near the top of the 4d bands leaving 0.36 unfilled 4d state per Pd atom and it intersects the broad 5sp bands. Also, the hydrogen occupying the octahedral sites can generate a group of new low-lying states. The electrons from the dissolved hydrogen atoms begin to fill the low-lying H-induced new states and the unfilled 4d states easily without much affecting the existing Fermi energy. At $x \gtrsim 0.6$, these two types of states become completely saturated (i.e., no more paramagnetism). Additional uptake of H involves filling of the hitherto unfilled 5sp bands above the 4d bands. Owing to the low density of states, the Fermi energy must now be substantially raised.

Superconductivity is brought about by the filled 5sp bands above the top of the 4d bands.[9] At $x = 1$, there is approximately 0.4 to 0.6 conduction electron per Pd atom and the system behaves much like a free electron metal. If $x \rightarrow 2$, the hydrogen begins to occupy the sites of the tetrahedral sublattice. In this configuration the hydrogen favors bonds of the electron-sharing type and PdH no longer resembles a free electron metal, i.e., the superconductivity vanishes. Thus it is in the octahedral sublattice where one finds the source of the superconductivity in PdH. A recent measurement[10] of the specific heat at liquid He temperature further indicates that the conduction electrons are coupled to the (low-energy) acoustic phonons. Although the current theories based on these ideas are still not able to give a quantitative explanation for the superconductivity in PdH and PdD, they do yield T_s for H and D which are qualitatively correct and also anomalous (i.e., reversed isotopic dependence).

III. THEORETICAL CONSIDERATION

The diffusion coefficient D of hydrogen has been commonly viewed in the past through a universal relation of the following form:

$$D = D_o \exp\{-U/kT\}, \qquad (1)$$

where, according to classical rate theory, U is the activation energy and D_o is some constant independent of temperature (or at best weakly temperature-dependent).[4] Many experimental results for diffusion have been fitted to the above relation. While eq. (1) approximately represents the observed diffusion for a considerable range of temperature, the two coefficients D_o and U do not behave as predicted by the rate theory.[6] Since hydrogen is extremely light compared with the host palladium, the diffusion processes cannot be properly understood in the classical context. It is necessary to utilize quantum theory to account for the diffusion of hydrogen.

The diffusion coefficient D has been measured frequently by one of two ways: Gorsky effect and neutron scattering. The existence of anelasticity in the PdH system gives rise to a simple relationship between D and the relaxation time τ,

$$D\ \tau = \text{constant} \tag{2}$$

where the constant depends on the geometry of the host sample.[11] Thus, by measuring τ directly through the anelasticity of the PdH system (the Gorsky effect)[12] or somewhat indirectly through the neurton scattering[3], D can be experimentally determined. Since our theoretical approach utilizes the scattering theory, we shall briefly explain the latter connection. The differential scattering cross section σ is related to the transition probability per unit time W_{if} (whose inverse gives the rate or relaxation time) as[13]

$$\frac{d^2\sigma}{d\Omega dE_f} = I\ W_{if} \tag{3}$$

where I contains all the inessential factors such as the nuclear form factor, and i and f denote the initial and final states, respectively, and Ω is the solid angle and E_f the final energy. The transition probability is given by quantum mechanics as

$$W_{if} = 2\pi/\hbar \cdot |\langle i|H|f\rangle|^2 \tag{4}$$

where the usual energy conservation and counting over the final degenerate states are assumed. Since H includes the hydrogen-hydrogen interaction mediated by, presumably, the palladium lattice, the experimental cross section contains information about the basic mechanisms of diffusion. Conversely, the transition probability calculated from some given H can provide an interpretation for the observed diffusion through (2) and also to a less extent through (1).

If, as according to (4), the initial and final states are known, it is in principle possible to calculate the transition probability, hence the diffusion coefficient. The problem of a harmonic solid serves as one such example. Accordingly, efforts have been made to construct a quantum theory of diffusion by considering a very dilute concentration of hydrogen dissolved in a harmonic lattice of palladium in which hydrogen is coupled to the lattice linearly only. Flynn and Stoneham,[4] notably, have obtained an expression for the transition probability in the form of (1), but with different meanings for the two coefficients D_o and U than given by the classical rate theory.

