Viscosities of liquid CdTe near melting point from *ab initio* molecular dynamics calculations

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Abstract

Recent experimental results for the viscosity of liquid CdTe exhibit disparate behavior as a function of temperature. While some measurements show the expected Arrhenius like behavior, other measurements show an anomalous temperature dependence indicating an increase in viscosity with increasing temperature. We present *ab initio* molecular dynamics simulations of liquid cadmium telluride near its melting point and use the Stokes-Einstein relation to extract values of the viscosity constant. We find no anomalous behavior; the viscosity decreases monotonically with temperature and is consistent with an Arrhenius like behavior. Although calculated values are slightly smaller than those measured, the predicted activation energy agrees well with experiment.

Among II-VI semiconductors, CdTe is of special technological interest. Cadmium telluride and its alloys are used to fabricate a wide array of electro-optic devices, high performance infrared detectors and room-temperature radiation detectors. For example, infrared sensors based on epitaxial layers of $Hg_{1-x}Cd_xTe$ (HgCdTe) typically are grown on single-crystal CdTe substrate. In order to continue the advance of such applications, large, high-quality single crystals of CdTe are required. However, the growth of such material has proven to be extremely difficult.[1,2] These difficulties have motivated growth experiments in the microgravity environment of earth orbit.[3] A more complete understanding of the physics of the melt state should provide important information to solve such technical difficulties of CdTe growth. Liquid CdTe (*l*-CdTe) also presents an interesting subject for fundamental studies.

One of the most important properties of a liquid is its shear viscosity. Experiments on the viscosity of *l*-CdTe have yielded very different behavior for the viscosity. Glazov and Chizhevskaya[4] reported results for the viscosity of *l*-CdTe in pioneering work done in the late 1960's on liquid semiconductors. They measured a monotonic decrease of the viscosity with temperature following an Arrhenius-like behavior. This behavior is common for most liquids. In contrast, Shcherbak *et al.*[5] found an anomalous trend of the viscosity with temperature. They found an *increase* with the viscosity with *increasing* temperature above the melting point. Starting at a temperature close to the melting point, Shcherbak *et al.* found a two-fold increase in the viscosity when the temperature was increased approximately 20 K.

Here we examine the behavior of the viscosity of *l*-CdTe as a function of temperature. In particular, we use *ab initio* molecular dynamics simulations to predict the viscosity within the experimental temperature range. Unlike earlier simulations of liquids, it is possible to calculate quantum interatomic forces, which can be incorporated in a molecular simulation. Until recently such simulations were very difficult and computationally demanding. However, *ab initio* simulations do not require *ad hoc* descriptions of the interatomic forces. Charge transfer, coordination changes and rehybridization are accurately reproduced with quantum forces. The required forces were computed quantum mechanically from *ab initio* pseudopotentials constructed within the local density approximation.[**?**]

We used a plane-wave pseudopotential representation, with norm-conserving pseudopotentials[6] for both Cd and Te species and with a plane-wave energy cutoff of 12 Ry. The Cd pseudopotential was constructed using the "partial core" approximation[7] to account for the outer $4d$ states. We considered a system of 64 atoms in a cubic cell with periodic boundary conditions. Characterization of the valence charge density was limited to the Γ point of the Brillouin zone. The mass density was fixed at the experimental value[8] for l-CdTe: $\rho = 5.64$ g/cm^3. Additional computational details can be found in the literature.[?]

We prepared the liquid ensemble using Langevin dynamics.[9] The equations of motion of the ions were integrated for a time step of 4 fs using the Beeman algorithm.[10] Starting from a random configuration, the system was thermalized at a temperature of 6000 K for 2 ps in order to eliminate any memory effect from the initial configuration. After the randomization process at the elevated temperature, we cooled the system to a temperature of 1370 K for 2.5 ps. The target temperature was fixed to be near the melting point of l-CdTe, 1373 K. We gradually reduced the Langevin viscosity associated with the heat bath to zero over a time period of 1 ps. This transforms our canonical ensemble to a microcanonical ensemble. Once the system is converted to a microcnanonical ensemble, we need to establish the actual temperature. We do this by averaging over the kinetic energy of the system using the equipartition theorem.

