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A tight-binding molecular dynamics study of phonon anharmonic effects in diamond and graphite

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Abstract. We study the temperature dependence of phonon frequency shifts and phonon linewidths in diamond and graphite using tight-binding molecular dynamics simulations. The calculation of one-phonon spectral intensities of several modes through velocity–velocity correlation functions allows a quantitative and nonperturbative study of these anharmonic effects. Our results for the zone-centre optical mode of diamond, for which experimental data are available, agree very well with first-order Raman-scattering measurements.

1. Introduction

Diamond and graphite are technologically important materials. Because most applications of diamond and graphite involve high temperatures, understanding the properties of these materials as functions of temperature is essential. Temperature-dependent phonon properties and their relationship with the anharmonicity of the interatomic interactions are also very interesting from the fundamental point of view.

The temperature dependences of phonon frequency shifts and linewidths in semiconductors have been measured by neutron-scattering and light-scattering techniques [1]. In the case of diamond, the temperature variation of the first-order Raman spectrum has been investigated more than fifty years ago [2, 3] and more recently [4–6]. The last two studies were performed over a wide range of temperatures up to 1900 K [5, 6]. Downshifts in the Raman spectra of graphite as the temperature increased have also been observed [7].

Theoretical calculation of phonon frequency shifts and linewidths in solids is a subject of interest and a challenge. Traditionally, the calculations have mainly been restricted to perturbative approaches, where anharmonic coupling constants are derived either by fitting to experimental data [8–10], or by first-principles calculations [11]. Besides the fact that perturbation expansion is practical for lowest orders only (up to the fourth order in the force constant), it becomes inadequate for strongly anharmonic systems and at high temperatures. Recently, molecular dynamics (MD) simulation has emerged as a useful technique for studying temperature-dependent properties of materials provided that the potential model gives an accurate description of the interatomic interactions of the system. Anharmonic effects have been studied by means of molecular dynamics simulations performed with empirical classical potentials in the case of alkali metals [12] and rare-gas solids [13], where the interatomic interaction is adequately described by simple pair potentials. In the case of carbon systems, a realistic description of the covalent bonding is necessary. Using tight-binding potentials for silicon and carbon based on the model proposed by Chadi

