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Tight binding molecular dynamics studies of the viscosity of liquid selenium

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Abstract. A tight binding technique is employed to study the influence of the size of the unit cell on molecular dynamics simulations of liquid selenium at 870 K. Systems with 69, 138, 276 and 552 atoms have been studied within the Fermi operator expansion method. The Green–Kubo formula has been used to calculate the shear viscosity for all systems from the off-diagonal component of the stress tensor. No dependence on the cell size could be found within the error bars defined by statistical accuracy. For the two smallest systems calculations up to 60 ps have been performed where the viscosities become identical. These findings indicate that the recently reported disagreement of DFT calculations and experiments on the viscosity of liquid selenium at 870 K must be attributed to a deficiency in the chosen exchange correlation functional rather than size effects.

1. Introduction

Liquid selenium (*l*-Se) is a much studied system exhibiting very unusual properties. The trigonal crystal structure of the solid consists of infinite helical chains in which neighbouring atoms are connected by strong covalent bonds. The bonding between the chains is much weaker which explains the system's low melting temperature ($T_m = 490$ K). The nature of these weak interchain bonds is still not completely clear [1]. Upon melting the chain-structure is essentially preserved and diffraction measurements show that the coordination number in the liquid is almost exactly equal to two even at high temperatures [2, 3].

The viscosity of *l*-Se drops from ~ 5 Pa s close to the melting point to ~ 4 mPa s at 1000 K. [1, 4] This rapid decrease may be governed by two parameters. The first is the chain length assuming that the Se chains become more and more disrupted as the temperature is raised, the second is the temperature dependence of the interaction between chains. The nature of these two parameters, as well as the amount of their contribution to the viscosity, have been discussed using several experimental and theoretical techniques.

Perron *et al* [4] applied a free volume model based on their viscosity studies of *l*-Se doped with Te to reduce the average chain length and Ge, Sb to increase interchain bonding in order to analyse the contributions of both parameters. However, their model could not account quantitatively for the experimental results.

Warren and Dupree [5] used NMR measurements to derive the average chain length in *l*-Se, and reported values from $\sim 10^4$ at the melting point to ~ 10 at 1600 K. Their analysis is based on the assumption that the majority of defects (one- or three-fold coordinated Se atoms terminating the chains) are paramagnetic centres. Recent molecular dynamics (MD) simulations based on

density functional theory (DFT) within the generalized gradient approximation (GGA) [6] gave average chain lengths differing from those from the NMR data at 870 K. [7] Spin-polarized calculations of the percentage of paramagnetic centers were also presented and it was estimated to be about 10%. So the disagreement in the number of atoms per chain at 870 K (62 atoms from DFT-GGA calculations [7], ~ 1000 atoms from the NMR-experiments [5]) could be caused by an underestimation of the number of chain-ends (and therefore overestimation of the chain length) by Warren and Dupree [5] because they only counted defect atoms with unpaired electrons.

On the other hand, although DFT-GGA calculations have proven to produce structure factors and radial distribution functions in fair agreement with diffraction data for *l*-Se in low- [7, 8] and high-temperature [9, 10] regimes, there is the possibility of finite-size effects which might affect the calculation of chain lengths. The unit-cell in [7] contained only 69 atoms and the restraints implied by periodic boundary conditions may prevent the formation of Se chains with 1000 atoms. This point is further supported by the fact that the same calculation procedure yielded a chain length of 23 atoms for 1370 K where the agreement with the NMR data (~ 20 atoms) is very close.