Once we have established the microcanonical temperature, we run the simulation for approximately 2 to 5 ps. Over this time interval, we can obtain the required atomic displacements for an accurate determination of the viscosity. Typically, we run the system for a given time interval and then reheat the the system to 3000 K, thermalize it at 3000 K over a 2.5 ps interval, and quench it again to the desired temperature. This eliminates any memory of the previous run.

Owing to the stochastic nature of this process, the heat bath temperature can be different in the transformation from canonical to microcanonical ensembles. However, the resulting temperatures from the kinetic energy are close to the target temperature. We examined five temperature regimes spanning over 200 K: 1324 K, 1349 K, 1411 K, 1468 K, and 1554 K.

Using these ensembles, we can calculate a number of properties of the melt such as the structure factors, the diffusion constants and the viscosity. We obtain the partial static structure factors, $S_{\alpha\beta}(q)$, from standard relations:[11]

$$S_{\alpha\beta}(q) = \frac{1}{\sqrt{N_\alpha N_\beta}} \langle \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \exp[-i\mathbf{q} \cdot (\mathbf{R}_{i,\alpha} - \mathbf{R}_{j,\beta})] \rangle \, , \tag{1}$$

$(\alpha, \beta = \mathrm{Cd}, \mathrm{Te})$, where N_α is the number of paricles of species α, $\mathbf{R}_{i,\alpha}$ is the position of particle i of that species, and $\mathbf{q}$ is a wave vector compatible with the periodic boundary conditions [*i.e.*, $\mathbf{q} = (2\pi/L)(n_x, n_y, n_z)$, where n_x, n_y, and n_z are intergers and L is the length of the cubic supercell]. The angular brackets denote average over both the trajectories of the particles and over all the wave vectors $\mathbf{q}$ with the same modulus q. From the partial structure factors, $S_{\mathrm{CdTe}}(q)$, $S_{\mathrm{CdCd}}(q)$, and $S_{\mathrm{TeTe}}(q)$, we can calculate the total structure factor, $S(q)$, as weighted by neutron-scattering factors:

$$S(q) = \frac{{b_{\mathrm{Cd}}}^2 S_{\mathrm{CdCd}}(q) + 2b_{\mathrm{Cd}} b_{\mathrm{Te}} S_{\mathrm{CdTe}}(q) + {b_{\mathrm{Te}}}^2 S_{\mathrm{TeTe}}(q)}{{b_{\mathrm{Cd}}}^2 + {b_{\mathrm{Te}}}^2}, \tag{2}$$

where b_{Cd} and b_{Te} are the corresponding experimental neutron scattering lengths ($b_{\mathrm{Cd}} = 0.51$ and $b_{\mathrm{Te}} = 0.58$).[12]

In Fig. 1, we compare the computed total structure factor $S(q)$ for *l*-CdTe at T = 1411 K with x-ray data obtained by Prigent *et al.*[13] at T = 1390 K. Our calculated total structure factor was smoothed with a Gaussian with a full width at half maximum of 0.1 Å^{-1}. The agreement between theory and experiment for the first, third, and fourth peaks at $\sim$ 1.7 Å, $\sim$ 3.0 Å, and $\sim$ 5.0 Å is quite good. The intensity of the first three peaks of the theoretical total structure factor $S(q)$ is somewhat sensitive to the temperature.[14] For example, as the temperature decreases, the intensity of the second peak also decreases relative to the first and third peaks. Thus, it is possible that a small temperature change in the simulation may bring the simulation into better agreement with experiment. In contrast, a ~10% change in the volume does not change the nearest neighbor coordination.[14]

We also calculated the self-diffusion constants from the mean-square displacements using Einstein's formula, and from the normalized velocity autocorrelation functions using the Green-Kubo relation.[11] The diffusion constant of species α is given by the mean-square displacement from

$$D_\alpha = \lim_{t->\infty} \frac{\langle [R_\alpha(t)]^2 \rangle}{6t}\,, \tag{3}$$

where $\alpha = \mathrm{Cd}, \mathrm{Te}$. The mean-square displacement at time t is given by

$$\langle [R_\alpha(t)]^2 \rangle = \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} [\mathbf{R}_{i,\alpha}(t) - \mathbf{R}_{i,\alpha}(0)]^2\,, \tag{4}$$

where the initial time may be set arbitrarily, provided the simulation is run sufficiently long.

