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LETTER TO THE EDITOR

Spectral shapes of solid neon

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Abstract. We present a path integral Monte Carlo calculation of the first three moments of the displacement–displacement correlation functions of solid neon at different temperatures, for longitudinal and transverse phonon modes. The Lennard-Jones potential is considered. The relevance of the quantum effects on the frequency position of the peak and principally on the line-width of the spectral shape is clearly pointed out. The spectrum is reconstructed via a continued fraction expansion; the approximations introduced using the effective potential quantum molecular dynamics are discussed.

Rare gas solids (RGS) are the simplest real systems in which we can study lattice vibrations. Argon and the heavier RGS can be well approximated as a set of harmonic oscillators at low temperatures, while classical behaviour is reached before the melting point. Quantum corrections on the thermodynamic quantities, like kinetic energy and specific heat, can be taken into account by means of the effective potential (EP) approach [1] only for small quantum coupling g ($g < 0.25$), defined as the ratio between the characteristic frequency and the strength of the binding potential. For neon ($g = 0.694$) anharmonic effects are present even for determining the ground state [2, 3]. Indeed, precise calculations of kinetic energy, to be compared with accurate experiments done by deep inelastic neutron scattering (DINS) [4], needed a rather sophisticated path integral Monte Carlo (PIMC) computation, the EP approach being inadequate. These results show that quantum effects are very important also at rather high temperatures [2].

Information about phonon dynamics is given by spectral shape, namely the space and time Fourier transform of the (symmetrized) displacement–displacement correlation function:

$$\mathcal{S}_{\mathrm{S}}^{\alpha\beta}(\boldsymbol{k},\omega) = \frac{1}{2\pi}\sum_{\boldsymbol{r}}\int \mathrm{d}t\; C^{\alpha\beta}(\boldsymbol{r},t)\;\exp\left[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)\right] \tag{1}$$

with

$$C^{\alpha\beta}(\boldsymbol{r},t) = \left[\left\langle x_{i+\boldsymbol{r}}^{\alpha}(t)x_{i}^{\beta}(0)\right\rangle + \left\langle x_{i+\boldsymbol{r}}^{\alpha}(0)x_{i}^{\beta}(t)\right\rangle\right]. \tag{2}$$

x_i^α is the αth component of the displacement of the ith atom from its equilibrium position. Even though this quantity has been investigated for many years [5], complete information is

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not available for various rare gas solids and in particular for neon. The perturbative many-body approach can give the frequency and lifetime of phonons only at low temperatures. Classical molecular dynamics (CMD) can describe the behaviour of argon and krypton at the highest temperatures, but it is no longer valid for lower temperatures or stronger coupling. As shown in the following, the spectra of neon present significant quantum effects up to the melting point and the high quantum coupling prevents us from using the EP method in the entire temperature range.

We approach the calculation of the spectra of neon as given in equation (1), by PIMC, evaluating the first three even frequency moments

$$\langle\omega^{2n}\rangle_{\boldsymbol{k}}^{\alpha\beta} = \int_{-\infty}^{\infty} \mathrm{d}\omega\ \omega^{2n} \mathcal{S}_{\mathrm{S}}^{\alpha\beta}(\boldsymbol{k},\omega) \tag{3}$$

while the odd moments vanish for symmetry reasons. As it is well known, this involves the PIMC calculation of static correlations obtained by multiple commutators of $x_{\boldsymbol{k}}^{\alpha}(t) = N^{-1/2}\sum_i \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{i})x_i^{\alpha}(t)$ with the Hamiltonian:

$$\langle\omega^{2n}\rangle_{\boldsymbol{k}}^{\alpha\beta} = \frac{1}{2}\left\langle \left.\frac{\mathrm{d}^n x_{\boldsymbol{k}}^{\alpha}}{\mathrm{d}t^n}\right|_{t=0} \left.\frac{\mathrm{d}^n x_{-\boldsymbol{k}}^{\beta}}{\mathrm{d}t^n}\right|_{t=0} + \left.\frac{\mathrm{d}^n x_{-\boldsymbol{k}}^{\alpha}}{\mathrm{d}t^n}\right|_{t=0} \left.\frac{\mathrm{d}^n x_{\boldsymbol{k}}^{\beta}}{\mathrm{d}t^n}\right|_{t=0} \right\rangle. \tag{4}$$

Here we will refer only to $\boldsymbol{k} = 2\pi/a_0(1,0,0)$ for which one longitudinal and two degenerate transverse modes are present, so that we omit polarization indexes.