The interaction between chains also remains a controversial topic. Bichara and coworkers [11, 12] as well as Molina *et al* [13] studied *l*-Se by means of tight binding (TB) Monte Carlo simulations and argued that the average two-fold coordination of Se atoms found in the diffraction data is caused by the number of one- and three-fold coordinated defects balancing each other while the total number of defects increases substantially with increasing temperature. This picture—which is in line with early DFT-calculations based on the local density approximation (LDA) [14]—suggests a branched network of chains with rather short chain lengths. However, Kirchhoff *et al* [7] showed that LDA descriptions of *l*-Se suffer from unphysical low-wavelength density fluctuations as a consequence of underestimating the equilibrium volume. In recent synchrotron diffraction experiments for *l*-Se [15] which go up to the critical temperature there is no indication of the substantial amount of three-fold coordinated defects which is predicted to be as high as 30% in [12]. The GGA-DFT results of Kresse *et al* [7] indicate that three-fold coordinated defects only form a percentage of $\sim 2\%$ for all temperatures studied and thus cannot act as a dense network of bridgeheads connecting the Se chains.

The viscosity of *l*-Se at 870 and 1370 K has been derived from GGA-DFT calculations using the Green–Kubo relations, recently [16]. While at 1370 K the agreement with experiment was reasonable within the statistical error bars of the calculations (the viscosity was calculated to be 0.30 ± 0.04 mPa s and measured to be 0.55 mPa s [4]), at 870 K the difference spanned an order of magnitude (0.52 ± 0.04 mPa s calculated, 6.0 mPa s measured [4]). Because of the relationship between viscosity and chain length in a molecular liquid and the fact that both quantities taken from the GGA-DFT calculations differ with related experiments by about a factor of 10 for *l*-Se at 870 K, it seems possible that both disagreements have a common source in some kind of deficiency in the simulations. This might either be the small size of the simulated cell or the form of the exchange correlation functional within GGA describing an aspect of bonding in the liquid incorrectly.

The aim of the present work is to investigate this point further by studying the dependence of the viscosity of *l*-Se at 870 K on the cell-size by using a TB order- N approach, since it would be extremely expensive to do first-principles MD calculations on systems of several hundred atoms with a duration long enough to calculate the viscosity. We are well aware that the size-dependence of transport coefficients in *l*-Se at 870 K has been studied before by means of classical MD [17]. However, in this approach intrachain bonds were fixed to remain between the same atom-pairs for the whole run and bond breaking and formation

events were therefore prohibited. We do not believe that transport coefficients of the system can be described correctly without taking these events into account, since the bond lifetime for *l*-Se is rather short [7].

The paper is organized as follows. Section 2 describes the details of our TB model. In section 3 its results are compared with previous GGA-DFT calculations for equilibrium properties of trigonal Se (*t*-Se) and for static structural properties and the self-diffusion coefficient of *l*-Se at 870 K. Calculations of the viscosity of *l*-Se at 870 K are presented in section 4, where again the results of the TB model and GGA-DFT are compared for a unit cell with 69 atoms. Size effects on the viscosity are also discussed in this section. The paper concludes with a summary in section 5.

2. Method and parametrization

For all calculations in the present work the well established TB order-*N* code OXON [18] has been used. A total energy E_{tot} is obtained by calculating the band energy E_{band} by summation over single-electron eigenstates of a Hamiltonian represented in an atomic-like basis set and adding a repulsive energy E_{rep} given as a sum of pair terms [18].

In principle the Hamiltonian can be diagonalized in \mathbf{k} space for the calculation of E_{band} . However, the number of computational operations required to do so would scale as the cube of the number of basis-functions and thus with the number of atoms in the system. In order to make the study of size-effects computationally feasible, it is therefore necessary to make approximations to exact TB to achieve linear scaling with the system's size. There are two classes of approach introducing such approximations, the recursion (or moment) methods, which formulate the problem in terms of continued fractions, and minimization methods, which formulate the problem in terms of the minimization of an energy functional. A review and comparison of these methods (as well as TB in general) is given in [18].