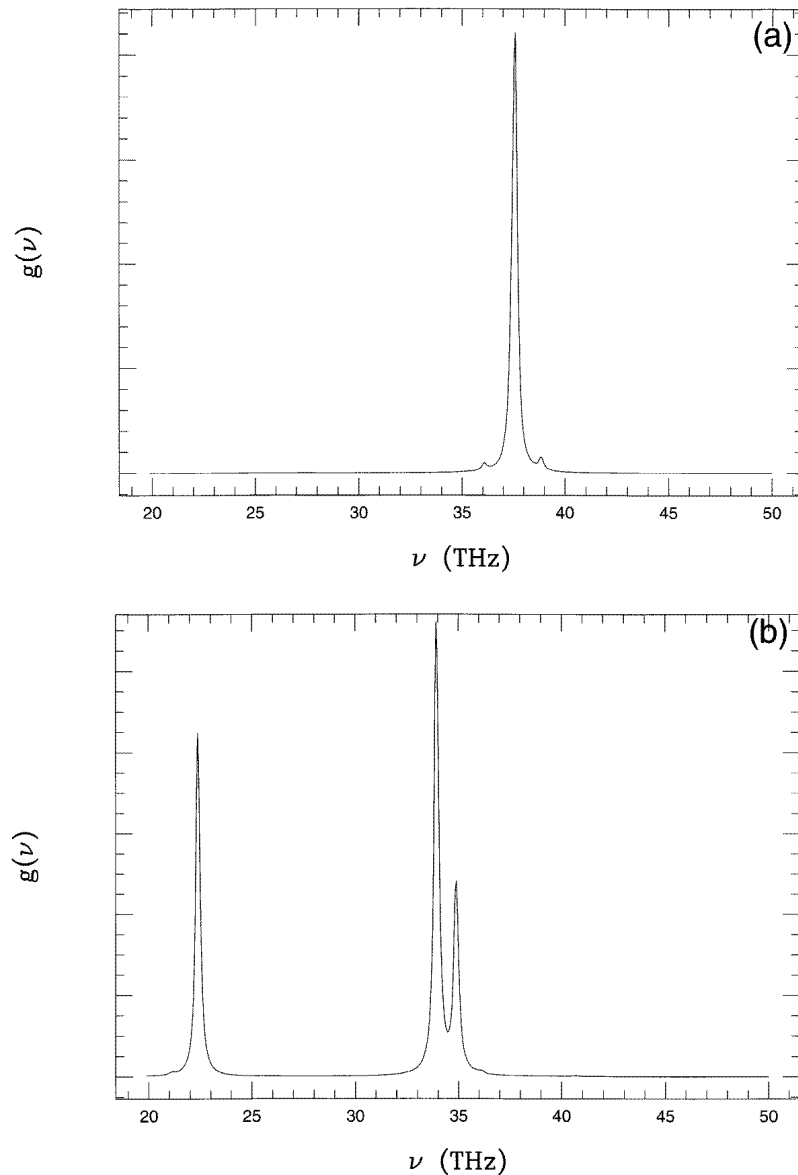


Figure 1. The spectral intensities of the LTO(Γ), (a), and TO(X), LOA(X), TA(X), (b), modes of diamond at a simulation temperature of 700 K.

[14], Wang, Chan, and Ho have performed tight-binding molecular dynamics (TBMD) simulations to study the anharmonic phonon frequency shifts and linewidths in silicon and in diamond as functions of temperature. The results for silicon were in very good agreement with experimental data obtained from Raman-scattering experiments [15]. In the case of diamond, the frequency shifts were underestimated.

In this paper, we present results for the anharmonic properties of diamond and graphite obtained by means of TBMD simulation, using an accurate tight-binding model for the carbon-carbon interactions developed by Xu, Wang, Chan, and Ho [16]. We calculated the