When the spectra are sufficiently narrow, the normalized second moment, $\delta_{1\boldsymbol{k}}$ and the irreducible part of the fourth moment, $\delta_{2\boldsymbol{k}}$:

$$\delta_{1\boldsymbol{k}} = \frac{\langle\omega^2\rangle_{\boldsymbol{k}}}{\langle\omega^0\rangle_{\boldsymbol{k}}} \qquad \delta_{2\boldsymbol{k}} = \frac{\langle\omega^4\rangle_{\boldsymbol{k}}}{\langle\omega^2\rangle_{\boldsymbol{k}}} - \delta_{1\boldsymbol{k}} \tag{5}$$

can be directly related to the peak position and width of the spectra [6].

A reconstruction of the spectra can be done by the continued fraction expansion of the Laplace transform of the normalized correlation function

$$\Xi_0(\boldsymbol{k},z) = \int_0^{\infty} \mathrm{d}t\ \frac{C(\boldsymbol{k},t)}{C(\boldsymbol{k},0)}\ \mathrm{e}^{-zt} \tag{6}$$

with

$$\mathcal{S}_{\mathrm{S}}(\boldsymbol{k},\omega) = \Re\,\Xi_0(\boldsymbol{k}, z = \mathrm{i}\omega)\ C(\boldsymbol{k}, t = 0). \tag{7}$$

The continued fraction expansion can be stopped at the third stage with a suitable termination $\Xi_2(\boldsymbol{k},z)$

$$\Xi_0(\boldsymbol{k},z) \simeq \frac{1}{\pi}\ \frac{1}{z + \dfrac{\delta_{1\boldsymbol{k}}}{z + \delta_{2\boldsymbol{k}}\,\Xi_2(\boldsymbol{k},z)}}\ . \tag{8}$$

In this letter, we shall present some of these spectra, showing the validity of the approach. Neutron scattering data are not available to date and we suggest and discuss here the possibility of performing such an experiment.

We have considered samples of solid neon, with 256 atoms interacting through a (12–6) Lennard-Jones pairwise potential

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{9}$$

and periodic boundary conditions. The dynamic interaction is limited to the 12 nearest neighbours, while for the outer shells the static approximation is used. For every temperature

Table 1. Moments ($M_{2n} \equiv \langle \omega^{2n} \rangle_{\boldsymbol{k}}$) of $\mathcal{S}_S(\boldsymbol{k}, \omega)$ for $T = 10$ K at vanishing pressure, for the wave vector $\boldsymbol{k} = 2\pi/a_0(1, 0, 0)$. They are expressed in reduced units. $b = 2.787$ Å and $\omega_0 = 0.289$ meV. Classical second moments are exact since they are equal to the reduced temperature.

	Transverse		
	Classical	EP	PIMC
$M_0/b^2(\times 10^{-4})$	8.427 ± 0.005	30.02 ± 0.01	28.28 ± 0.06
$M_2/(b^2\omega_0^2)$	0.272 6281	0.7027 ± 0.0002	0.788 ± 0.002
$M_4/(b^2\omega_0^4)$	98.13 ± 0.05	168.5 ± 0.1	314 ± 3
	Longitudinal		
	Classical	EP	PIMC
$M_0/b^2(\times 10^{-4})$	3.955 ± 0.002	20.732 ± 0.008	19.02 ± 0.05
$M_2/(b^2\omega_0^2)$	0.272 6281	0.9902 ± 0.0003	1.141 ± 0.004
$M_4/(b^2\omega_0^4)$	205.0 ± 0.2	467.3 ± 0.3	849 ± 6

Table 2. Moments ($M_{2n} \equiv \langle \omega^{2n} \rangle_{\boldsymbol{k}}$) of $\mathcal{S}_S(\boldsymbol{k}, \omega)$ for $T = 20$ K at vanishing pressure, for the wave vector $\boldsymbol{k} = 2\pi/a_0(1, 0, 0)$. They are expressed in reduced units. $b = 2.787$ Å and $\omega_0 = 0.289$ meV. Classic second moments are exact since they are equal to the reduced temperature.

