ELSEVIER

31 July 1995

PHYSICS LETTERS A

Physics Letters A 203 (1995) 362–366

Comparison of quantum Monte Carlo and semiclassical Monte Carlo results in investigations of the thermal stability of Davydov solitons

L. Cruzeiro-Hansson [a], V.M. Kenkre [b]

[a] *Department of Crystallography, Birkbeck College, Malet Street, London WC1E 7HX, UK*

[b] *Center for Advanced Studies and Department of Physics, University of New Mexico, Albuquerque, NM 87131, USA*

Received 3 May 1995; accepted for publication 26 May 1995

Communicated by A.P. Fordy

Abstract

We study the problem of the thermal stability of the Davydov soliton, in the context of its viability as providing a mechanism for energy transfer in proteins, by making a quantitative comparison between the full quantum model and the semiclassical model which has been used frequently for analytic and numerical calculations. Our goal is to gain insight into the range of validity of the semiclassical model in the particular context of finite temperatures. Our results indicate that, at biologically relevant temperatures, for the parameters chosen, the semiclassical model gives practically the same results as the full quantum mechanical model.

In many biological processes involving systems such as proteins, the release of useful energy occurs in regions (the active sites) lying at non-negligible distances from regions in which the energy is consumed. The question thus arises how this energy, which is not enough to create excited electronic states, can travel without being dispersed or dissipated into heat. In Davydov's model [1] it is assumed that the energy released in the hydrolysis of adenosine triphosphate (ATP) leads to the creation of amide I vibrations in the hydrogen-bonded spines of protein α-helices. The interaction of the amide I excitation with the vibrations of the neighboring hydrogen bonds leads, within the approximations of the analyses employed, to a nonlinear effect and to soliton states. The nonlinear effect is closely related to that inherent in polaron dynamics [2].

The Davydov model has been recently the subject of many analytical and numerical studies [3]. An outstanding question in the field is that of the thermal stability of the soliton [4–8]. From Langevin simulations of the Davydov model it was initially concluded that Davydov solitons are not thermally stable at biological temperatures [4]. Further studies have, however, uncovered a more complex picture [6] and it has been suggested [11] that the soliton lifetimes estimated in Ref. [4] might be lower bounds rather than accurate estimates. These investigations as well as a number of other related studies of the thermal stability of the soliton [5,7–10] have been based on the semiclassical approximation. An analysis of the validity of this approximation is obviously important as pointed out recently by a number of authors [12,13]. While it is not our purpose here to settle this validity issue in

0375-9601/95/$09.50
SSDI 0375-9601(95)00411-4

complete generality, we make what we believe to be a useful contribution in this field by reporting results of our Monte Carlo studies of the Davydov model, with specific assumed values for the physical parameters involved, vis-à-vis known results of quantum Monte Carlo studies [14] of the same model for the same parameters.

The Hamiltonian $\hat{H}$ under consideration is [1]

$$\hat{H} = \hat{H}_{\rm qp} + \hat{H}_{\rm ph} + \hat{H}_{\rm int}, \tag{1}$$

where $\hat{H}_{\rm qp}$ is the quasiparticle Hamiltonian, associated with the amide I vibration, $\hat{H}_{\rm ph}$ is the phonon Hamiltonian and $\hat{H}_{\rm int}$ is the Hamiltonian for the interaction between the quasiparticle and the lattice phonons. The quasiparticle Hamiltonian $\hat{H}_{\rm qp}$ is

$$\hat{H}_{\rm qp} = \sum_{n=1}^{N} [\epsilon \hat{a}_n^\dagger \hat{a}_n - J(\hat{a}_n^\dagger \hat{a}_{n-1} + \hat{a}_n^\dagger \hat{a}_{n+1})], \tag{2}$$

where ϵ is the amide I energy, $-J$ is the dipole–dipole interaction energy between neighbouring sites and $\hat{a}_n^\dagger$ ($\hat{a}_n$) is the creation (annihilation) operator for an amide I excitation in site n.