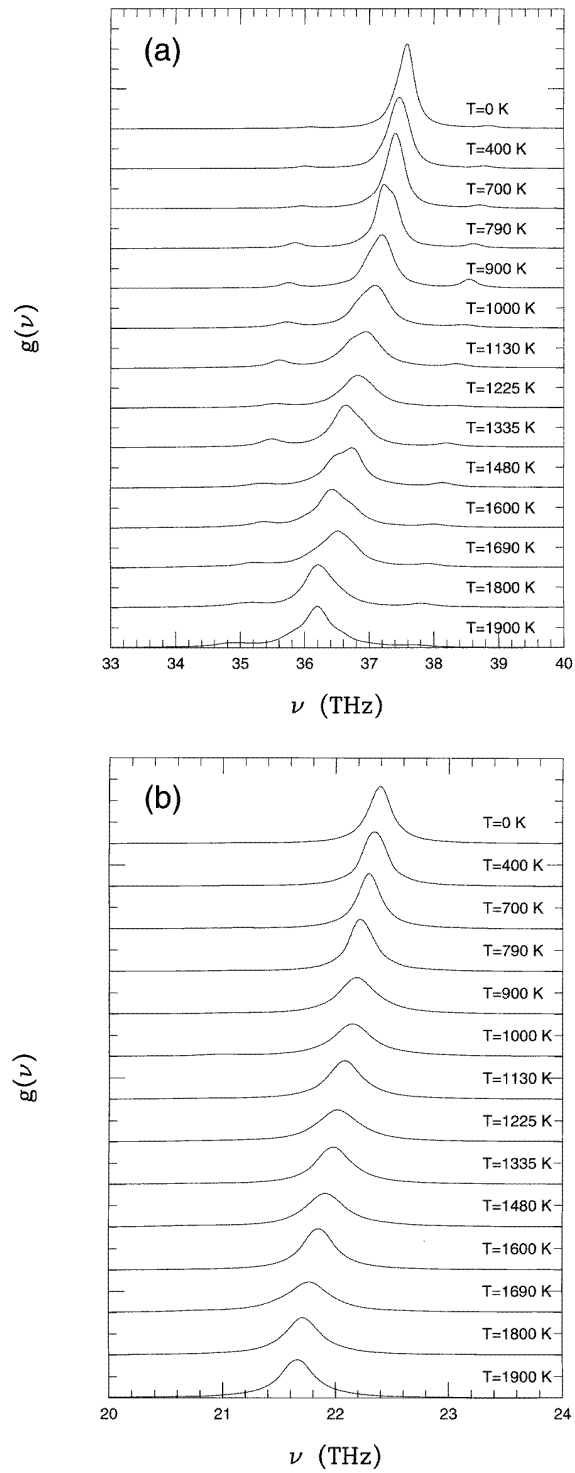


Figure 2. The spectral intensities of the LTO(Γ), (a), and TA(X), (b), modes of diamond as functions of temperature.

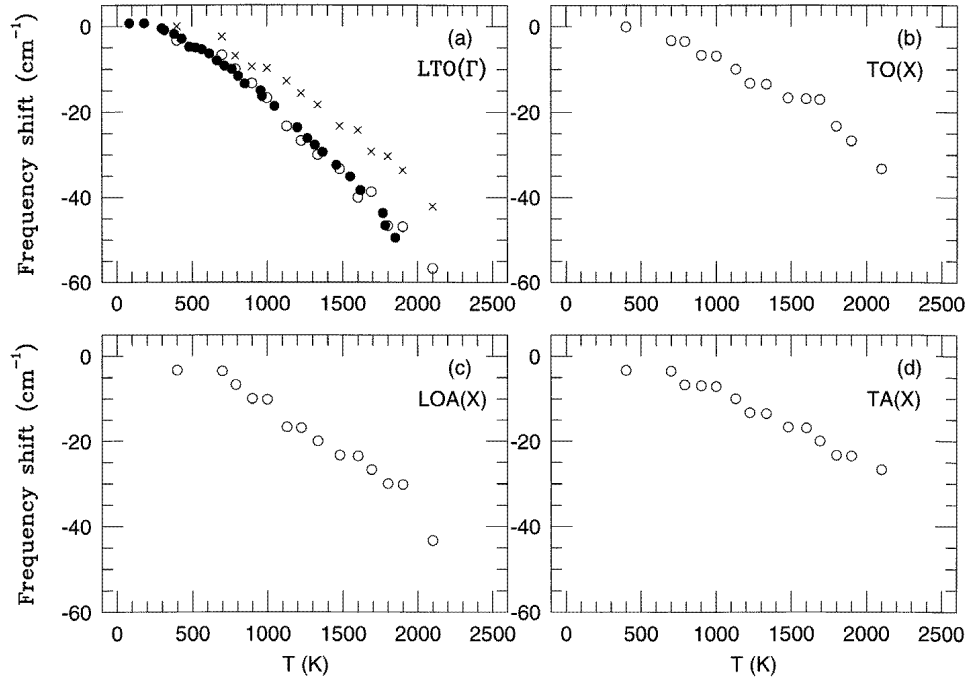


Figure 3. The frequency shifts as functions of temperature for the LTO(Γ), (a), TO(X), (b), LOA(X), (c), and TA(X), (d), modes. The solid circles in (a) represent Raman-scattering measurements from reference [5], and the crosses represent results obtained with the same TB model in the quasi-harmonic approximation.

frequency shifts and linewidths as functions of temperature for diamond and graphite. The results for the zone-centre optical mode of diamond, for which Raman-scattering data are available, are in very good agreement with experiment.

2. Simulation details

TBMD simulation is a method that incorporates quantum mechanical effects into the MD simulation through explicit evaluation of the electronic structure of the system at each MD step [17]. In addition to accurately describing covalent systems, TBMD allows for relatively long MD simulations with a relatively large number of atoms.