In the current work the Fermi operator expansion (FOE) method [20] has been used, because it works extremely well for metallic systems, while also modelling semiconductors [19]. As for any recursion method there are two parameters defining the level of accuracy compared to exact TB. The first is the number of moments m , which can be thought of as equivalent to m hops along closed paths, while the second is the size of the cluster of atoms over which the hops are made. The cluster of size n is here defined as a shell of neighbours that can be reached by n hops. For all calculations in this work n was equal to three and m equal to 150, because this setting ensured good convergence of forces and stresses, which is crucial for calculating viscosities.

It should be noted that the FOE method requires the use of a finite electron temperature and an infinite number of moments would be required to reach $T = 0$. However, the energy can be extrapolated to its $T = 0$ value by using the energy functional $U - \frac{1}{2}TS$, where U is the internal energy, and S is the electron entropy [21].

The form of the repulsive pair potential, distance dependence and all parameters of E_{band} and E_{rep} were based on the work of Raty *et al* [12]. In this approach the repulsive energy is given as

$$E_{\text{rep}} = \frac{1}{2} \sum_{i,j \neq i} V_0 \left(\frac{r_0}{r_{ij}} \right)^p \left(1 + \frac{a - r_{ij}}{r_0} \left(\frac{r_{ij}}{a} \right)^{-b} \right) F_1(r_{ij}) \quad (1)$$

the distance dependence of the hopping integrals in the band term is defined by

$$\beta_\lambda(r) = \beta_{\lambda,0} \exp \left(-q_\lambda \frac{r}{r_0} \right) F_0(r) \quad (2)$$

and Fermi-functions are used for the damping of both terms,

$$F_v(r) = \frac{1}{1 + \exp((r - \delta_v)/\sigma_v)} \quad v = 0, 1. \quad (3)$$

The band integrals $\beta_{\lambda,0}$ and the parameters defining the distance dependence of the band term ($q_\lambda, \delta_v, \sigma_v$) were fitted to the electronic density of state calculated by a first-principle approach in [12] and are therefore very reliable. The parameters defining the repulsive term, however, were determined in order to stabilize the correct crystalline structure of selenium with the band structure term approximated at the fourth moment level ($m = 4$). Since the cohesive energy in these calculations differed from the experimental one by a factor of 1.7, the temperatures were scaled by this factor to prevent the described systems from being ‘too cold’. Since at the present time the number of moments used for the expansion of the Hamiltonian is much higher ($m = 150$) than in [12], the contribution of the band structure term becomes different and the parameters of the repulsive term have been readjusted to correctly describe the first two peaks in the *ab initio* radial distribution function $g(r)$ for *l*-Se at 870 K. In this way a temperature scaling could be avoided. All parameters of the model used in the present work are listed in table 1.

Table 1. Parametrization of the Hamiltonian used in equations (1)–(3) in the text.

	$ss\sigma$	$sp\sigma$	$pp\sigma$	$pp\pi$	repulsive
$\beta_{\lambda,0}$ (eV)	-74.68	83.79	49.92	-6.36	—
q	4.05	3.52	2.97	1.80	—
V_0 (eV)	—	—	—	—	3.88
p	—	—	—	—	6.51
r_0	2.37	2.37	2.37	2.37	2.37
a	—	—	—	—	1.98
b	—	—	—	—	6.00
δ_v	3.36	3.36	3.36	3.36	3.33
σ_v	0.15	0.15	0.15	0.15	0.12

Within a canonical or (N,V,T) ensemble the equations of motion were solved using a Verlet algorithm [22] with a Gaussian thermostat [23] where the timestep was 3 fs for all studied systems. All calculations in this work were performed for the temperature $T = 870$ K and the density $\rho = 3.57$ g cm⁻³ to make a direct comparison with recent *ab initio* calculations [16] possible.

3. Validity of the model for trigonal selenium and liquid selenium at 870 K

All results presented in this section are based on calculations with three atoms in the unit cell for the bulk properties and 69 atoms for the liquid. The total simulation time for the properties of the liquid was 15 ps.