The work such as by Flynn and Stoneham represents interesting first steps into understanding the quantum processes of diffusion and is thus a valuable contribution. But it is a model for the PdH system at infinite dilution. It is thus not expected to be useful at moderate densities (i.e., A and B phases) of our interest where the interaction between hydrogens mediated by the lattice is an important, possibly dominant, factor in the quantum processes of diffusion. That the lattice mediated hydrogen-hydrogen interaction is an essential factor is evident from the now well-established existence of second order phase transition in the PdH system,[8] which has been compared to that in the homogeneous gas-liquid system.[14] For a Hamiltonian containing this kind of strong and complex interaction, one does not know the initial or final states. Even if the initial state can be prepared in some way, there may be innumerably many degenerate or nearly degenerate final states which must be included in (4) for the transition probability--a well-known difficult problem in itself. There is an alternative approach originally pioneered by van Hove[15] and later developed by others[16] suitable for studying dynamics of strongly interacting systems (such as the diffusion in the PdH system at densities of our interest). We shall turn to this approach to provide an understanding for the quantum processes of diffusion and also to devise a practical means of calculating dynamic quantities.

IV. DIFFUSION MODEL

There are two main problems for studying diffusion from first principles. First, the Hamiltonian must be constructed by taking into account all the interactions important for diffusion in the PdH system. Second, given such a Hamiltonian one must still be able to apply nonequilibrium statistical mechanics to obtain solutions to a quantum version of the diffusion equation. Recently we have developed mathematical techniques to treat certain time-dependent problems[17], which may be applicable to our diffusion problem.

In constructing a diffusion model for the PdH system at high hydrogen concentrations, one must thus include long-range forces between hydrogen atoms embedded in a nonrigid lattice. Since the transition of hydrogen atoms from one interstitial site to another is essentially of discrete steps, we construct our model in terms of a set of discrete operators a_i and a_i^+, respectively, the destruction and creation operators of the hydrogen atoms at the interstitial site i. These operators satisfy the algebra of spins.[18] In terms of these operators, our model is given as follows[19]: Up to an additive constant and with a harmonic lattice for Pd whose equilibrium coordinates are given by $\{x_\alpha^o\}$,

$$H = -\sum_{(ij)} \left[\frac{\hbar^2}{2md^2} - U_{ij}(\{x_\alpha\})\right] (a_i^+ a_j + a_i a_j^+) + \frac{K}{2}\sum_\alpha (x_\alpha - x_\alpha^o)^2, \qquad (5)$$

where m is the proton mass, d is the lattice spacing (e.g., $d \sim 3A$), $U_{ij}(\{x_\alpha\})$ is a function of the instantaneous Pd coordinates $\{x_\alpha\}$ and K is the spring constant. The first term represents the transition energy of protons in a nonrigid lattice. In a nonrigid lattice, the transition of protons, however, is influenced by the lattice through its distortion. We denote by $U_{ij}(\{x_\alpha\})$ the coupling of the proton transition to the Pd lattice. The second term represents the usual lattice energy. Here, the equilibrium positions $\{x_\alpha\}$ may be thought of as being equivalent to the positions of a rigid lattice.

Our Hamiltonian does not include the proton localization energy, nor any short-range interaction energy. It contains only the simplest hydrogen lattice coupling necessary for diffusion. Still, our Hamiltonian is not simple since the proton and Pd coordinates are coupled. To decouple them, we expand $U(\{x_\alpha\})$ about the equilibrium positions, retaining the first-order terms in the Pd lattice displacement only. We then have

$$H = H_o(\{x_\alpha^o\}) + H_1(\{x_\alpha\}) \tag{6}$$

where H_o is the transition energy evaluated at the equilibrium positions of Pd and H_1 is given by

$$\begin{aligned} H_1 &= +\Sigma(x_\alpha - x_\alpha^o)U_{ij}^\alpha \cdot \{a_i^+ a_j + a_i a_j^+\} \\ &\quad + \frac{K}{2}\Sigma(x_\alpha - x_\alpha^o)^2, \end{aligned} \tag{7}$$

where

$$U_{ij}^\alpha = \frac{\partial}{\partial x_\alpha} U_{ij}(\{x_\alpha^o\}). \tag{8}$$

The hydrogen and Pd coordinates are still coupled in H_1, but they can be decoupled by a unitary transformation,

$$\tilde{H} = T\,H\,T^{-1}, \tag{9}$$

where we choose

$$T = \pi_{\alpha}\exp\{-iK^{-1}P_{\alpha}\Sigma U^{\alpha}_{ij}\ (a_i^{+}a_j + a_i a_j^{+})\} \tag{10}$$

where P_α is the momentum of the Pd atom. The unitary-transformed Hamiltonian is as follows:

$$\tilde{H} = H_o + \tilde{H}_p(\{x^o_\alpha\}) + \tilde{H}_L \tag{11}$$

where

$$\tilde{H}_p = -\frac{1}{2K}\sum_{\alpha}\sum_{(ij)}\sum_{(mn)} U^{\alpha}_{ij}\,U^{\alpha}_{mn}$$

$$\times\ (a_i^{+}a_j + a_i a_j^{+})(a_m^{+}a_n + a_m a_n^{+}) \tag{12}$$

and $\tilde{H}_L$ contains the Pd coordinates only, i.e., a pure Pd lattice energy, which therefore may be included in the additive constant. We have taken advantage of the invariance of the partition function under unitary transformations to uncouple the hydrogen and Pd coordinates. Furthermore, our choice for T gives H_o and $\tilde{H}_p$ in terms of the Pd equilibrium coordinates only. That is, the hydrogen transition in our transformed model takes place in a rigid lattice. The model, however, has more complex hydrogen-hydrogen interactions than the original model.

