Spectral shapes of solid neon

Gaia Pedrolli, Alessandro Cucolo, Alessandro Macchi, Valerio Tognetti

Dipartimento di Fisica dell’Università di Firenze and Istituto Nazionale di Fisica della Materia (INFM),
Largo E. Fermi 2, I-50125 Firenze, Italy

Ruggero Vaia

Istituto di Elettronica Quantistica del Consiglio Nazionale delle Ricerche, via Panciatichi 56/30, I-50127 Firenze, Italy,
and Istituto Nazionale di Fisica della Materia (INFM).

(March 24, 2022)

We present a Path Integral Monte Carlo calculation of the first three moments of the 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 lowest temperatures, while the 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 approach (EP) 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 energy. Indeed, precise calculations of kinetic energy, to be compared with accurate experiments done by Deep Inelastic Neutron Scattering (DINS) computation, being the EP approach inadequate. These results show that quantum effects are very important also at rather high temperatures.

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

$$S_\alpha^{\alpha\beta}(\mathbf{k}, \omega) = \frac{1}{2\pi} \sum_r \int dt \, C^{\alpha\beta}(\mathbf{r}, t) \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)]$$

(1)

with

$$C^{\alpha\beta}(\mathbf{r}, t) = \left\langle x^{\alpha}_i(t)x^{\beta}_i(0) \right\rangle + \left\langle x^{\alpha}_{i+r}(0)x^{\beta}_i(t) \right\rangle.$$

(2)

$x^{\alpha}_i$ is $\alpha$-th component of the displacement of the $i$-th atom from its equilibrium position. Even though this quantity has been investigated since long time, complete information is not available for various rare gas solids and in particular for neon. The perturbative many-body approach can give frequency and lifetime of phonons only at low temperatures. Classical molecular dynamics (CMD) can describe the behaviour of argon and krypton at highest temperatures, but it is no more 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 to use 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,

$$\langle \omega^{2n}\rangle^{\alpha\beta}_k = \int_{-\infty}^{\infty} \omega^{2n} S_\alpha^{\alpha\beta}(\mathbf{k}, \omega),$$

(3)

while the odd moments vanish for symmetry reasons. As it is well known, this involve the PIMC calculation of static correlations obtained by multiple commutators of $x^{\alpha}_k(t) = N^{-1/2} \sum_1 \exp[i(\mathbf{k} \cdot \mathbf{r})]x^{\alpha}_i(t)$ with the Hamiltonian:

$$\langle \omega^{2n}\rangle^{\alpha\beta}_k = \frac{1}{2} \left\langle \left| \frac{d^n x^{\alpha}_k}{dt^n} \right|_0 \left| \frac{d^n x^{\beta}_k}{dt^n} \right|_0 + \frac{d^n x^{\alpha}_k}{dt^n} \frac{d^n x^{\beta}_k}{dt^n} \right\rangle_0,$$

(4)

with the derivatives taken at $t = 0$. Here we will refer only to $\mathbf{k} = 2\pi/a_0(1, 1, 0)$ 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, $\delta_{1k}$ and the irreducible part of fourth moment, $\delta_{2k}$:

$$\delta_{1k} = \frac{\langle \omega^2 \rangle_k^{\alpha\alpha}}{\langle \omega^0 \rangle_k^{\alpha\alpha}}; \quad \delta_{2k} = \frac{\langle \omega^4 \rangle_k^{\alpha\alpha}}{\langle \omega^2 \rangle_k^{\alpha\alpha}} - \delta_{1k},$$

(5)

can be directly related with the peak position and width of the spectrum.

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

$$\Xi_0(\mathbf{k}, z) = \int_0^\infty dz \frac{C(\mathbf{k}, t)}{C(\mathbf{k}, 0)} e^{-zt}$$

(6)

with

$$S_\alpha(\mathbf{k}, \omega) = \Xi_0(\mathbf{k}, z = i\omega) C(\mathbf{k}, t = 0).$$

(7)
The continued fraction expansion can be stopped at the third stage with a suitable termination $\Xi_2(k, z)$

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

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

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

$$V(r) = 4\epsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right),$$ \hspace{1cm} (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 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 number 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. The melting temperature of neon at zero pressure is 24.5 K.

Detailed explanations of the total procedure and results for the first three even moments, 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, by which we correct the raw PIMC data, subtracting the exact contributions of the harmonic part for finite $P$ and $N$, and adding both 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 $\delta_{2k}$. 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 and 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 $\delta_{2k}$. For narrow spectra ($\delta_{2k} \ll \delta_{1k}$), the phonon frequencies are $\omega_k \sim \sqrt{\delta_{1k}}$ while the phonon lifetimes are $\Gamma_k \sim \sqrt{\delta_{2k}}/2$. These quantities, shown in table and can be probed by inelastic neutron scattering.