Table 2 compares the equilibrium structural parameters of *t*-Se calculated from our TB Fermi operator expansion approach (TB-FOE) with results from GGA-DFT calculations [8] and experimental data. The overall agreement is satisfactory although the bulk modulus is three to four times larger than in experiment. Since the experimental value, however, is quite small, this is a very sensitive quantity to calculate and even the GGA-DFT result differs from experiment by a factor of two.

Figure 1 shows the structure factor $S(k)$ and pair distribution function $g(r)$ of *l*-Se at 870 K, where again our present TB-FOE results are compared with DFT-GGA calculations

Table 2. Comparison of equilibrium structural parameters (volume per atom Ω , c/a ratio, internal parameter u and bulk modulus B) of t -Se derived from TB-FOE and DFT-GGA [8] results and from experimental data [24].

	Ω (\AA^3)	c/a	u	B (GPa)
TB-FOE	31.47	1.135	0.224	50.2
DFT-GGA	28.77	1.16	0.226	7.1
Experimental data	27.26	1.136	0.225	14.9

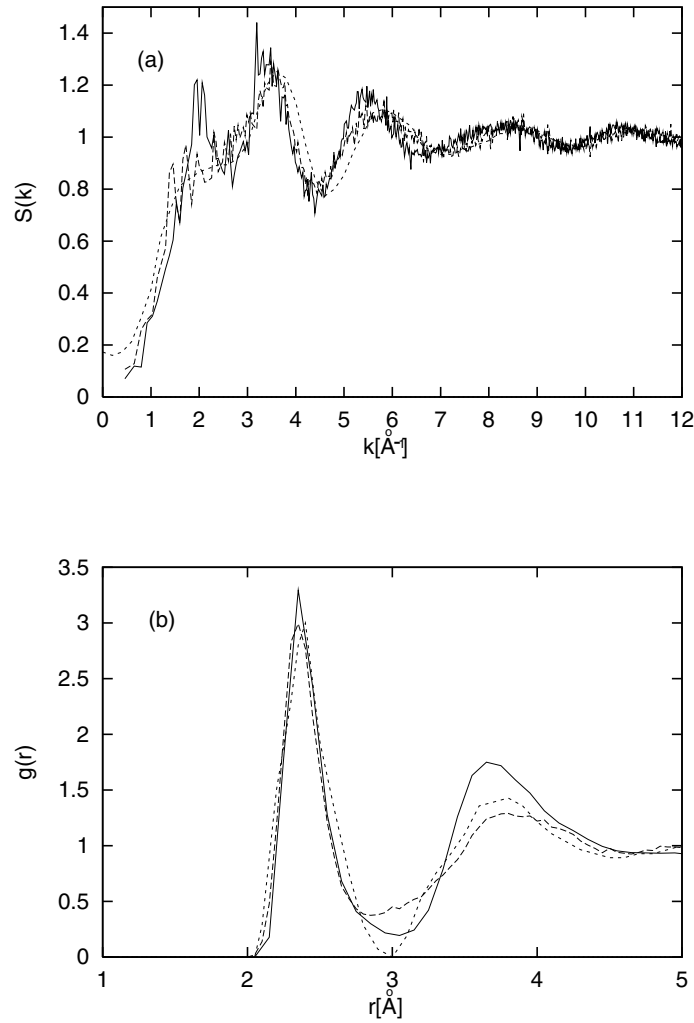


Figure 1. (a) Structure factor $S(k)$ and (b) radial distribution function $g(r)$ for l -Se at 870 K, TB-FOE results are given as solid lines, DFT-GGA references as dashed lines, neutron scattering [2] as dotted lines.

from [8]. The dotted lines show data from neutron scattering experiments [2], which have been extensively compared with the DFT-GGA results in [8]. The static structure factor provides

the most direct means of comparison with diffraction data and is derived from

$$S(k) = \langle |\hat{\rho}_k|^2 \rangle \quad (4)$$

in our calculations. Here, the dynamical variable $\hat{\rho}_k$ represents the density of atoms at wave vector k

$$\hat{\rho}_k = N^{-1/2} \sum_{i=1}^N \exp(i\mathbf{k} \cdot \mathbf{R}_i) \quad (5)$$

where the sum goes over all N atoms in the system. Again the overall agreement between TB-FOE and DFT-GGA results is reasonably good, although the first peak of $S(k)$ (figure 1a) at about 2 \AA^{-1} is overestimated by the TB method compared with the DFT-GGA reference.

