

An effective pair potential for liquid semiconductor, Se: Structure and related dynamical properties

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Abstract. The effective pair potential of liquid semiconductor Se is extracted from its experimental structure factor data using an accurate liquid state theory and this shows important basic features. A model potential incorporating the basic features of the structure factor extracted potential is suggested. This model potential is then used to describe through low-order perturbation theory, the structure and related dynamical properties like self-diffusion coefficient and shear viscosity of this complex liquid over a wide range of temperatures.

Keywords. Liquid semiconductor; pair potential; structure and dynamical properties.

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1. Introduction

The crystalline structure of Se is made by stacking helical chains and results from a Peierls distortion of a simple cubic structure [1]. The atomic and electronic structures of fluid Se at high pressure and high temperature are still not fully understood. The theoretical understanding of the process is hindered by the bonding properties of Se [2]. The bonds within the chains are covalent with an energy ~ 2 eV/atom whereas the bonds between chains are an order of magnitude smaller but long-range dispersion forces are not negligible and must be taken into account. From the measurement of shear viscosity and NMR near the melting point an average chain length of 10^4 – 10^5 atoms can be estimated but this number drastically decreases with the increase of temperature and pressure [3]. Clearly the effective pair potential must be complex and liquid-state statistical mechanical calculation appears to be quite puzzling. The complexity of the average intermolecular interaction is reflected in the liquid structure factor of Se which is very different from that of simple liquid metals in as much as the first diffraction peak is considerably reduced in magnitude compared to second one while subsequent oscillations persist significantly on the high- Q side [4]. This oscillation on high- Q implies that a considerable fraction of the ring or chain structure found in crystalline structure

remains in the liquid state. Also it is important to note that the structure factors of solid amorphous (a-) and liquid (l-) Se are quite similar. The structural features are likely to be exhibited in the effective pair potential of Se. With this view in mind we have first extracted effective pair potential of Se in liquid state from its x-ray structure factor data [4] using an accurate liquid-state theory (the modified hypernetted chain (MHNC) method) [5]. The diffraction data is due to Waseda *et al* [4] and presented in tabulated form in Waseda's book. The data have however been properly interpolated in smaller intervals and also at smaller Q below $Q = 0.5 \text{ \AA}^{-1}$.

2. Effective pair potential from structure factor data

The assumption of the existence of an effective pair potential, $\phi(r)$, allows one to write the pair distribution function (PDF), $g(r)$, as

$$g(r) = \exp[-\beta\phi(r) + h(r) - c(r) + B(r)], \quad (1)$$

where $h(r) = g(r) - 1$, $c(r)$ and $B(r)$ are the direct correlation function (DCF) and 'bridge function' respectively. $g(r)$ and $c(r)$ are obtainable from structure factor data. $B(r) \approx B_{\text{hs}}(r, \eta)$ for small r where $B_{\text{hs}}(r, \eta)$ is the 'bridge' function of the hard sphere system, η , being the packing density and for large r , since $c(r) \sim -\beta\phi(r)$ it is easy to see that

$$B(r) \cong B_{\text{hs}}(r, \eta) + (1/2)[h^2(r) - h_{\text{hs}}^2(r)]. \quad (2)$$

In MHNC for all r one assumes $B(r)$ to be equal to $B_{\text{hs}}(r, \eta)$ with the packing density η given by the Lado criterion [6],

$$\int [g(r) - g_{\text{hs}}(r, \eta)] \delta B_{\text{hs}}(r, \eta) / \delta \eta \, dr = 0. \quad (3)$$

Thus, in the MHNC approximation $\phi(r)$ is given by

$$\phi(r) = -k_{\text{B}}T[\ln g(r) + c(r) - h(r) - B_{\text{hs}}(r, \eta)]. \quad (4)$$

The computed $\phi(r)$ is shown in figure 1a. Though the method has limitation it yields important basic features showing small potential minimum with a strong repulsive barrier beyond the nearest-neighbor distance restricting atoms lying on neighboring chain from approaching closer. At large separation the potential is small and attractive again. The nature of the potential is very different from that in simple metallic liquids which show deeper minimum with characteristic Friedel oscillation [7]. The features exhibited in $\phi(r)$ for Se is representative of the two-fold coordinated chain structure. The results for other approximate liquid-state theories like PY, HNC methods [7] are similar in showing basic features.

