Collective excitations and dynamic structure factor of liquid tellurium

R V Gopala Rao & R Venkatesh
Department of Chemistry, Banaras Hindu University, Varanasi 221 005, India

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Using the potential function and its derivatives evaluated by Rao and Venkatesh from the experimental structure factors, the longitudinal ($\omega_L$) and transverse ($\omega_T$) phonon frequencies have been computed through the equations of Takeno and Goda. The $\omega_0(k)$ maximum is found to occur midway between zero and the first peak of the structure factor. The dynamic structure factor has been calculated in the viscoelastic approximation. In the current correlation function, the position of the maximum of the current density at a particular $k$ is designated as $\omega_L$, $\omega_T$ versus $k$ has been obtained at various wave vectors. The $\omega_L$ versus $k$ exhibits a flat portion spreading over the three peaks of the complex structure factor of liquid Te even though $\omega_0(k)$ increases slowly with $k$. $\omega_L$ gives a peak at nearly the same position as $\omega_L(k)$.

1. Introduction

In recent years neutron diffraction of liquid tellurium has been performed by many authors. The molecular dynamics (MD) calculations of the structure factor of liquid Te based on effective interatomic forces derived from pseudo-potential theory have been investigated by Hafner. Enderby and coworkers pointed out that liquid Te occupies a position between semi-metals and semiconductors, and with increasing temperature, liquid Te becomes distinctly more metallic. Hafner found interesting results while evaluating the potential function of liquid Te. The potential function exhibits a strong inflection in the repulsive region. He attributed this to an interplay of the repulsive hard core diameter and Friedel wave length ($2\pi/2k_F=\lambda_F$). This interaction between these two lengths splits the first nearest neighbouring shell into two subshells and thus a repulsive minimum corresponding to the first nearest neighbouring distance (nn) occurs while a negative attractive minimum appears and this corresponds to second nearest neighbour distance.

Liquid Te exhibits peculiar properties in its potential function and shows increased metallic properties with increased temperature. We now give in a concise way the theory of the calculations of phonon frequencies, elastic constants, the definition of which can easily be found in textbooks like Kettle and Bhatia. Further we also give the evaluation of the dynamic properties of the liquid in the viscoelastic approximation so as to find its resemblance with other metallic liquids like Rb.

Results and Discussion. The potential function $\Phi(r)$ as derived by Rao and Venkatesh has been used as such in the computation of potential energy derivatives. We have also calculated the elastic constants, phonon frequencies through Takeno and Goda’s equations. The computed dynamic structure factor calculated in the viscoelastic approximation is found to have similar characteristics as those obtained for liquid rubidium.

2. Theory

2.1. Calculation of phonon frequencies

We use Takeno and Goda’s equations in the evaluation of longitudinal and transverse phonon frequencies in the liquid. These are given by Eqs (1) and (2).

$$\omega_L^2(k) = \frac{4\pi}{M} \int dr \Phi(r) \left( \frac{\sin kr}{kr} \right)^2 + \frac{1}{3} \frac{\sin kr}{kr}$$

$$\omega_T^2(k) = \frac{4\pi}{M} \int dr \Phi(r) \left( \frac{\sin kr}{kr} \right)^2 + \frac{1}{3} \frac{\sin kr}{kr}$$

Equations (1) and (2) require the derivatives of the potential function. The Rao-Joardar’s equation for
the potential energy $\phi(r)$ is given by

$$\beta \phi(r) = \frac{1}{2 \pi^2 \rho} \int_0^{r/2} \left[ \frac{S(k) - 1}{S(k)} \right] \left( kr \cos kr' - \sin kr' \right) dk$$

$$\int_0^{2 \pi / \rho r} \left[ \frac{S(k) - 1}{S(k)} \right] \sin kr' dk$$

Here $\rho$ is the number density of the liquid and $S(k)$ is the structure factor.

Using Leibnitz theorem and differentiating Eq. (3) we get the first derivative as

$$\beta \frac{d\phi(r)}{dr} = \beta \phi'(r) = -\frac{1}{2 \pi^2 \rho} \left( \frac{A_1}{A_2} \right)$$

and on further differentiation of Eq. (4), we obtain the second derivative of the potential function as

$$\beta \phi''(r) = -\frac{1}{2 \pi^2 \rho} \left[ \frac{A_1}{A_2} \right]$$

where

$$A_1 = \frac{1}{r^2} \int \left[ \frac{S(k) - 1}{S(k)} \right] k \left( kr \cos kr' - \sin kr' \right) dk$$

$$A_2 = 1 + \frac{1}{2 \pi^2 \rho r} \int \left[ \frac{S(k) - 1}{S(k)} \right] \sin kr' dk$$

$$A_3 = \frac{2}{r^2} \int \left[ \frac{S(k) - 1}{S(k)} \right] (kr \cos kr' - \sin kr') dk$$

$$-\frac{1}{r^2} \int \left[ \frac{S(k) - 1}{S(k)} \right] k \sin kr' \sin kr'' dk$$

$$A_4 = -\frac{1}{2 \pi^2 \rho r^2} \int \left[ \frac{S(k) - 1}{S(k)} \right] \sin kr' \sin kr'' dk$$

In Eqs (1) and (2) we require the radial distribution function $g(r)$ for the computation of phonon frequencies. This is obtained by Fourier transformation of experimental structure factors. The phonon frequencies are shown in Fig. 1.