Finally, we have calculated the spectra with the available $\delta_{1k}, \delta_{2k}$ by means of the continued fraction (8) and with a suitable “Gaussian termination”\[9]. $\Xi_2(k, t)$ = exp ($-\Gamma t^2$). The parameter $\Gamma$, is determined by the insight on the corresponding spectra obtained by CMD\[10].

As an example, some spectra are shown in figures and . In these figures we report also the similar spectra, obtained by EP molecular dynamics (EPMD)\[11].

We therefore can conclude that:

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

ii) The evaluation of the spectral width requires a particular care and a fully quantum treatment of the fourth moment. EPMD, as observed in [4], 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 can be tested measuring the integrated intensity, while the afore-mentioned features of the line shapes can be directly compared with experimental spectra.

We would like to thank Prof. S. W. Lovesey for useful discussions. One of us (V. T.) wants also to thank him for hospitality in the very stimulating atmosphere of the Rutherford Appleton Laboratory.

\footnotetext{1}{See: Cuccoli A, Giachetti R, Toggetti V, Vaia R and Verrucci P 1995 J. Phys.: Condens. Matter 7 7891 and reference therein}

\footnotetext{2}{Cuccoli A, Macchi A, Pedrolli G, Toggetti V and Vaia R 1997 Phys. Rev. B 56 51}

\footnotetext{3}{Acocella D, Horton G K and Cowley E R 1995 Phys. Rev. Lett. 74 4887}

\footnotetext{4}{Glyde H R 1994 Excitations in Liquid and Solid Helium (Oxford: Clarendon Press)}

\footnotetext{5}{Maradudin A A, Flinn P A and Coldwell-Horsfall R A 1961 Annals of Physics 15 377}

\footnotetext{6}{Lovesey S W and Meserve R A 1972 J. Phys. C 6 79}

\footnotetext{7}{Brown J S 1966 Proc. Phys. Soc. 89 897}

\footnotetext{8}{Pedrolli G 1998 PhD thesis, unpublished}

\footnotetext{9}{Cuccoli A, Macchi A, Pedrolli G, Toggetti V and Vaia R 1995 Phys. Rev. B 51 12369}

\footnotetext{10}{Tomita K and Tomita H 1971 Progr. Theor. Phys. 45 1407}

\footnotetext{11}{Cuccoli A, Toggetti V, Maradudin A A, McGurn A R and Vaia R 1993 Phys. Rev. B 48 7015}

\footnotetext{12}{Cao J and Voh G A 1994 J. Chem. Phys. 100 5106}

\footnotetext{13}{Cuccoli A, Giachetti R, Toggetti V and Vaia R 1998 cond-math/9712067 and J. Phys. A, in press.}

---

**Table I.** Moments of $S_n(k, \omega)$ for $T = 10$ K at vanishing pressure, for the wave vector $k = 2\pi/a_0(1,0,0)$. They are expressed in reduced units. $b = 2.787$ Å and $\omega_0 = 0.289747$ meV. Classical second moments are exact since they are equal to the reduced temperature.

|          | Transverse | Longitudinal |
|----------|------------|--------------|
|          | classical  | EP           | PIMC         |
| $M_0/b^2$ | ($\times 10^{-4}$) | 8.427 ± 0.005 | 30.02 ± 0.01 | 28.28 ± 0.06 |
| $M_2/(b^2\omega_0^2)$ | 0.2726281 | 0.7027 ± 0.0002 | 0.788 ± 0.002 |
| $M_4/(b^4\omega_0^4)$ | 98.13 ± 0.05 | 168.5 ± 0.1 | 314. ± 3. |

---

**Table II.** Moments of $S_n(k, \omega)$ for $T = 20$ K at vanishing pressure, for the wave vector $k = 2\pi/a_0(1,0,0)$. They are expressed in reduced units. $b = 2.787$ Å and $\omega_0 = 0.289747$ meV. Classical second moments are exact since they are equal to the reduced temperature.

|          | Transverse | Longitudinal |
|----------|------------|--------------|
|          | classical  | EP           | PIMC         |
| $M_0/b^2$ | ($\times 10^{-4}$) | 20.92 ± 0.02 | 36.50 ± 0.05 | 34.7 ± 0.3 |
| $M_2/(b^2\omega_0^2)$ | 0.545256 | 0.8387 ± 0.0006 | 0.870 ± 0.002 |
| $M_4/(b^4\omega_0^4)$ | 182.3 ± 0.3 | 218.6 ± 0.4 | 347. ± 3. |

---

**Table III.** $\sqrt{\delta_1}$ 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 |
|----------|------------|--------------|
| $T$      | $\sqrt{\delta_1}$ | $\sqrt{\delta_2}/2$ | $\sqrt{\delta_1}$ | $\sqrt{\delta_2}/2$ |
| 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 |