3. Model potential and structure factor

Though l-Se potential is far from anything described by any simple model qualitative descriptions of the structural features and structure related properties could

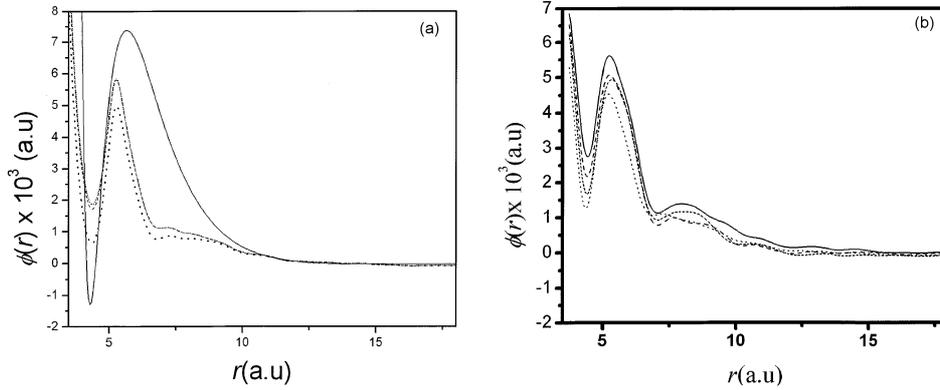


Figure 1. (a) $\phi(r)$: (—) model; $S(Q)$ derived potential: (- - -) MHNC, (- · - ·) HNC, (· · ·) PY. (b) $S(Q)$ derived potential: (—) 250°C, (- - -) 350°C, (- · - ·) 450°C, (· · ·) 550°C.

be possible due to the following considerations. Firstly, Se is a covalently bonded semiconductor like Ge, Sb etc. whose structure factor data show a shoulder on the high-angle side of the first diffraction peak which resembles a split peak. In Se the first smaller peak is more like a shoulder to the major second peak. For Ge etc., from the nature of the bonding the potential is a function of the mutual orientation of the atoms and if the spatial average over the neighbors is taken, the effective pair potential comprises double minima [8]. An approximate potential, hard-core with a ledge, produces the basic feature of shouldered peak quite successfully [9]. Secondly, the hydrogen bonded alcohols have chain molecular association indicative of high-angle oscillations in the inter-molecular structure function data [10] somewhat similar to the one in Se. The centre structure has split peak and average pair potential too has a double minimum [11]. Finally, a-Se and l-Se have basic similarities in the structure factor data. The a-Se properties have been discussed quite reasonably in terms of effective pair potential [12]. An interaction potential comprising bireciprocal L-J form and an additional Born–Mayer-type term have been used to describe properties including those representing collective motion. So it is not beyond expectation that a similar discussion should be possible for l-Se too.

We therefore propose an approximate model potential for liquid Se consistent with the basic features of its structure. The atoms in the chains are strongly bound whereas the interaction between the chains is weak van der Waals type. The application of hydrostatic pressure promotes transfer of electrons from the intra-chain bonding orbitals to bonding states between chains and can bring about a change in the relative charge distribution between inter-chain and intra-chain bonds [13]. We therefore propose a model potential comprising Mie m, n ($m = 6$ and $n = 12$) potential in conjunction with a repulsive term. The repulsive term is suggested corresponding to empty-core pseudopotential in Thomas–Fermi screening approximation [14] to account for the ionic behavior. Thus,

$$\phi(r) = a(r_0/r)^n - b(r_0/r)^m + (z_s^2 e^2 / r) \cosh^2(kr_c) \exp(-kr), \quad (5)$$

where a , b , r_0 , z_s , k and r_c are the constants obtained through structure factor data fit and listed in table 1. The model potential is shown in figure 1a. The basic features agree approximately with the one extracted from the experimental structure factor data.

For structure factor calculation in low-order perturbation theory, we use the WCA separation [15] of the potential into short-range reference term, $\phi_{\text{ref}}(r)$ and long-range perturbation term, $\phi_1(r)$

$$\text{and } \left. \begin{aligned} \phi_{\text{ref}}(r) &= \phi(r) - \phi_{\text{min}} & \text{for } r < r_0 \\ &= 0 & \text{for } r > r_0 \\ \phi_1(r) &= \phi_{\text{min}} & \text{for } r < r_0 \\ &= \phi(r) & \text{for } r > r_0 \end{aligned} \right\}. \quad (6)$$