The first peak in the radial distribution function $g(r)$ (figure 1b) is almost identical in both descriptions, the first minimum and second maximum, however, differ. These last two features are related to the weak bonding between Se chains. To describe these bonds correctly is a formidable task and also the DFT-GGA description is not in perfect agreement with the experimental data taken from [2].

Table 3. Average percentage of defects at 870 K taken from instantaneous coordination analysis calculated from TB-FOE and DFT-GGA [7]. Also shown is the calculated number of nearest neighbours N_c , and the self diffusion coefficient D , with the values in parentheses showing D calculated from VACF; for details see text.

	One-fold	Three-fold	N_c	D ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)
TB-FOE	22.0	19.7	1.96	4.2 (4.4)
DFT-GGA	3.4	8.5	2.00	3.5 (3.8)

In table 3 the average concentrations of one-fold and three-fold coordinated defects are given. The DFT-GGA values are taken from [8], where the effect of the chosen cut-off distance r_c and quenching for removing vibrational contributions are discussed in detail. Values in the table were derived from instantaneous coordination analysis from six selected snapshots of the MD runs. These numbers are based on a cut-off distance $r_c = 2.90 \text{ \AA}$ as is the average coordination number N_c given in the third column. The defect concentrations derived from the TB-FOE model are significantly higher than those of the DFT-GGA reference. This is in agreement with the TB Monte Carlo simulations of Bichara *et al* [11, 12] and also with the TB MD results from Molina *et al* [13]. The effect of quenching in removing vibrational contributions has also been studied and we found that the total number of defects was not reduced as in the DFT-GGA case [7] but the percentage of three-fold coordinated Se atoms increased with a decreasing number of one-fold coordinated atoms. Nevertheless, the average coordination numbers N_c taken from TB-FOE and DFT-GGA data agree sufficiently well with each other and reproduce the value of ~ 2 found in diffraction experiments [3].

Atomic transport in liquids is characterized by the self-diffusion coefficient. One way of defining it is through the time-dependence of the mean-square displacement in the Einstein relation

$$2tD = \frac{1}{3} \langle |\mathbf{R}_i(t) - \mathbf{R}_i(0)|^2 \rangle \quad (6)$$

in the long-time limit $t \rightarrow \infty$, where $\langle \cdot \rangle$ denotes an average over particles i and over time-origins. Alternatively, it can be defined as the time-integral of the velocity autocorrelation function (VACF)

$$D = \frac{k_B T}{M} \int_0^\infty Z(t) dt \quad (7)$$

where M is the atomic mass,

$$Z(t) = \frac{\langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle}{\langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(0) \rangle} \quad (8)$$

and $\mathbf{v}_i(0)$ is the velocity of particle i . The corresponding spectral density is given by

$$\hat{Z}(\omega) = \int_0^\infty Z(t) \cos(\omega t) dt. \quad (9)$$

The diffusion coefficients calculated from the two approaches are compared with each other and the corresponding DFT-GGA results from [8] in table 3 where the overall agreement is found to be very good. Figure 2 shows a direct comparison of mean square displacements,

