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LETTER TO THE EDITOR

Quantum effects on double-Morse hydrogen-bonded chains

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Abstract. Thermodynamic quantities of a hydrogen-bonded chain model are calculated by means of the effective potential method assuming a non-linear double-Morse interaction. The relevance of the quantum effect is pointed out, especially through the modification of the intensity and position of the non-linear contribution to the specific heat.

Hydrogen-bonded one-dimensional systems have been a subject of interest for a long time as many organic solids—e.g., imidazole and proteins in cell membranes [1]—are composed of these chains. Moreover, many two- and three-dimensional systems, like ice [2] and rhodopsin in *Holobacterium holobium* [3], can be considered as aggregates of interacting hydrogen-bonded chains (for example, the Bernal-Fowler filament in ice).

The rather surprising transport properties of these compounds have been investigated, and a soliton mechanism for the coherent mobility of protons has been suggested [4, 5]. The proton is assumed to move in a double-well potential (like the ϕ^4 or double Morse) originated by its interaction with the two nearest-neighbour heavier ions; different kinds of the interaction potential have been considered in the literature [6, 7, 8, 9, 10, 11, 12].

The influence of strong quantum effects on the statistical and transport properties of the proton has been recently studied [12]. Indeed, these effects cannot be disregarded even at room temperature, because the thermal de Broglie wavelength is about 1 Å, i.e. still comparable with the characteristic interaction range (2.76 Å for the Bernal-Fowler chain in ice).

Quantum effects in the aforementioned ice chain were evaluated, and found to be significant [12], using the self-consistent harmonic approximation [13], with a trial Hamiltonian made up of independent harmonic oscillators, i.e. approximating the system in terms of Einstein's model. In order to do a more realistic calculation, the full dispersion relation will be considered in our complete quantum treatment of the harmonic excitations, while a one-loop approximation will be employed only as far as the quantum effects of the non-linearity are concerned, the classical non-linear behaviour being fully embodied in our approach. This is within the framework of the effective potential method [14, 15, 16, 17], which successfully describes the thermodynamics and spectral shapes of quantum non-linear chains [18].

In this letter we apply the method to the hydrogen-bonded chain, showing the relevance of the quantum effects in the thermodynamic quantities, and in particular, by means of the calculation of the non-linear part of the specific heat, the quantum character of the solitons is investigated.

As has usually been done in previous work, we describe the hydrogen-bonded chain as an alternating two-sublattice system: one sublattice is formed by protons (or deuterons), while the other one hosts the heavy ions (oxygen in ice crystals), and they interact through a non-linear potential. Therefore, the following Hamiltonian may be used to model the system:

$$H = \frac{1}{2} \sum_{i=1}^N \frac{P_i^2}{M} + \frac{1}{2} \sum_{i=1}^N \frac{p_i^2}{m} + \sum_{i=1}^N \{V_{\text{OH}}(x_i - X_i) + V_{\text{OH}}(X_{i+1} - x_i) + V_{\text{O}}(X_i) + V_{\text{OO}}(X_{i+1} - X_i) + V_{\text{HH}}(x_{i+1} - x_i)\}. \quad (1)$$

The first two terms are the kinetic energy of the heavy and light sublattice, respectively, V_{OH} is the hydrogen–oxygen interaction potential, while the other potential terms represent: a site potential for the oxygens (V_{O}), which mimics the interaction with a substrate; the oxygen–oxygen (V_{OO}) and hydrogen–hydrogen (V_{HH}) interactions; X_i and x_i denote the distance of the heavy and light ions, respectively, from a common, fixed origin.