The structure factor calculation is made for short-range reference part by Jacobs–Anderson (JA) method and long-range perturbation part contribution obtained in RPA [15]. According to JA method the reference structure factor $S_0(Q)$ corresponding to the given potential $\phi_{\text{ref}}(r)$ takes the form

$$\frac{1}{S_0(Q)} = \frac{1}{S_{\text{hs}}(Q)} - \rho_0 B_l(Q). \quad (7a)$$

Here, $S_{\text{hs}}(Q)$ is the structure factor for a system of hard spheres, ρ_0 is the number density and $B_l(Q)$ is the Fourier transformation (FT) of the WCA blip function, which allows core softness and defined by [15]

$$B_l(Q) = \frac{4\pi}{Q} \int_0^\alpha r y_\sigma(r) [e^{-\beta\phi_{\text{ref}}(r)} - e^{-\beta\phi_{\text{hs}}(r)}] \sin(Qr) dr, \quad (7b)$$

where $y_\sigma(r)$ is the hard sphere DCF within the core diameter, σ and PDF outside the core and $\phi_{\text{hs}}(r)$ is the corresponding hard sphere potential. PY theory [7] is used for hard sphere term. The hard-core diameter for this calculation could be fixed by WCA criterion [15] but we have preferred fixing this by overall structure factor fit between experimental and model data. The two values, however, are not very different. In RPA, the structure factor $S(Q)$ is given by

$$S(Q) = \frac{S_0(Q)}{1 + \beta\rho_0 S_0(Q)\phi_1(Q)}, \quad (7c)$$

where $\phi_1(Q)$ is the FT of the perturbation potential $\phi_1(r)$. The calculated structure factor $S(Q)$ as function of wave vector Q is shown in figure 2 along with

Table 1. Potential parameters (temp. = 250°C).

a (a.u.)	0.052
b (a.u.)	0.155
r_0 (a.u.)	4.2155
z_s	1.68
k (a.u. ⁻¹)	0.605
r_c (a.u.)	1.36

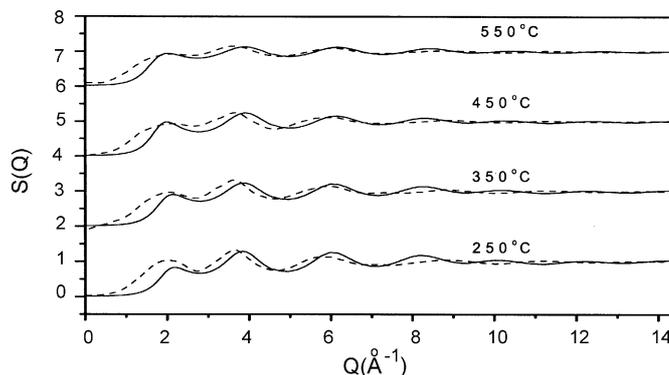


Figure 2. $S(Q)$: (—) model, (---) experimental.

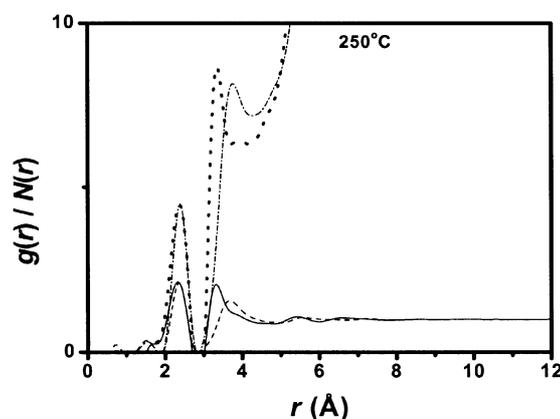


Figure 3. $g(r)$: (—) model, (---) experimental. $N(r)$: (···) model, (-·-·) experimental.

experimental data. Evidently the basic features are well-produced by the model potential calculation. The first peak region as well as the high- Q oscillations are well-represented by the model calculation. The high- Q oscillations are representative of the bonding structure of l-Se. The calculation has also yielded the free electron parameters like effective valency, ion-core radius and Thomas–Fermi screening constant vector of Se. These are shown in table 1. These values as well as other parameters appear quite reasonable. They agree fairly well with those obtained from other sources. We have also evaluated the PDF or radial distribution function (RDF), $g(r)$ and atomic distribution function, $N(r)(= 4\pi r^2 \rho_0 g(r))$ as a function of r by Fourier transform of the structure factor, $S(Q)$. The truncation effect is minimized by using a window function [16]. The results are shown in figure 3 together with the experimental data and agreement is evidently reasonable. We have also obtained the first and second nearest-neighbor numbers and corresponding distances and these are tabulated in table 2 along with experimental liquid and amorphous data [4]. The model results agree reasonably with the experimental data.