From the calculated phonon frequencies we evaluate the elastic constants $C_{11}$ and $C_{44}$ while $C_{12}$ can be evaluated through Cauchy’s relation. We also calculate the elastic constants through Schofield’s $I_1$ and $I_2$ integrals. The $I_1$ and $I_2$ integrals are defined as

$$I_1 = \frac{\rho}{2k_B T} \int g(r) r \phi'(r) dr$$

$$I_2 = \frac{\rho}{2k_B T} \int g(r) r^2 \phi''(r) dr$$

These $I_1$ and $I_2$ integrals are related to elastic constants as:

$$C_{11} = \rho k_B T \left( 3 + \frac{2 I_1}{5} + \frac{I_2}{5} \right)$$

$$C_{12} = \rho k_B T \left( 1 + \frac{4 I_1}{15} + \frac{I_2}{15} \right)$$

The calculated values of elastic constants are given in Table I. The computed potential function derivatives can be used in the calculation of the characteristic frequency $\omega_0$ with which most of the atoms of the liquid oscillate. The appropriate equation is

$$\frac{\langle V^2 \phi \rangle}{3M} = \frac{4\pi \rho}{M} \int dr r^2 g(r) \left( \phi''(r) + 2\phi'(r) \right)$$
Table 1 - Elastic constants of liquid Te in units of $10^{42}$ dyne/cm$^2$

<table>
<thead>
<tr>
<th>Characteristic constant</th>
<th>$C_{11}$</th>
<th>$C_{44}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>From $C_L$ and $C_T$</td>
<td>0.75</td>
<td>0.21</td>
</tr>
<tr>
<td>From phonon frequencies</td>
<td>0.53</td>
<td>0.13</td>
</tr>
<tr>
<td>From $I_1$ and $I_2$ integrals</td>
<td>0.51</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Table 2 - Characteristic and average frequencies of liquid Te ($10^{13}$ s$^{-1}$).

<table>
<thead>
<tr>
<th>Characteristic frequency ($\omega_p$)</th>
<th>$\omega_p$ maximum values</th>
<th>Debye frequency $\omega_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.55</td>
<td>1.54</td>
<td>1.95</td>
</tr>
</tbody>
</table>

$$\omega_p^2 = \left( \frac{\nabla^2 \phi}{3M} \right)$$ \hspace{1cm} (15)

The average value of the frequency $\omega_{av}$ has been computed through Eq. (16)

$$\frac{3}{\omega_{av}^2} = \frac{1}{\omega_p^2} + \frac{2}{\omega_T^2}$$ \hspace{1cm} (16)

The asymptotic equation obtained by Takeno and Goda$^6$ for longitudinal $C_L$ and transverse $C_T$ velocities is given by

$$C_L = \left( \frac{4 \pi \rho}{3M} \int dr \cdot r^3 \tilde{g}(r)(3r \phi''(r) + 4 \phi'(r)) \right)^{1/2}$$ \hspace{1cm} (17)

$$C_T = \left( \frac{4 \pi \rho}{3M} \int dr \cdot r \tilde{g}(r)(r \phi''(r) + 4 \phi'(r)) \right)^{1/2}$$ \hspace{1cm} (18)

From the computed velocities the elastic constants, $C_{11}$ and $C_{44}$, have been calculated and these are given in Table 1. The computed Debye temperature $\theta_D$ from the velocities and that obtained from low temperature heat capacities are found to be 189K and 149K respectively. The agreement is only fair. The Debye frequency $\omega_0$ obtained from heat capacities is given in Table 2.

2.2. Computation of dynamic structure factors

We now describe the computation of the dynamic structure factor of liquid Te in the viscoelastic approximation$^{13,14}$. The dynamic structure factor $S(k,\omega)$ is given by

$$S(k,\omega) = \frac{1}{\pi} \frac{\tau(k) \nu_k^2 k^2 [\omega_p^2(k) - \omega_0^2(k)]}{\left[ (\omega \tau(k) [\omega^2 - \omega_p^2(k)]) + (\omega^2 - \omega_0^2(k)) \right]}$$ \hspace{1cm} (19)

$$\omega_0(k) = \frac{\nu_k^2}{[S(k)]^{1/2}}$$ \hspace{1cm} (20)

$$\nu_{th} = (k_B T / M)^{1/2}$$ \hspace{1cm} (21)

Here $\tau(k)$ is the relaxation time in the Lovesey approximation$^4$ which is given by

$$\tau(k) = \frac{\pi \nu_k^2}{2 \left[ \omega_p^2(k) - \omega_0^2(k) \right]^{1/2}}$$ \hspace{1cm} (22)