The binding energy of a system in the tight-binding approximation is given by

$$E_{\text{binding}} = E_{bs} + E_{rep}. \quad (1)$$

The first term in the right-hand side is the electronic band-structure energy:

$$E_{bs} = \sum_n \langle \psi_n | H_{TB} | \psi_n \rangle \quad (2)$$

i.e. the sum of the eigenvalues over all occupied electronic states. The electronic eigenvalues are obtained by solving the empirical tight-binding Hamiltonian, H_{TB} . The matrix elements of H_{TB} are adjustable parameters that are determined by fitting to *ab initio* results. The off-diagonal elements are two-centre hopping parameters, scaled with the interatomic separation, r , with a specific functional form. The second term in the right-hand side of equation (1)

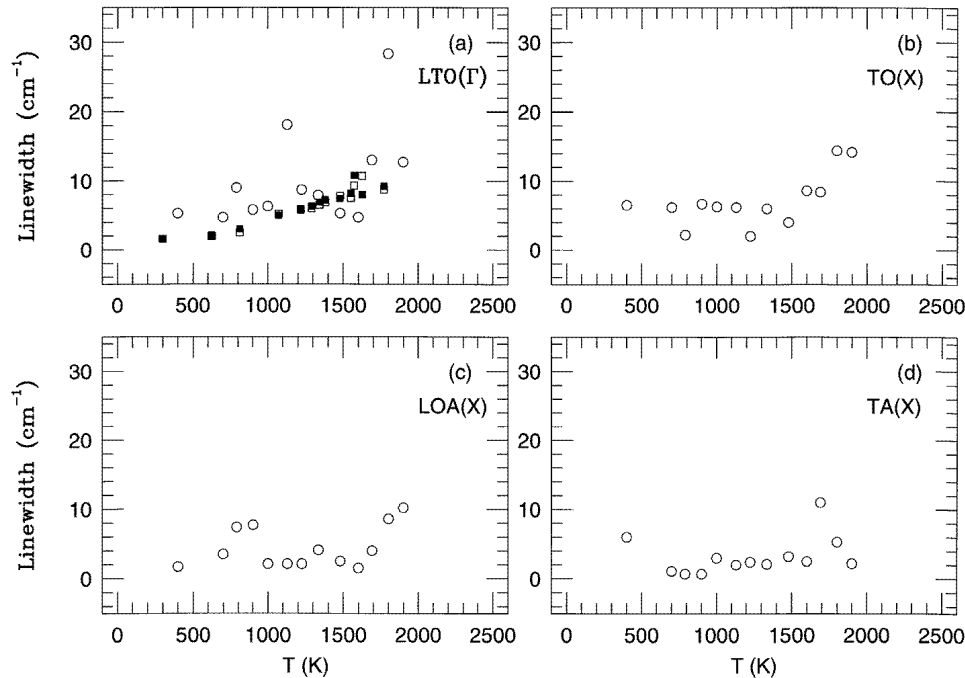


Figure 4. The linewidths as functions of temperature for the LTO(Γ), (a), TO(X), (b), LOA(X), (c), and TA(X), (d), modes. The solid and open squares are from the Stokes and anti-Stokes first-order Raman spectra of reference [5].

is the repulsive term, E_{rep} , which is described by a sum of short-ranged functions of the interatomic distance. By following Goodwin *et al* [18], who developed a tight-binding model for silicon, Xu *et al* [16] obtained a set of parameters for carbon with good accuracy and transferability, i.e. they fit simultaneously to first-principles (LDA) results for energy-versus-volume curves of an infinite linear chain of C, graphite, diamond, and simple cubic and face-centred cubic structures, with an emphasis on the diamond, graphite, and linear chain structures. Unlike in the model given by Goodwin *et al*, two distinct functions of the same form were used to scale the off-diagonal matrix elements and the pairwise repulsive potential [16]. This model is highly transferable, reproducing accurately the energy-versus-volume diagram of carbon polytypes, as well as properties that do not enter explicitly into the fitting procedure, such as the phonon frequencies, Grüneisen parameters, and elastic constants for carbon in the diamond and graphite structures. It has been used successfully in molecular dynamics studies of different atomic environments (small carbon microclusters [16], the liquid phase [19], amorphous carbon [20], and fullerenes [21]).