Table 2.

	l-Se (250°C)		
	Present	Experimental	a-Se
σ (Å)	3.104	–	–
η	0.47	–	–
r_1 (Å)	2.38	2.36	2.34
n_1	2.29	2.36	2.00
r_2 (Å)	3.36	3.76	3.75
n_2	7.51	6.80	6.40

We have then studied the temperature effects on the structure through the model potential. The potential parameters are almost temperature independent. The effective valence, ion-core radius are only slightly temperature sensitive. The hard-core diameter σ and the packing density η are however strongly temperature dependent and reduce quite sharply. The results are also shown in figure 2. The temperature effects on RDFs are shown in figure 4a and the model calculation reasonably works. The temperature effects on the first and second nearest-neighbor numbers (n_1 and n_2) are depicted in figure 4b along with core diameter and packing density. The model potential approach shows significant decrease in the nearest-neighbor numbers contrary to only slightly temperature-dependent numbers from the experimental $S(Q)$ data.

4. Structure-related dynamical properties

The statistical theory of fluids allows computation of a macroscopic dynamical property like self-diffusion coefficient from the knowledge of effective pair potential and structure factor data [4]. As it is well-known that the soft-part of the intermolecular potential has a dominant role in determining the magnitude of the self-diffusion coefficient we hope that the positive barrier of the Se potential would have significant role to play in the nature of the self-diffusion coefficient. With this objective in mind we have computed the self-diffusion coefficient D of l-Se based on Helfand–Rice–Nachtrieb (HRN) prescription [17] given by

$$D = k_B T / (\zeta^H + \zeta^S + \zeta^{SH}), \quad (8)$$

where ζ^H , ζ^S and ζ^{SH} are the friction constants due to repulsive hard core interaction, soft interaction between the neighboring atoms and cross effect between the repulsive core and the soft long forces respectively. Explicit expressions could be found elsewhere [4]. In a liquid where diffusion takes place, the motion of a given atom is impeded by its neighbors and several atoms must be moved in order for diffusion to take place. This fact can be taken into account in an *ad hoc* way by allowing atomic mass to be larger than the actual mass. Because of the very nature of the repulsive barrier we hope that this caging effect [18] must be more appropriate for system like l-Se and that the atomic mass m is to be replaced by an

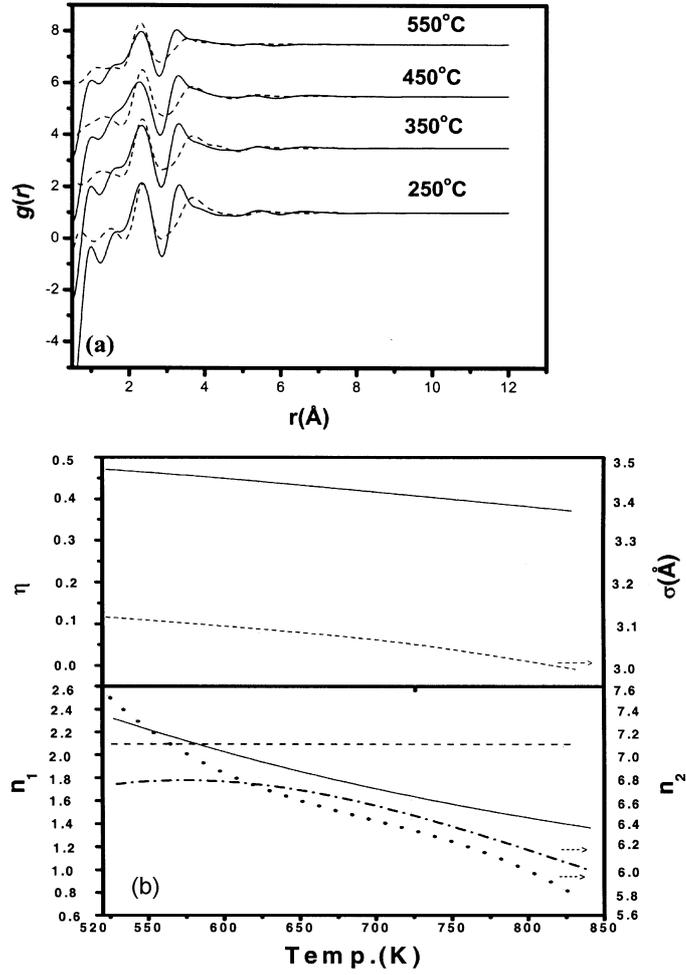


Figure 4. (a) $g(r)$: (—) model, (- - -) experimental. (b) η : (—), σ : (- - -), n_1 (calc.): (—), n_1 (expt.): (- - -), n_2 (calc.): (···), n_2 (expt.): (- · - · -).