When the static approximation for the heaviest ions is considered, the hydrogen ion moves in a local, degenerate double-minimum potential; quartic [6], ϕ^4 [4, 5], sine–Gordon [7, 8] and double-Morse (DM) [10, 11, 12] potentials have been used. The DM seems to be the most realistic interaction potential between hydrogen and oxygen, so we have chosen this as the inter-sublattice coupling:

$$v_{\text{DM}} = \sum_{i=1}^N [\varepsilon(1 - e^{[-d(x_i - X_i - r)])^2})^2 + \varepsilon(1 - e^{[-d(X_{i+1} - x_i - r)])^2})^2] \\ = \sum_{i=1}^N \{V_{\text{OH}}(x_i - X_i) + V_{\text{OH}}(X_{i+1} - x_i)\} \quad (2)$$

where ε determines the well depth, d^{-1} the well width (and implicitly the anharmonic character of the system), and r is the equilibrium distance between the oxygen and hydrogen ions.

The usual choice for the other interactions is a simple parabolic potential, so the last row of equation (1) reads simply:

$$\frac{1}{2} \sum_{i=1}^N [k_{\text{O}}(X_i - iR)^2 + k_{\text{HH}}(x_{i+1} - x_i - R)^2 + k_{\text{OO}}(X_{i+1} - X_i - R)^2]. \quad (3)$$

Unless very crude approximations are used, the complete Hamiltonian model (1) is rarely considered, but it is common practice to neglect some of the parabolic interactions, which have a common feature of contributing to fixing the lattice constant of the chain, which makes the respective interaction constants not completely independent from each other. As we are interested in the statistical properties of the system, we find it sensible to neglect the on-site potential $V_{\text{O}}(X_i)$, whose main effect is simply to prevent the longitudinal sliding of the chain, i.e. to introduce an energy gap in the phonon dispersion relation, which causes a finite activation energy of the translation mode. As far as the oxygen–oxygen and hydrogen–hydrogen interactions are concerned, there is *a priori* no really good reason to neglect one of them; however, the actual computation of the thermodynamics of the chain is greatly simplified if only one is retained, and this appears to be sufficient to describe the main statistical properties of the system. We have considered both the cases where only V_{HH} or V_{OO} is present, and the results we get are very similar if the respective force constant is adjusted in order to match the dispersion relation given by the parameters already employed in the literature [12] and reported in table 1.

Table 1. The set of potential parameters used in the thermodynamics calculations.

ε (kcal mol ⁻¹)	d (Å ⁻¹)	r (Å)	R (Å)	k_{OO} (N m ⁻¹)	k_{HH} (N m ⁻¹)
10.7	7.8	0.94	2.76	36.6	22.0

The use of the effective potential method allows us to reduce the evaluation of the quantum thermodynamic properties of the system described by the Hamiltonian (1) to the computation of those of the classical system whose interaction potential is given by

$$\begin{aligned}
 V_{\text{eff}} = & V_O + V_{OO} + V_{HH} + \sum_{i=1}^N [\varepsilon(1 - 2e^{-d(x_i - X_i - r) + D/2} + e^{-2d(x_i - X_i - r) + 2D}) \\
 & + \varepsilon(1 - 2e^{-d(X_{i+1} - x_i - r) + D/2} + e^{-2d(X_{i+1} - x_i - r) + 2D})] \\
 & - \frac{\varepsilon}{g^2}(f_1^2 + f_2^2)D + \frac{1}{\beta} \sum_{qs} \ln \left(\frac{\sinh f_{qs}}{f_{qs}} \right)
 \end{aligned} \quad (4)$$

where the following quantities have been introduced:

$$\left\{ \begin{array}{l}
 f_1^2 = g^2 \frac{\partial^2 V_{\text{eff}}}{\partial (x_i - X_i)^2} \Big|_{x_i = x_{\min}, X_i = X_{\min}} \\
 f_2^2 = g^2 \frac{\partial^2 V_{\text{eff}}}{\partial (X_{i+1} - x_i)^2} \Big|_{x_i = x_{\min}, X_{i+1} = X_{\min}} \\
 D = \sum_{qs} (U_{nH,qs} - U_{nO,qs})^2 \alpha_{qs} \\
 \alpha_{qs} = \frac{\hbar}{2\omega_{qs}} (\coth f_{qs} - 1/f_{qs}) \quad f_{qs} = \frac{\hbar\omega_{qs}\beta}{2}
 \end{array} \right. \quad (5)$$