In the case of diamond, our TBMD simulations were performed with 64 carbon atoms in a cubic box. The volume is fixed at a given temperature according to the lattice thermal expansion [1]. The atoms are initially arranged in the diamond structure (with small random displacements to start the simulation), and periodic boundary conditions are used. A fifth-order predictor–corrector algorithm is used for the solution of the equations of motion with a time step $\Delta = 0.7 \times 10^{-15}$ s (with this time step, energy is conserved within 8.1×10^{-5} eV over 16400 steps at a simulation temperature of 100 K). The phonon anharmonic effects were studied through the temperature dependence of one-phonon spectral intensities, which

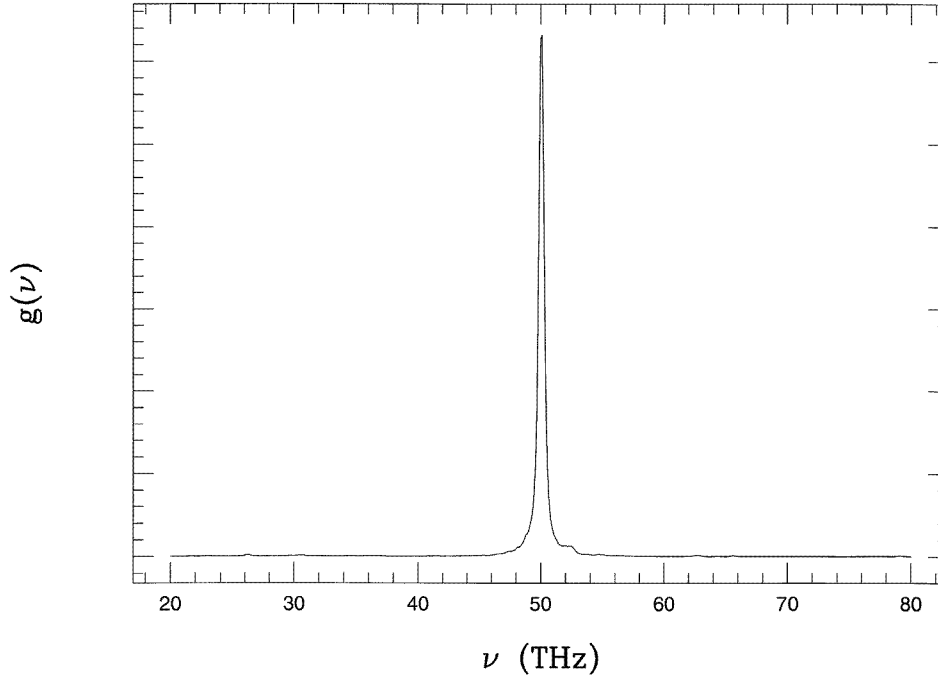


Figure 5. The spectral intensity of the E_{2g_2} mode of graphite at a simulation temperature of 750 K.

were calculated as Fourier transforms of velocity–velocity correlation functions in the course of the molecular dynamics simulation:

$$g(k, \omega) = \int dt e^{i\omega t} \sum_n e^{ikR_n} \left(\frac{\langle v_n(t)v_0(0) \rangle}{\langle v_n(0)v_0(0) \rangle} \right) \quad (3)$$

where $v_n(t)$ is the velocity of the atom n at time t , R_n is the lattice position of the atom n , and k is the phonon wave vector. With $k = (2\pi/a)(1, 1, 1)$, we studied the optical phonon at the centre of the Brillouin zone (LTO(Γ)), and with $k = (2\pi/a)(1, 0, 0)$, both optical and acoustic phonons at the zone-boundary wave vector X (TO(X), LOA(X), TA(X)) are calculated. At each temperature, we run 6000 steps with stochastic temperature control and 2000 steps without temperature control, to equilibrate the system, followed by 16 384 steps (corresponding to 11.5 ps), to evaluate the velocity–velocity correlation functions and phonon spectral intensities. The frequency resolution is comparable to that of optical experiments.