This, therefore, completes the method of calculation of $S(k,\omega)$. $S(k,\omega)$ for five typical set of momentum vectors have been calculated and these are shown in Fig. 2.1 to 2.5. From the dynamic structure factor the longitudinal current density correlation function $J_L(k,\omega)$ have been evaluated through the following equation$^{13}$

$$J_L(k,\omega) = \left( \frac{\omega_p^2}{k^2} \right) S(k,\omega)$$ \hspace{1cm} (23)

For various values of $\omega$ the current density correlation function has been computed at fixed value of $k$. As is obvious, Eq. (23) contains a factor $\omega^2$ and hence has a maximum at each $k$. We designate the position of the maximum of current density as $\omega_m$. The values of $\omega_m$ as obtained for several values of $k$ are plotted in Fig. 3. In the same figure the experimental structure factor $S(k)$ of liquid Te and also $\omega_0(k)$ have been given.

3. Results and Discussion

The computed values of $\omega_m(k)$ and $\omega_0(k)$ are given in Fig. 1. $\omega_m(k)$ shows oscillation upto large $k$ indicating the collective modes of the nature of vibration, while $\omega_0$ as expected does not show any such oscillations. The position of $\omega_0(k)$ maximum is found to be 0.9Å$^{-1}$ while the structure factor first maximum occurs at 1.95Å$^{-1}$.

In Fig. 2.1 to 2.5 the dynamic structure factor $S(k,\omega)$ versus $\omega$ for five typical momentum vectors for liquid Te are shown. The figures indicate clearly the general resemblance of these to that of liquid Rh$^{13}$. It is impor-
Figs 2.1 to 2.5 - The dynamical structure factor $S(k, \omega)$ calculated in viscoelastic approximation for $k=1.0\,\AA^{-1}$, $2.0\,\AA^{-1}$, $3.6\,\AA^{-1}$, $4.0\,\AA^{-1}$ and $5.0\,\AA^{-1}$ at $T=723\,K$. 
Fig. 3 - The dispersion relation $\omega_m(k)$ as obtained from maximum of the longitudinal current density correlation function, $h_0(k)$ and experimental structure factor $S(k)$ versus $k$. $h_0$ (---); $h_0$ (o o o); $S(k)$ (--------).

It is important to observe that at $k=4.0\text{Å}^{-1}$ and $k=5.0\text{Å}^{-1}$ we get a clear maximum. It may be pointed out that this complex liquid shows three clear maxima of comparative heights [$1.39$ at $1.95\text{Å}^{-1}$, $1.11$ at $3.30\text{Å}^{-1}$ and $1.08$ at $4.08\text{Å}^{-1}$] in the static structure factor while in metallic liquid Rb, the first peak is very conspicuous compared with second which is insignificant. In Fig. 3 we observe that $h_0$ versus $k$ plot gives a flat portion from $1.80\text{Å}^{-1}$ to $3.40\text{Å}^{-1}$. We also give the structure factor in the same figure. In the liquid Rb the first peak is predominant [$S(k)$ = 3.06] while the second peak height is only 1.25. The $h_0$ curves increase with $k$ but slowly unlike in liquid argon and liquid Rb. This clearly shows the complex nature of Te. Both $h_0$ and $h_0$ exhibit first peak at $k = 1.0\text{Å}^{-1}$ which is nearly equal to half the value of the highest peak position of the structure factor where maximum correlation in the momentum space occurs. This is evident on examining Fig. 2 of ref. 13. Here the first peak occurs at $1.63\text{Å}^{-1}$ in $S(k)$ at 350K, while $\omega_m$ (vide Fig. 6 of ref. 13) maximum occurs at $0.82\text{Å}^{-1}$ which is close to half the position of the structure factor principal peak. The nature of $\omega_m$ and $\omega_m$ curves appear to be similar and is expected since they are both influenced by $S(k)$. We observe no flat portion in $\omega_m$ but a minimum where $S(k)$ shows maximum as expected from Eq. (20). The dashed portion of Fig. 3 is only an extension of $S(k,\omega)$ as Eqs (19) and (20) give imaginary values.

4. Conclusions
The longitudinal phonon frequency exhibits collective excitons at large $k$ while transverse phonons do not. The position of the maximum longitudinal phonon frequency appears at $0.9\text{Å}^{-1}$ and is just half of the first peak position of structure factor ($=1.95\text{Å}^{-1}$). The dynamic structure factor shows a sharp peak at high $k$ while at middle values of $k$ a flat portion is seen and at low $k$ it falls off exponentially.

$\omega_m$ versus $k$ shows a flat portion after exhibiting a peak. This flat portion ranges over the three peaks of the liquid structure factor. $\omega_m$ versus $k$ increases slowly in steps with increasing $k$. This is perhaps due to the important role played by the electron density and its interaction with hard core diameter of the atom. It is important to note that the first peak of $\omega_m$ and $\omega_m$ as can be seen from Fig. 3 also occur at $k=1.0\text{Å}^{-1}$ and is nearly equal to the position of longitudinal phonon frequency maximum.

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