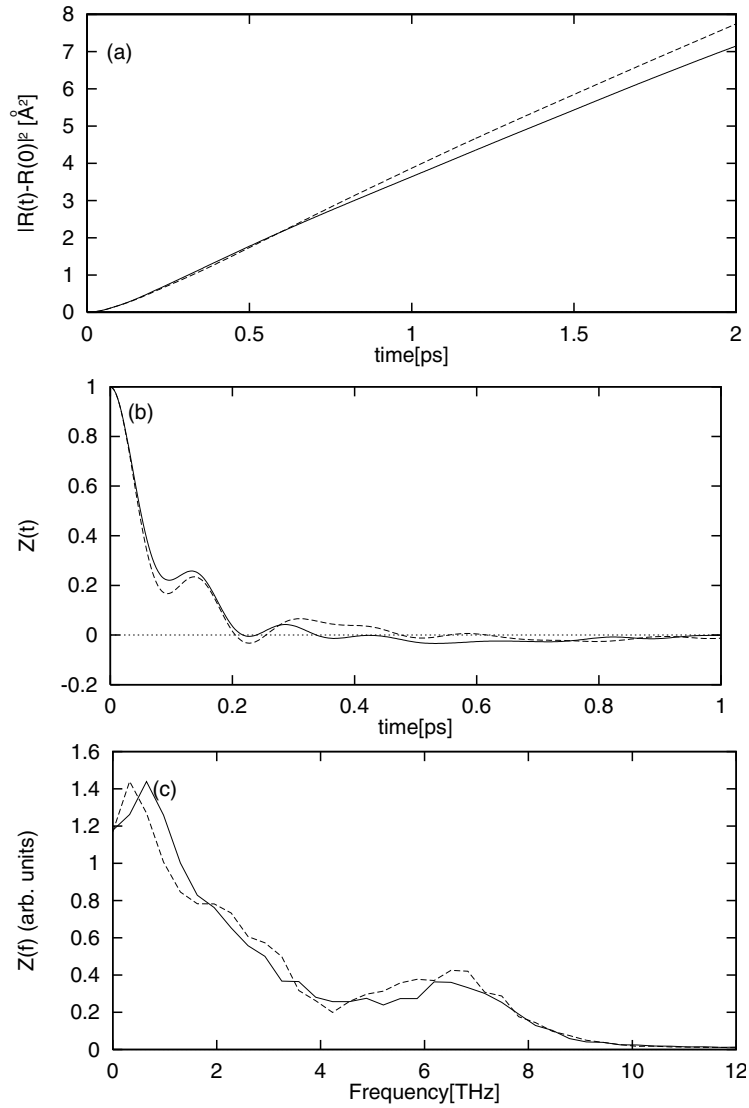


Figure 2. (a) Mean square displacement, (b) velocity auto-correlation function $Z(t)$, and (c) the corresponding spectral density $\hat{Z}(f)$ for l -Se at 870 K. Meaning of line type as in figure 1.

VACFs and spectral densities derived from both methods where excellent agreement is found apart from a slight shift in the first peak of $\hat{Z}(\omega)$.

In summarizing this section, our TB-FOE model reproduces the DFT-GGA results for *l*-Se and *l*-Se at 870 K quite well where substantial differences were found for the concentration of defects.

4. Results and discussion of the calculations of the viscosity

Exploiting the Green–Kubo relations, i.e. the relations between transport coefficients and correlation functions involving fluxes of conserved quantities [25], the shear viscosity η can be derived from

$$\eta = \frac{V}{k_B T} \int_0^\infty dt \langle P_{xy}(t+t_0) P_{xy}(t_0) \rangle \quad (10)$$

where V is the volume of the unit cell and P_{xy} denotes an off-diagonal component of the stress-tensor. The components of the stress-tensor are defined by

$$P_{xy}(t) = -\frac{1}{V} \sum_{i=1}^N (M v_i^x(t) v_i^y(t) + \sum_{j>i}^N r_{ij}^x(t) f_{ij}^y(t)) \quad (11)$$