Using the same method, we studied the frequency shifts and the broadening of the linewidths as functions of temperature for the in-plane E_{2g_2} mode of graphite. Since the interplanar distance in graphite is larger than the cut-off distance for the C–C interactions in our model, a single graphite plane was used. A rhombus-shaped sample consisting of 98 carbon atoms, with periodic boundary conditions, was used in the simulation.

Since molecular dynamics follows classical statistical mechanics, quantum corrections are necessary, particularly for the low-temperature regime. A simple way of taking into account these corrections is by rescaling the MD averaged temperature T_{MD} to a scaled temperature T determined by requiring the mean kinetic energy of our system to be the

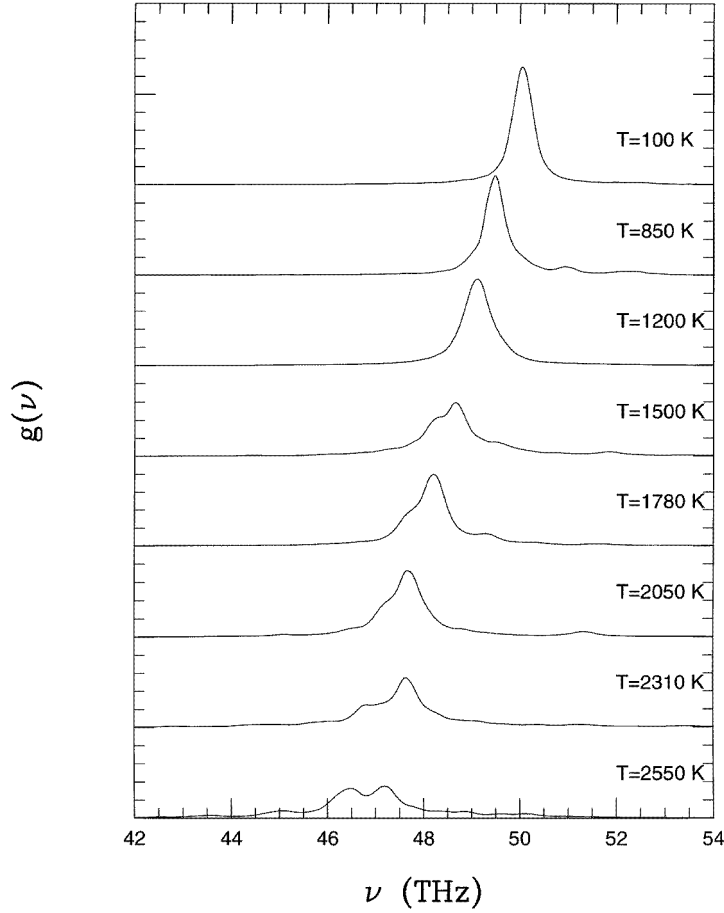


Figure 6. The spectral intensity of the E_{2g_2} mode of graphite as a function of temperature.

same as that of the corresponding quantum system at temperature T , including zero-point motion [15]:

$$T_{MD} = \frac{1}{k_B} \int h\nu D(\nu) \left[\frac{1}{2} + \frac{1}{e^{h\nu/k_B T} - 1} \right] d\nu. \quad (4)$$

According to this scaling relation, T_{MD} and T approach each other at high temperature, while at $T = 0$, $k_B T_{MD}$ corresponds to the zero-point energy of the system (in the diamond case, this happens at $T_{MD} = 700$ K).

3. Results and discussion

Typical spectral intensities are shown in figure 1 for the LTO(Γ), TO(X), LOA(X), and TA(X) modes of diamond at a simulation temperature $T_{MD} = 700$ K. The spectral peaks are sharp and well defined at the frequencies of 37.6, 33.9, 34.9, and 22.4 THz, which are very close to the zero-temperature dynamical-matrix calculation results obtained using the same potential model [16].