$U_{nl,qs}$ is the unitary matrix which diagonalizes the harmonic approximation of the system, and α_{qs} is the pure quantum square fluctuation of the qs mode, whose eigenfrequency is ω_{qs} . The parameter D determines the renormalization of the non-linear interaction due to the pure quantum fluctuations, while x_{\min} and X_{\min} are the positions of the ions corresponding to the translation-invariant global minimum configuration of V_{eff} , which is determined in a self-consistent way together with all the other parameters defined in equations (5). We observe that the effective potential (4) is defined in such a way as to preserve the symmetry properties of the original interaction potential; moreover, all of the quadratic part of the interaction is unaffected by the renormalization procedure, as the effective potential formalism treats the harmonic excitations of the system in a fully quantum way.

The quantum non-linear effects in the system are determined by the coupling constant $g = (\hbar/\varepsilon)\sqrt{k_{OH}/\mu_{OH}}$, where $k_{OH} = 2d^2\varepsilon$ is the force constant of the harmonic approximation of a Morse oscillator, and $\mu_{OH} = \sqrt{mM}$ is the reduced mass of an oxygen-hydrogen couple. With our choice of the parameters we have $g = 0.5$ when the lighter particle is a proton, and $g = 0.42$ when it is a deuteron.

As mentioned before, the thermodynamic calculations of our system are greatly simplified when only V_{OO} or V_{HH} is considered, so the kernel of the transfer matrix becomes

symmetric and the extended Gürsey method [19, 20, 21], based on the bilateral Laplace transform (BLT), can be used.

Considering only V_{OO} seems to be more realistic because the greater oxygen mass should constrain the chain to a fixed lattice constant R and screen the proton-proton interaction. However, in the adiabatic approximation, i.e. when the dynamics of only the hydrogen subsystem is considered, taking a parabolic V_{HH} and a DM V_{OH} , the model can be mapped into a double sinh-Gordon system [10] which admits kink-antikink solutions. The activation energy of these kinks is given by

$$E_p = \frac{2}{dR} \sqrt{2mDc_0^2} (dr_0 - \tanh dr_0) \quad (6)$$

where c_0 is the sound velocity and r_0 is the position of one of the two symmetric minima of the double-Morse potential. E_p turns out to be of the order of 2500 K for a chain with parameters as given in table 1.

For such a system the soliton phenomenology is easier to perform; however, as the thermodynamics turns out to be practically the same, the soliton considerations can also be sensibly extended to the more realistic V_{OO} potential.

We have calculated the internal energy and the specific heat of the chain at fixed length, $L = NR$, in the range of temperatures from $T = 25$ K to $T = 5400$ K in order to see the behaviour of the quantum effects when the highest temperatures (of the classical region) are approached.

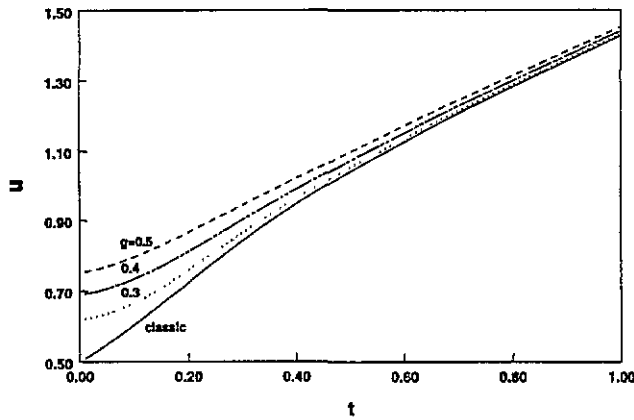


Figure 1. The internal energy per particle at constant length of the classical (full line) and quantum (broken lines) DM chain. The different broken lines correspond to different values of the coupling constant g .