effective larger mass m^* . The effective mass for diffusion includes the mass of the atom itself plus the mass of the neighboring atoms that have to be moved in order for diffusion to take place. Thus the idea of correlation length l^* arises and this is given by the distance over which some rearrangement takes place to accommodate the movement of one atom. The relation between l^* and m^* is such that a volume of dimension l^* contains a number of atoms equal to m^*/m and considering hard sphere particles expression is given by

$$m^* = m\eta g(\sigma)(l^*/\sigma)^3, \quad (9)$$

where $g(\sigma)$ is the PDF at contact and other terms are as already defined. Like number average chain length [19], we assume l^*/σ to fall exponentially with temperature. The value at 250°C and its fall are determined by fitting the self-diffusion

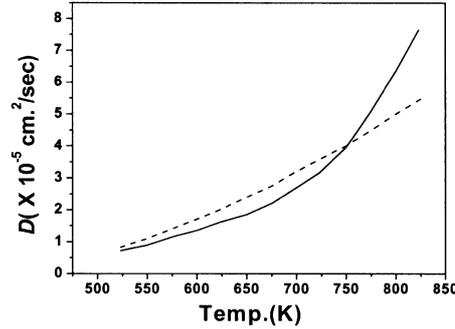


Figure 5. Self diffusion coefficient vs. temperature. Calculated: (—), simulation/QENS: (- -).

coefficient data at 250°C and its rate of increase at 250°C with temperature as available in the literature. The calculated self-diffusion coefficient as a function of temperature is shown in figure 5 along with simulation data [20] and estimation from quasi-elastic neutron scattering (QENS) data [21] wherever available. Unfortunately there is no direct experimental measurement of self-diffusion coefficient of l-Se available in the literature. The friction constants are also shown which indicate the relative contributions of short-range and long-range interactions.

Like self-diffusion coefficient the shear viscosity is another important macroscopic dynamical property in which l-Se has its distinction from other liquids and liquid metals. Near the melting point it is extremely large but drastically reduces with increase of temperature. The number average chain length in l-Se is derived from observed shear viscosity data [19]. Eyring developed a theory for rate process which gives a connection between self-diffusion (D) and shear viscosity (μ) coefficients for dense liquids [18]. This relationship has been often used to estimate the self-diffusion coefficient from shear viscosity data [21]. The desired relationship is [18]

$$\mu = k_B T a^2 \rho / D, \quad (10a)$$

where a is the spacing between atoms and ρ is the position-dependent number density. Approximating a by the correlation length and ρ by the RDF at contact value we have the shear viscosity formula given by

$$\mu = k_B T l^{*2} \rho_0 g(\sigma) / D \quad (10b)$$

ρ_0 being the atomic number density. The latter approximation is done similar to the one done for effective mass calculation [18]. Using calculated D 's we have evaluated μ from eq. (10b) and the results are shown in figure 6 as a function of temperature. It is indeed surprising to note that Eyring's rate theory results agree so well with observed shear viscosity data.

5. Results and discussion

It is gratifying to note that like a-Se, it is possible to conceive of a model effective pair potential for l-Se. The characteristic features of the effective pair potential

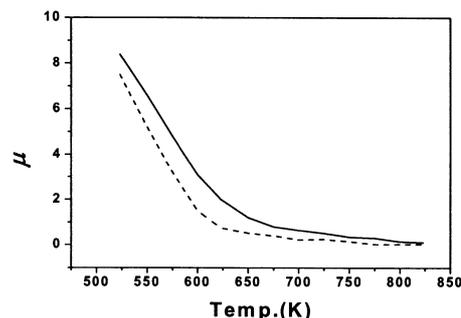


Figure 6. Shear viscosity vs. temperature. Calculated: (—), experimental: (- - -).