where N is the number of atoms in the unit cell, v_i^x is the x component of the velocity of atom i , r_{ij}^x is the x component of the vector separation between atoms i and j , and f_{ij}^y is the y component of the force on atom i due to atom j . There are five independent components of the traceless stress-tensor, P_{xy} , P_{yz} , P_{zx} , $\frac{1}{2}(P_{xx} - P_{yy})$ and $\frac{1}{2}(P_{yy} - P_{zz})$. From each of those components the stress autocorrelation function (SACF) can be constructed by averaging $P_{xy}(t+t_0)P_{xy}(t_0)$ over time origins t_0 . For the SACFs and their time-integrals averages over the five independent components are presented in the following. The Green–Kubo formalism has been successfully applied to first principles calculations of the viscosity of liquid Al and Fe in [16, 26].

Figure 3(a) shows a comparison of the SACF of *l*-Se at 870 K calculated from TB-FOE (solid line) and DFT-GGA (dashed line), where the latter corresponds to the data presented in [16]. Both simulations have been performed for a unit cell with 69 atoms and a total simulation time $t = 15$ ps. Again the agreement is fairly good, and the first oscillations reflecting the complex molecular structure of *l*-Se are found almost at the same times with similar peak-heights. It must be noted that the form of SACF is qualitatively different from that of metallic liquids like *l*-Al and *l*-Fe [16, 26], where it steadily decays towards zero and oscillations are due to statistical noise only. At times larger than ~ 0.3 ps, also for *l*-Se statistics becomes predominant and the functions begin to differ. The time-integrals of SACF are also given in figure 3(b) together with the statistical error as a function of t estimated by using the scatter of the SACFs calculated by splitting the simulations into many short intervals and combining this estimate with an analytical expression. The calculated error is larger for the TB-FOE method than for DFT-GGA indicating longer correlation of the movement of the atoms in the liquid. Asymptotic values for the viscosity, however, estimated from the time-integrals in figure 3(b) are similar for the two methods.

Having assured ourselves that the TB-FOE model describes the SACF and its time-integral with reasonable accuracy for *l*-Se at 870 K with respect to the DFT-GGA reference, we now proceed to study size-effects. Figure 4(a) shows the time-integrals of the SACFs and its estimated errors derived from calculations with total simulation time $t = 15$ ps and a size of 69, 138, 276 and 552 atoms in the unit cell. It can be seen that the viscosity increases when the cell is doubled, but decreases again for the next larger system and finally reaches its highest

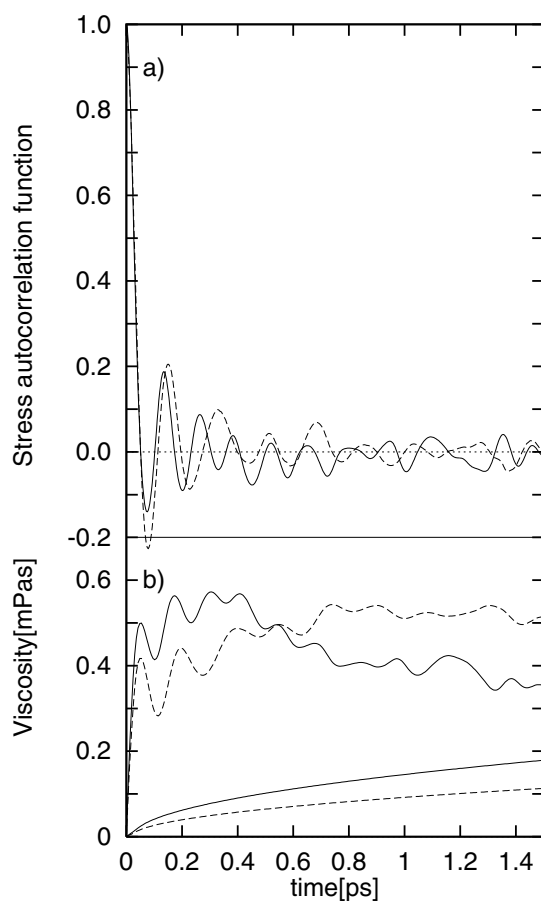


Figure 3. (a) Stress auto-correlation function and b) its time integral with the corresponding statistical error from TB-FOE (solid line) and DFT-GGA results (dashed line), $t = 15$ ps.

value for the largest system studied. However, the statistical error increases in size with the number of atoms as well.