In figure 1, the internal energy is shown for the classical and quantum systems as a function of the reduced temperature $t = k_B T / \epsilon$. The latter is plotted for different couplings starting from hydrogen ($g = 0.5$) and deuterons ($g = 0.4$). At the lowest temperatures, the quantum effects are apparent through the zero-point energy. For increasing temperatures the quantum curves approach the classical one as rapidly as the quantum coupling is decreasing.

Analogous considerations can be made for the specific heat at constant length c_v , as shown in figure 2. It is worthwhile noticing that in the classical case a well pronounced peak is present, which strongly decreases when g increases. This peak can be ascribed to solitons: in the classical case, its position turns out to be at $t \simeq 0.2$ ($T = 1100$ K), in agreement with a soliton gas phenomenology. As usual [22], the quantum effects manifest

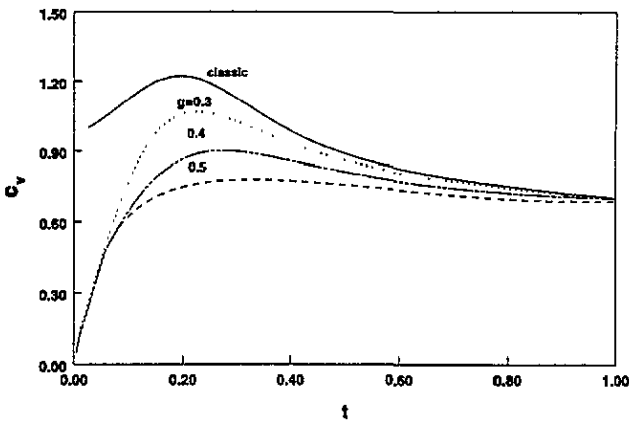


Figure 2. The specific heat per particle at constant length of the classical and the quantum DM chain as a function of temperature; symbols as in figure 1.

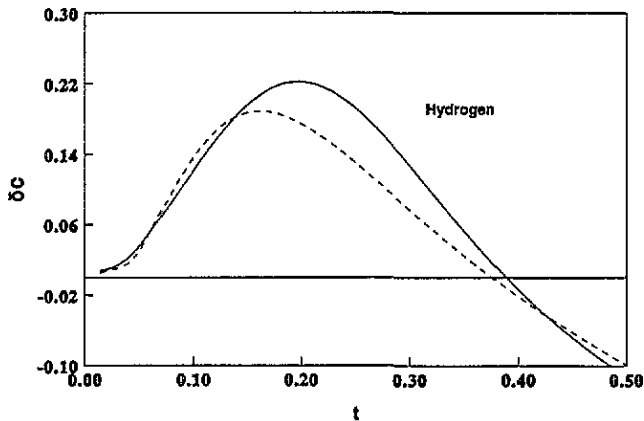


Figure 3. The pure non-linear contribution to specific heat per particle at constant length of the classical (—) and quantum (- - -) hydrogen-bonded chain ($g = 0.5$).

themselves in the decreasing of the intensity of the peak and the shifting of its position to lower temperatures, due to the lower energy of the kinks. These effects are better pointed out in figure 3, where the non-linear contribution to the specific heat δc is reported.

The results shown seem to confirm the presence of soliton excitations and their important role in the transferring of the protons along the chain. On the other hand the quantum character of the system is apparent at any realistic temperature. This leads to two important modifications of the peak of the non-linear contribution to the specific heat. These features can be explained by taking into account the fact that the quantum fluctuations decrease the energy of the barrier, enhancing the activated jumps across the two minima of the potential. Due to the increased number of activated solitons they can no longer be considered to be pure non-interacting particles and their interaction has to be taken into account [22]. The lower intensity of the peak, together with the shift to lower temperatures, reflects the interaction among the non-linear excitations with a related loss of coherence of propagation.

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