The interaction energy $\tilde{H}_p$ has the feature that it may be reduced to a product of two essentially independent bilinear factors. Each bilinear term represents the creation-annihilation of a mode localized over a samll region of space. If one regards this creation-annihilation process as correlated (i.e., a quasiparticle of diffusion or a "diffuson"), the interaction energy consists of pairing of these diffusons over the entire lattice. If the pairing is effective over a long range and largely unchanging, e.g., $U_{ij}\ U_{mn} = U^2$ for any pairs of ij and mn, our diffusion model corresponds to the generalized van der Waals model in a field[17]. Some recent measurements[8] indicate that the interaction responsible for the phase transition in the PdH system has this reducible form, presumably arising from the Pd's deformable lattice.

If our Hamiltonian contains only H_o, to obtain the experimental values of T_c the effective proton mass associated with the transition here must at least be a few orders of magnitude smaller than the actual proton mass. Thus, the source of the observed phase transition, according to our model, cannot be H_o but must be $\tilde{H}_p$. We observe that this lattice energy does not strongly depend on the proton mass since $\tilde{H}_p$ mainly represents the elasticity of the Pd lattice. Our model, therefore, predicts that critical temperatures for Pd-hydride systems should exhibit little or no isotope effect. That is, T_c's for PdH and PdD should be nearly the same. This conclusion seems to be borne out by recent experiments[20]. These results indicate that for metal-hydride systems the phonon-proton coupling (represented in our model by U) plays a central role. This function U, as may be expected, is rather complicated since it must include the structure and dynamics of the lattice. If, for example, Pd atoms move closer towards the path of an H atom, the lattice motion retards the movement of the H atom. If Pd atoms move away from the path, the lattice motion enhances the transition. Hence, the diffusion of hydrogen in the Pd lattice clearly depends on the coupling of the Pd and H coordinates and also on the nonrigidity of the lattice.

V. TIME CORRELATION FUNCTION

We shall define the order parameter for the system as follows[21]:

$$\rho_k = \sum_i (e^{ik\cdot r_i} a_i + e^{-ik\cdot r_i} a_i^+) \qquad (14)$$

where the sum extends over all the equilibrium lattice points r_i and k is the wavevector. Under the constant-coupling approximation discussed in IV and with no external field, one can re-express the transformed Hamiltonian (11) in terms of the order parameter entirely.[22] The re-expressed form my be shown to closely resembe the van der Waals Hamiltonian. That is,

$$\tilde{H} \to A\rho^2 + B\rho^4 \ , \qquad (15)$$

where A and B are coupling constants (the wavevectors are suppressed for simplicity). The van der Waals Hamiltonian has been recently investigated in detail[17]. Thus, it is possible to gain a considerable insight into our model from our knowledge of the van der Waals system. In particular, the long-range order $\langle\rho\rangle$ for (11) must approximately satisfy the following relation:

$$\langle\rho\rangle = \frac{1}{2} \tanh \{2A\beta\langle\rho\rangle + 2B\beta\langle\rho\rangle^3\} \qquad (16)$$

where $\beta = 1/kT$ and $3B < 4A^3\beta^2$. For $B = 0$, we know the time correlation function for (11) exactly: For $T > T_c$, where $T_c = A/2k$,

$$\langle\rho(t)\rho\rangle = \langle\rho^2\rangle \exp\{-\frac{1}{2}(At)^2\} \ , \qquad (17)$$

where

$$2\langle\rho^2\rangle = (2 - \beta A)^{-1}. \qquad (18)$$

For $T < T_c$,

$$\langle\rho(t)\rho\rangle = \langle\rho^2\rangle\exp(-At^2/\beta), \qquad (19)$$

where $\langle\rho^2\rangle = \langle\rho\rangle^2$ if $T \rightarrow 0$ (a more general expression may be found elsewhere)[17].

The time correlation function follows Gaussian form for temperature above and below T_c. This behavior may be taken as an ideal behavior. The true time correlation function for our model (11) is expected to approach the ideal form under appropriate limits already described. It is thus reasonable to suggest that the time correlation for our model is weak at long-time intervals. That is, over a long time the hydrogen transition becomes uncorrelated and random-walk-like. But at short-time intervals and especially below T_c the transition may be strongly correlated with the correlated distances ranging much beyond the average size of diffusons.

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