In order to reduce this error we have performed calculations for a total simulation time $t = 60$ ps for the two smallest systems, and the results are depicted in figure 4(b). The calculations are now much better converged with respect to the simulation time, and the asymptotic values of the viscosity for the two system sizes become almost identical. So we conclude that size effects are negligibly small.

Table 4. Average percentage of defects for cells with 69, 138, 276 and 552 atoms calculated from TB-FOE.

Number of atoms per cell	69	138	276	552
One-fold	22.0	19.9	0.4	17.6
Three-fold	19.7	24.0	23.5	20.6

The first four columns in table 4 show the average percentage of defects for the different cell sizes, and also in these numbers no distinct dependence on the cell size can be found.

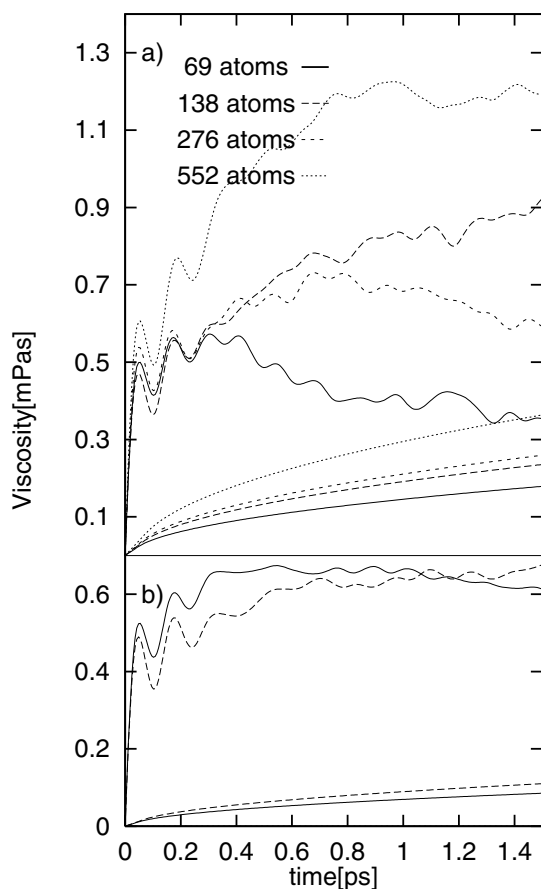


Figure 4. Time integrals of stress auto-correlation functions with the corresponding statistical error, (a) total simulation time $t = 15$ ps for systems with 69, 138, 276 and 552 atoms, (b) $t = 60$ ps for systems with 69 and 138 atoms. Line type goes from solid to dotted with increasing number of atoms in the cell.

Our findings are in disagreement with earlier classical MD calculations [17], where a size dependence of properties of *l*-Se is found. It must be noted, though, that in the force field model of [17] bond breaking and formation events were not accounted for, therefore limiting the reliability of the model.

5. Conclusions

The main purpose of this work was to find out whether finite size effects or a deficiency of the form used for the exchange correlation functional is responsible for the recently reported [16] disagreement between GGA-DFT calculations and measurements on the shear viscosity of liquid selenium at 870 K. In order to elucidate this question a TB order- N method based on the Fermi operator expansion technique has been employed for viscosity calculations via the Green-Kubo relations from cells with 69 up to 552 atoms. No size effects at all could be found within this range of cell sizes. Furthermore, the viscosity calculated from the TB model was in good agreement with the GGA-DFT results. Therefore we conclude that only improved

exchange correlation functionals within DFT or methods going beyond DFT could describe the viscosity of *l*-Se in a satisfactory way.

Acknowledgments

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