extracted from experimental structure factor data agree generally with the model potential. The structure factor data are more or less similar in both x-ray [4] and neutron diffraction [22] and naturally expected to yield similar effective pair potential. The model potential parameters listed in table 1 appear quite reasonable when compared with those of a-Se [12]. The structure factors and its temperature effects are represented quite well by the model (figure 2). Mie potential parameters almost remain independent of temperature while z_s , k and r_c of the electron-ion contribution change slightly. The hard-core parameters, however, decrease monotonically with increase of temperature (figure 4b). In figure 1b we show the effective pair potential (at large r only) derived from experimental structure factor data at four different temperatures. There is some systematic decrease in the minimum and the repulsive barrier height at elevated temperatures. The basic features, however, remain unchanged. In the model calculation the temperature effect is mainly taken care by the change in reference hard core diameter. The model RDF and atomic distribution function $N(r)$ at 250°C are shown in figure 3 while the temperature effects are shown in figure 4a. The major basic features are clearly produced. Though the peak positions are nearly temperature independent, the first and second nearest-neighbor numbers are somewhat temperature dependent, unlike only slight effects observed in the quantities extracted from experimental diffraction data. The computer simulation results at higher temperatures (597–1097°C), however, show similar decrease in the number of first neighbors [20] and this is consistent with the fact that the chain structure might be somewhat disrupted in the liquid state at higher temperatures. This is also consistent with the way the coefficient of shear viscosity drops down at higher temperatures.

In figure 5 the results depicted for self-diffusion coefficient indeed agree well with the data from quasi-elastic neutron scattering (QENS) data and also simulation data [20,21] wherever available. The directly measured data for l-Se are not available in the literature. The calculated values at higher temperatures appear to be somewhat large but these values agree reasonably with simulation results [20]. It is to be noted that the caging effect in fact takes into account the multiple scattering effects that are ignored in the evaluation of equations in (8). In figure 7 we have also shown the variations of various ζ 's as functions of temperature. Evidently it is ζ^S which contributes very significantly to the total ζ at all temperatures. The

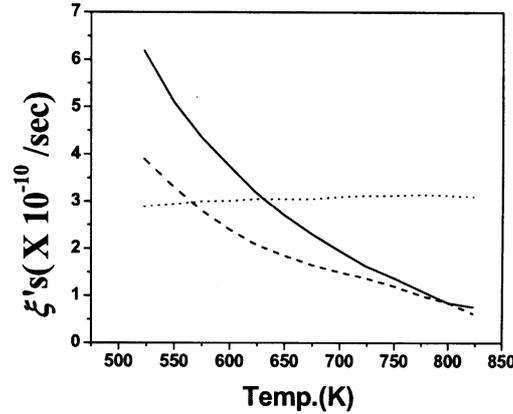


Figure 7. ζ^H : (—), ζ^S : (---), ζ^{SH} : (...).

correlation length l^* has been assumed to vary with temperature exponentially somewhat similar to the number average chain length. So the effective mass m^* decreases rapidly.

In figure 6, we show the results for shear viscosity calculated through eq. (10b). The directly measured data on the shear viscosity are available in the literature and the values are shown for comparison. It is evident that Eyring's rate theory expression with the consideration of effective mass due to caging effect yields viscosity results quite well. The large and rapid decrease in the viscosity with rise of temperature is well-produced by this formula involving self-diffusion constant. The agreement also supports the calculated values of self-diffusion coefficient through eq. (8).

6. Conclusion

We have performed a detailed liquid-state theory calculation on l-Se where highly non-central forces are known to operate and a pair-wise interaction potential model were expected to be inappropriate [23] and as such little work from this point of view was done so far. However, such effective pair potential approach on the study of various static and dynamical properties of a-Se has been there in the literature for long [12]. Since the structure factors of Se in liquid and amorphous states agree in basic features as also indicated by identical nearest-neighbor numbers we hope that such approach should yield useful results for Se in liquid state. It is true that there exists some disagreement in actual values between the structure factor extracted potential and the model potential. The Mie form ($m = 6$ and $n = 12$) has been chosen in consistency with a-Se potential [12] and simulation work for l-Se [24]. It is expected that a better form of model potential more in coincidence with structure factor extracted potential could produce better agreement between model calculation and experimental data. We have, however, stressed more on producing the characteristic features than finding perfect agreement between experimental and calculated values. Anyway, the present approach, though approximate, is

straightforward and thus useful as direct application of existing liquid-state theories to this complex system.

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