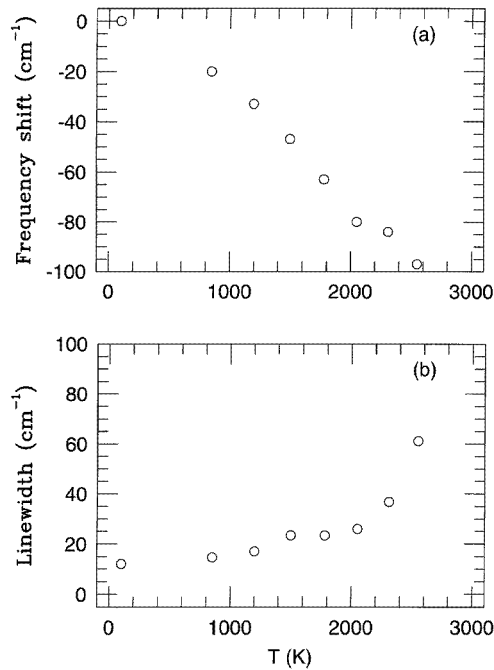


Figure 7. The frequency shift as a function of temperature for the E_{2g_2} mode of graphite (a), and the linewidth as a function of temperature (b).

In figure 2 the temperature-dependent spectral intensities are presented for the LTO(Γ) and TA(X) modes. The shifts in frequencies and the increases in linewidths with increased temperature are apparent. The shift and the broadening of the transverse acoustic mode are smaller than those of the optical mode.

The frequency shifts and the linewidths of the phonon modes as functions of temperature, as obtained after lorentzian fitting to our simulation data, are plotted in figures 3 and 4 respectively. For the frequency shifts of the LTO(Γ) mode, our results are compared with Raman-scattering data [5]. The agreement with the available experimental data is very good (figure 3(a)). We note that the frequency shifts obtained from a quasi-harmonic calculation (where the temperature dependence of the phonons is totally attributed to the change of force constants due to thermal expansion), as shown by crosses in figure 3(a), are smaller than the TBMD simulation results, indicating that the effects of phonon–phonon interactions are significant. The frequency shifts of the modes at the X point are smaller than those of the LTO(Γ) mode. We are not aware of any experimental results on the frequency shifts of these modes to compare with our simulation results. The linewidths estimated from our simulation data are somewhat scattered (figure 4). However, the trend of broadening of the linewidths with the increase of temperature is evident from the plots. The linewidth of the LTO(Γ) mode as a function of temperature also compares fairly well with the experimental data. We do not have any experimental data on the linewidths of the other modes to compare with our simulation results.

For the in-plane stretching E_{2g_2} mode of graphite, the spectral intensity at a simulation temperature $T_{MD} = 750$ K (corresponding to the corrected temperature $T = 100$ K), is presented in figure 5. The spectral intensities as functions of temperature obtained from our simulation are plotted in figure 6. From the temperature-dependent spectra, we estimate

the frequency shift and the linewidth of the mode as functions of temperature; these are presented in figure 7. The mode exhibits a significant shift in frequency and broadening in linewidth as the temperature is increased. The shifts in the frequency and the broadening in the linewidth are found to be larger than those of the LTO(Γ) mode of diamond. A downshift of the frequency of the E_{2g_2} mode of graphite has been reported in experiments for temperatures below 1000 K. It was estimated that the downshift of the frequency is 12 cm^{-1} when the temperature increases from 400 K to 890 K [7]. In our simulation, the frequency shift from $T = 100 \text{ K}$ to $T = 850 \text{ K}$ is about 20 cm^{-1} , which is in good agreement with the experimental measurements. We are not aware of any experimental data for higher temperatures with which to compare our simulation results.

4. Summary

We have performed extensive molecular dynamics simulations using a tight-binding potential to study the temperature dependence of the phonon frequency shift and linewidth of diamond and graphite. We show that the TBMD scheme provides a more efficient and accurate method of studying phonon anharmonic effects than the quasi-harmonic approximation (where the temperature dependence of the phonons is totally attributed to the change of force constants due to thermal expansion), and perturbative calculations, particularly at high temperatures. In MD simulations, anharmonic effects are automatically included through the time correlation functions. Our results for the zone-centre optical mode of diamond are in good agreement with Raman-scattering data.

Acknowledgments

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