	Transverse		
	Classical	EP	PIMC
$M_0/b^2(\times 10^{-4})$	20.92 ± 0.02	36.50 ± 0.05	34.7 ± 0.3
$M_2/(b^2\omega_0^2)$	0.545 256	0.8387 ± 0.0006	0.870 ± 0.002
$M_4/(b^2\omega_0^4)$	182.3 ± 0.3	218.6 ± 0.4	347 ± 3
	Longitudinal		
	Classical	EP	PIMC
$M_0/b^2(\times 10^{-4})$	9.67 ± 0.01	22.47 ± 0.02	21.3 ± 0.1
$M_2/(b^2\omega_0^2)$	0.545 256	1.1022 ± 0.0006	1.157 ± 0.006
$M_4/(b^2\omega_0^4)$	380.3 ± 0.5	560.1 ± 0.3	872 ± 8

Table 3. $\sqrt{\delta_1}$ and $\sqrt{\delta_2}/2$ roughly represent the peak position and the phonon lifetime, respectively. They are evaluated via PIMC simulations and they are expressed in meV.

	Transverse		Longitudinal	
T (K)	$\sqrt{\delta_1}$	$\sqrt{\delta_2}/2$	$\sqrt{\delta_1}$	$\sqrt{\delta_2}/2$
10	4.83 ± 0.02	1.58 ± 0.1	7.01 ± 0.02	1.78 ± 0.06
20	4.57 ± 0.02	1.74 ± 0.1	6.76 ± 0.02	2.07 ± 0.06

we resorted to three different Trotter numbers: $P = 8, 16, 24$. For each of them, 16 simulation runs of 100 000 steps per particle were performed, plus 20 000 steps per particle for initial thermalization. The density was adjusted in order to get a practically vanishing

pressure (the pressure is always less than 15 atm). The parameters of the Lennard-Jones potential are taken as $\epsilon = 36.68$ K and $\sigma = 2.787$ Å [7]. The melting temperature of neon at zero pressure is 24.5 K.

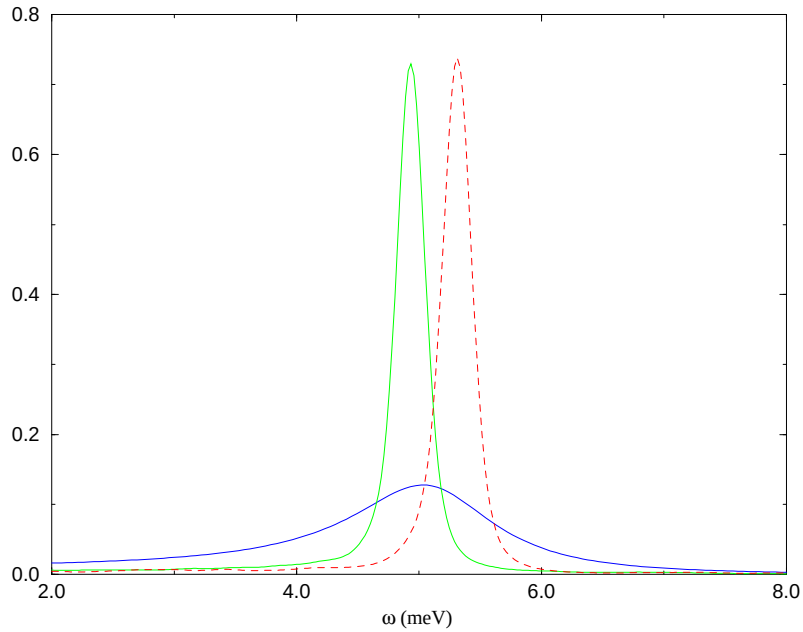

Figure 1. Transverse projection of the (normalized) space and time Fourier transform of the symmetrized displacement–displacement correlation function, $\mathcal{S}_S(\boldsymbol{k}, \omega)/C(\boldsymbol{k}, t = 0)$. At $T = 10$ K, $\rho = 1.494$ g cm^{-3} for $\boldsymbol{k} = 2\pi/a_0(1, 0, 0)$ and zero pressure. The dashed line refers to CMD results, the long-dashed one to EPMD results, and the solid line to results obtained via continued fraction expansion and PIMC evaluation of frequency moments.

Detailed explanations of the total procedure and results for the first three even moments [8], at different temperatures for longitudinal and transverse modes, will be presented in an extended paper. Here we want to point out that when the order of the frequency moment increases, more complicated static correlations are involved. Moreover accurate Trotter extrapolations are in order and finite-size effects are more and more important. We have used the procedure introduced by us [2, 9] by which we correct the raw PIMC data, subtracting the exact contributions of the harmonic part for finite P and N, and adding the exact harmonic results for infinite P and N. In this way, an accuracy of 0.2% is reached for the zeroth moment, which rises to 1% for the fourth moment. This corresponds to a maximum uncertainty of 4% for δ_{2k}. Classical simulations were also done for comparison, using both the classical and the effective potential.