The phonon Hamiltonian $\hat{H}_{\rm ph}$ is

$$\hat{H}_{\rm ph} = \sum_{n=1}^{N} [\hat{P}_n^2/2M + \tfrac{1}{2}\kappa(\hat{u}_n - \hat{u}_{n-1})^2], \tag{3}$$

where $\hat{u}_n$ is the displacement operator for site n, $\hat{P}_n$ is the momentum operator of site n, M is the mass of each site and κ is the elasticity constant of the lattice.

Finally, the interaction Hamiltonian $\hat{H}_{\rm int}$ is

$$\hat{H}_{\rm int} = \sum_{n=1}^{N} [\chi^+(\hat{u}_{n+1} - \hat{u}_n)\hat{a}_n^\dagger \hat{a}_n + \chi^-(\hat{u}_n - \hat{u}_{n-1})\hat{a}_n^\dagger \hat{a}_n], \tag{4}$$

where χ^+ (χ^-) is an anharmonic parameter related to the coupling between the amide I excitation.

The semiclassical version of the above fully quantum mechanical model is obtained by replacing all operators describing lattice coordinates and momenta by c-numbers. In order to carry out a comparison between the two versions of the model, it is necessary to choose a quantity denoting the extent of self-trapping which can be used in both approaches. In a lattice with periodic boundary conditions at thermal equilibrium, the probability for an excitation to be in site n is equal for all sites because all sites are equivalent. In other words, the average excitation per site is $1/N$, whether the underlying states that compound the average are localized or not. To distinguish between delocalized and localized regimes, one must modify the candidate quantity in order to break the effect of the translational symmetry of the lattice. The choice of such a quantity and its modification in the manner stated have already been carried out in the quantum mechanical Monte Carlo calculations of Wang et al. [14], where a suitable candidate was found to be the lattice displacements around the location of the quantum quasiparticle. We use the same quantity in our semiclassical Monte Carlo studies and compare the results.

In the semiclassical model, the average displacement of site n at temperature T, $\langle\langle u_n^{\rm c}\rangle\rangle$, is

$$\langle\langle u_n^{\rm c}\rangle\rangle = \frac{\int(\prod_{n=1}^{N} {\rm d}u_n)\ {\rm Tr}({\rm e}^{-\beta\hat{H}}\, u_n^{\rm c})}{\int(\prod_{n=1}^{N} {\rm d}u_n)\ {\rm Tr}({\rm e}^{-\beta\hat{H}})} = \frac{\int(\prod_{n=1}^{N} {\rm d}u_n)\sum_{i=1}^{N} u_n^{\rm c}(i)\,{\rm e}^{-\beta E_i}}{\int(\prod_{n=1}^{N} {\rm d}u_n)\sum_{i=1}^{N} {\rm e}^{-\beta E_i}}, \tag{5}$$

where $\beta = 1/k_{\rm B}T$, $k_{\rm B}$ being the Boltzmann constant and $E_i(\{u_n\})$ are the eigenvalues of the semiclassical Davydov Hamiltonian. The superscript c indicates that the displacements u_n are *correlated* with the positions of the maximum probability for the location of a quasiparticle in each of the eigenstates i. Thus $u_0^{\rm c}$ is the displacement at the site of the peak, $u_1^{\rm c}$ is the displacement on the right side of the peak, etc.

At infinite temperature, the average displacement difference correlated with the excitation predicted by the quantum mechanical model is $-2\chi/\kappa$, independent of the number of sites N and the quasiparticle interaction V [14]. By considering the simple case $N = 2$, it is possible to recover this result in the semiclassical approach. At very large temperature, the quasiparticle Hamiltonian (2) is negligible compared to the phonon (3) and interaction Hamiltonian (4). The Hamiltonian (1) is diagonal in the quasiparticle excitations and expression (5) becomes

$$\langle\langle u^{\rm c}\rangle\rangle = \frac{\int {\rm d}u\, u\, {\rm e}^{-\beta\kappa u^2/2}({\rm e}^{-\beta\chi u} - {\rm e}^{\beta\chi u})}{\int {\rm d}u\ {\rm e}^{-\beta\kappa u^2/2}({\rm e}^{-\beta\chi u} + {\rm e}^{\beta\chi u})} = -\chi/\kappa. \tag{6}$$