The necessity to account for quantum effects by an 'exact' method like PIMC has been ascertained, especially for higher-order moments. The fourth moment exhibits strong quantum effects at any realistic temperature which cannot be approached by the EP method. In tables 1 and 2 we report the first three even moments together with the analogous ones obtained by classical and EP Monte Carlo calculations. The fourth moment is related to the width of the spectra (phonon lifetime) through the quantity δ_{2k}. For narrow spectra ($\delta_{2k} \ll \delta_{1k}$), the phonon frequencies are $\omega_k \sim \sqrt{\delta_{1k}}$ while the phonon lifetimes are $\eta_k \sim \sqrt{\delta_{2k}}/2$. These quantities, shown in table 3, can be probed by inelastic neutron

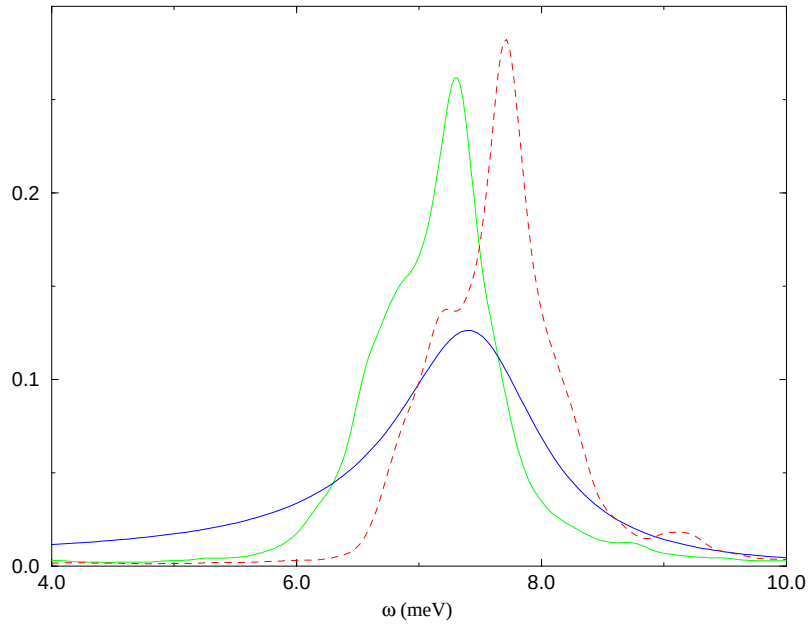

Figure 2. The same as in figure 1 for the longitudinal projection of the (normalized) space and time Fourier transform of the symmetrized displacement–displacement correlation function, $\mathcal{S}_S(\boldsymbol{k},\omega)/C(\boldsymbol{k},t=0)$, at $T=10$ K, $\rho=1.494$ g cm^{-3} for $\boldsymbol{k}=2\pi/a_0(1,0,0)$.

scattering.

Finally, we have calculated the spectra with the available δ_{1k}, δ_{2k} by means of the continued fraction (8) and with a suitable 'Gaussian termination' [10]: $\Xi_2(\boldsymbol{k},t) = \exp\left(-\Gamma t^2\right)$. The parameter Γ, is determined by the insight on the corresponding spectra obtained by CMD [11] .

As an example, some spectra are shown in figures 1 and 2. In these figures we also report the similar spectra, obtained by EP molecular dynamics (EPMD) [12].

We therefore can conclude that:

(i) Quantum effects in solid neon are relevant at all temperatures so that neon cannot be approached by classical models.

(ii) The evaluation of the spectral width requires particular care and a fully quantum treatment of the fourth moment. EPMD, as observed in [13], can correctly give the peak position only because it reproduces just the short-time behaviour and consequently the second moment; using this method the phonon damping is therefore calculated by considering classical processes only. This is not sufficient for giving a good description of the spectra, as on the other hand our approach is expected to do.

We conclude suggesting new accurate neutron scattering experiments in order to investigate quantum effects in solid neon. In particular our results on zero moment $M_0 \equiv C(\boldsymbol{k},t=0)$ can be tested measuring the integrated intensity, while the aforementioned features of the line shapes can be directly compared with experimental spectra.

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