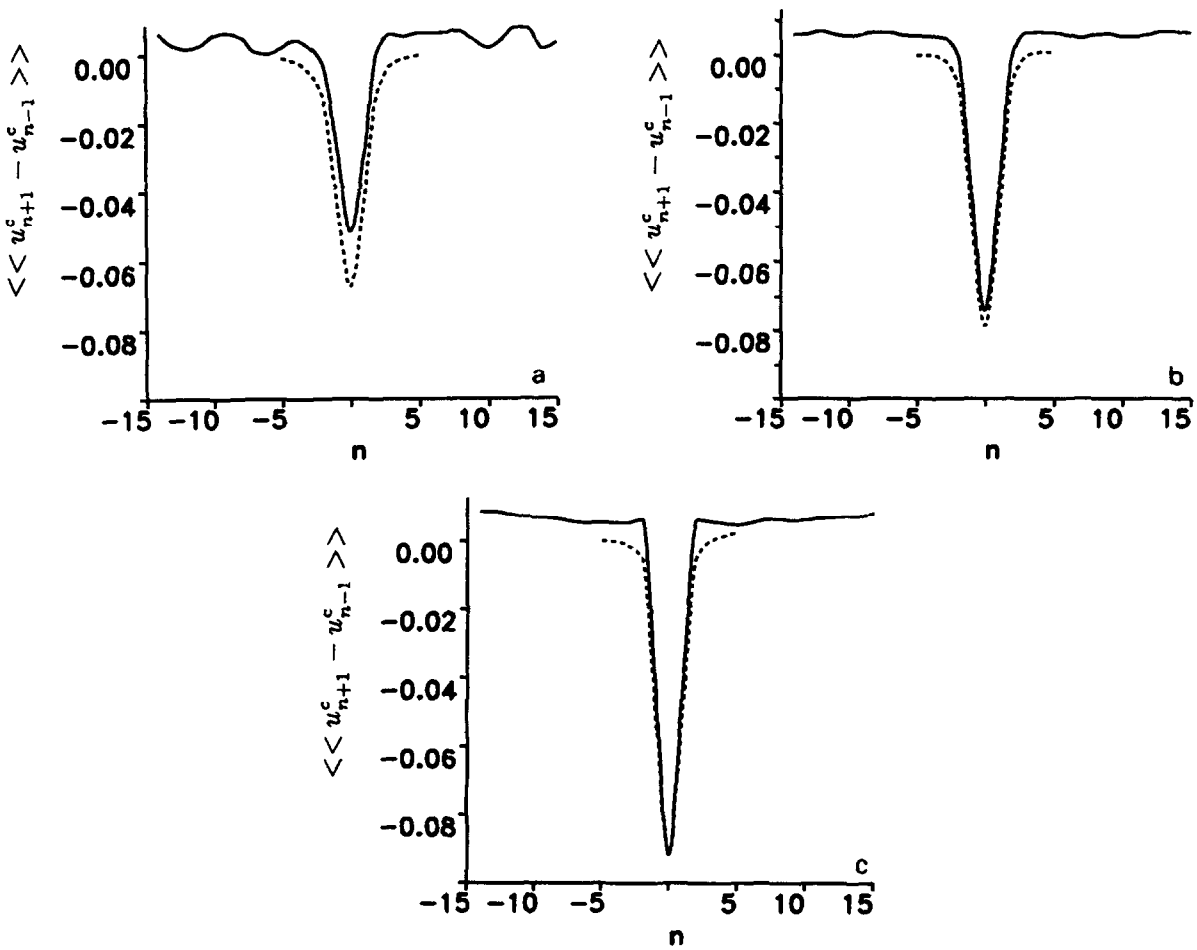

Fig. 1. Comparison of results for thermal stability of the Davydov soliton in the fully quantum mechanical model and in its semiclassical version. Plotted is the correlation between the lattice displacement and the quasiparticle excitation for (a) $T = 0.7$ K, (b) $T = 2.8$ K and (c) $T = 11.2$ K. The solid line is for the semiclassical model and the dotted line is for the full quantum mechanical model. $V = 1.55$ J, $\chi^+ = \chi^- = 62$ pN and $\kappa = 13$ N/m. The semiclassical simulation is for a lattice with $N = 30$ sites. The quantum mechanical values are reconstructed from Ref. [14].

Making the change $2\kappa \rightarrow \kappa$ necessary to go from the $N > 2$ to the $N = 2$ Hamiltonian we find that at sufficiently large temperatures the semiclassical model leads to the same result as the quantum mechanical model. This is expected since as temperature increases the lattice motions become more classical. Our interest in this note is to determine, with the help of our numerical experiments, how large the temperature has to be for the semiclassical model to be valid in this manner.

Expression (5) can be evaluated by Monte Carlo methods where the displacements u_n are generated and accepted with the usual Metropolis acceptance criteria [16] and where an eigenvalue problem of size N is solved for each Monte Carlo step that is accepted. The quantum Monte Carlo simulations were reported for 11 sites, in lattices of about 24 sites. Our own semiclassical calculations have used larger lattices consisting specifically of 30 sites. In Fig. 1 we compare our semiclassical results with the fully quantum mechanical ones of Ref. [14]. The larger oscillations in the correlated displacements away from the dip, in the semiclassical simulations, are due to statistical error. Indeed, it is found that as the temperature decreases,

the rate of convergence also decreases and thus many more configurations (at least six times more for the lowest temperature here) need to be collected. This parallels a well-known trend in the path integral Monte Carlo method.

Three results emerge from the comparison carried out in Fig. 1. The first is that, at low temperature, the semiclassical model underestimates the average distortion induced by the quasiparticle excitation. The second is that, as temperature increases, the difference is reduced. The third is that, for the parameters used in the full quantum model [14], above $T \approx 11.2$ K the semiclassical model leads to approximately the same results as the fully quantum model.

We point out here that while we have chosen exactly the same parameters as used by Wang et al. [14], and have found almost identical results for the correlation between the position of the excitation and the associated lattice displacements, particularly at high temperatures, there is a subtle difference in the manner of calculation of the fully quantum mechanical and the semiclassical correlations. The sampling procedure in the fully quantum mechanical simulation involves a reduction of the wave packet in each Monte Carlo step and the calculation of the correlation is done after this reduction. In the semiclassical simulation no reduction is performed and instead, for each snapshot, the maximum of the probability distribution is located and the lattice displacements around the maximum are averaged. A reduction of the wave packet will localize the excitation predominantly around the maximum, but occasionally it will also localize it in other, less probable, sites. These sites have displacements which, on average, are *smaller* than those around the maximum. Thus, if the semiclassical correlation had been calculated exactly as in the quantum Monte Carlo simulations [14] the semiclassical result would be even *smaller* than that calculated here. This would make the difference between the semiclassical and the full quantum correlation *larger* than is shown in the figure. The two ways of calculating the correlation become statistically equivalent when the excitation is very localized so that the reduction of the wave packet leads to an excitation localized at the maximum of the probability distribution. Thus, while this calculational difference introduces an uncertainty in the exact amount by which the quantum correlation exceeds the semiclassical at very low temperatures (i.e. an amount which is equal or greater than shown in Figs. 1a and 1b), the difference becomes negligible above 11 K, when the excitation is localized in essentially one site. The qualitative conclusion remains that the introduction of quantum effects in the lattice leads to stronger correlations between the excitation and the lattice distortion.

It is perhaps remarkable that the temperature above which our results show the semiclassical model to be practically valid is essentially the same as the temperature above which solitons are destroyed thermally according to the semiclassical Langevin simulations of Lomdahl and Kerr [4]. It has been argued [14] that the quantum results are in agreement with the latter Langevin simulations. On the other hand, it has been shown [11] that those Langevin simulations are equivalent to Monte Carlo simulations [15] in which the postulate of *a priori* random phases for the wavefunctions is violated [5], and thereby lead to an inappropriate statistical treatment. The correlation between the excitation and the lattice calculated in those Monte Carlo simulations *decreases*, in absolute terms, as the temperature increases [15]. This is the reverse of what is found here and in the quantum Monte Carlo simulations [14]. Thus, from this point of view, we conclude that the semiclassical Langevin simulations [4] and the quantum Monte Carlo simulations are at odds with each other.

L.C.-H. thanks the BBSRC for the Advanced Fellowship B/93/AF/1646 and for supercomputing facilities at ULCC (grant B01960). This work is partially supported by the NATO Scientific Affairs Division through a grant for collaborative research between the University of New Mexico, USA and Birkbeck College, University of London, UK.

References

[1] A.S. Davydov and N.I. Kislukha, Phys. Stat. Sol. B 59 (1973) 465;
A.S. Davydov, J. Theor. Biol. 38 (1973) 559.

[2] T. Holstein, Ann. Phys. 8 (1959) 325, 343

[3] P.L. Christiansen and A.C. Scott, eds., Davydov's soliton revisited. Self-trapping of vibrational energy in protein (Plenum, New York, 1990);
A. Scott, Phys. Rep. 217 (1992) 1.

[4] P.S. Lomdahl and W.C. Kerr, Phys. Rev. Lett. 55 (1985) 1235.

[5] P. Grigolini, H.-L. Wu and V.M. Kenkre, Phys. Rev B 40 (1989) 7045;
V.M. Kenkre and P. Grigolini, Z. Phys. B 90 (1993) 247.
[6] H. Motschmann, W. Förner and J. Ladik, J. Phys. Condens. Matter 1 (1989) 5083;
W. Förner, J. Phys. Condens. Matter 3 (1991) 4333; 4 (1992) 1915; 5 (1993) 823, 883, 3883, 3897; Phys. Rev. A 44 (1991) 2694; J. Comput. Chem. 13 (1992) 275.
[7] V.M. Kenkre and L. Cruzeiro-Hansson, Z. Phys. B 95 (1994) 379.
[8] V.M. Kenkre, S. Raghavan and L. Cruzeiro-Hansson, Phys. Rev. B 41 (1994) 9511.
[9] J.P. Cottingham and J.W. Schweitzer, Phys. Rev. Lett. 62 (1989) 1792;
J.W. Schweitzer, Phys. Rev. A 45 (1992) 8914.
[10] A.F. Lawrence, J.C. McDaniel, D.B. Chang, B.M. Pierce and R.R. Birge, Phys. Rev. A 33 (1986) 1188.
[11] L. Cruzeiro-Hansson, Physica D 68 (1994) 65; Phys. Rev. Lett. 73 (1994) 2927;
L. Cruzeiro-Hansson and V.M. Kenkre, in: Nonlinear excitations in biomolecules, ed. M. Peyrard (Springer, Berlin, Editions de Physique, Paris), in press; in: Computational physics. Nonlinear dynamical phenomena in physical, chemical and biological systems, eds. P.L. Christiansen and E. Mosekilde (IMACS, Bethlehem, PA, 1994).
[12] D. Vitali, L. Bonci, R. Mannella and P. Grigolini, Phys. Rev. A 45 (1992) 2285.
[13] V.M. Kenkre, in: Fluctuations and disorder in nonlinear systems, ed. L. Vazquez (Plenum, New York, 1995).
[14] X. Wang, D.W. Brown and K. Lindenberg, Phys. Rev. Lett. 62 (1989) 1796; in: Davydov's soliton revisited. Self-trapping of vibrational energy in proteins, eds. P.L. Christiansen and A.C. Scott (Plenum, New York, 1990) p. 83.
[15] L. Cruzeiro-Hansson, Phys. Rev. A 45 (1992) 4111.
[16] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller and E. Teller, J. Chem. Phys. 21 (1953) 1087.