In Figure 2 (inset), we plot the mean-square displacement as a function of time for Cd and Te atoms at the temperature of 1411 K. We followed the trajectory of each atom in the liquid for $\sim$ 1.2 ps by averaging over time origins for 3.2 ps. From the slopes of both curves, we obtain $D_{\mathrm{Cd}} = 11.3\times10^{-5}$ cm^2/s and $D_{\mathrm{Te}} = 5.8\times10^{-5}$ cm^2/s at the temperature of 1411 K. Table 1 shows the diffusion constants for the five different temperature regimes. Our theoretical diffusion constant for Te atom near the melting point, 1373 K, agrees well with available experimental data,[8] $D_{\mathrm{Te}} = 5.0\times10^{-5}$ cm^2/s.

We also calculated the normalized velocity autocorrelation function $Z_\alpha(t)$ for species α defined as

$$Z_\alpha(t) = \frac{\langle \mathbf{v}_{i,\alpha}(t) \cdot \mathbf{v}_{i,\alpha}(0)\rangle}{\langle \mathbf{v}_{i,\alpha}(0) \cdot \mathbf{v}_{i,\alpha}(0)\rangle}, \tag{5}$$

where $\mathbf{v}_{i,\alpha}(t)$ is the atomic velocity of the ith atom of that species at time t. The angular brackets denote an average over all atoms and over different time origins. The diffusion constant can be calculated as

$$D_\alpha = \frac{k_B T}{m_\alpha} \int\limits_0^\infty Z_\alpha(t)dt, \tag{6}$$

where m_α is the mass of an atom of species α, k_B is the Boltzmann constant, and T is the temperature calculated from the kinetic energy of the system. Plots of $Z_{\mathrm{Cd}}(t)$ and $Z_{\mathrm{Te}}(t)$ at T = 1411 K are presented in Fig. 2.

As shown in Fig. 3 and Table 1, the values of the diffusion constants obtained from the velocity autocorrelation functions agree to within 5-10 % those from the mean-square displacements. In principle, the autocorrelation functions and mean square displacements should yield identical numbers. In practice, there are differences because of finite sample sizes and simulation times. We note that diffusion constants of Cd and Te increase linearly with respect to temperature between $T = 1300$ K and 1600 K.

The diffusion constant and the shear viscosity, η, are connected through the Stokes-Einstein formula,[11]

$$\eta = \frac{k_B T}{2\pi a D} \tag{7}$$

where $D = (D_{Cd} + D_{Te})/2$ and a is the effective "diameter" of the diffusing particles. We define the particle size, a, as the first maximum in the *total* pair correlation function. The Stokes-Einstein relation is exact only for the Brownian motion of a macroscopic particle. However, molecular dynamics simulations of liquids have demonstrated that the viscosity as calculated from the Green-Kubo and generalized Einstein formulas[15] or the transverse-current autocorrelation function[16] is consistent with that obtained from the Stokes-Einstein relation.

Our calculated values for the shear viscosity are shown in Table 1. The theoretical shear viscosity of *l*-CdTe decreases gradually with increasing temperature as expected. The kinematic viscosity is given as $\nu = \eta/\rho$, where ρ is the mass density of the melt. From the mass density used in our simulations, we estimated the kinematic viscosity given in Table 1. In Fig. 4, we compare the calculated and measured kinematic viscosities. The temperature dependence of the viscosity is usually expressed as simple Arrhenius relationship,[17]

$$\nu = \nu_o \exp(-E/RT), \tag{8}$$

where E is an activation energy of viscous flow and R is the gas constant.

The experimental data in Fig. 4 from Shcherbak *et al.*[5] is not consistent with an Arrhenius behavior, whereas the work of Glazov and Chizhevskaya[4] is. Our work is clearly at variance with Shcherbak *et al.* and in fairly good agreement with Glazov and Chizhevskaya. The calculated activation energy assuming an Arrhenius behavior is approximately 28.5 kJ/mol. The experimental activation energy from Glazov and Chizhevskaya is 28.9 kJ/mol. However, the magnitude of the calculated viscosity is smaller than the Glazov and Chizhevskaya experimental values.

In summary, we report the structure factor and temperature dependence of the diffusion constants and shear viscosity of *l*-CdTe near its melting point from molecular dynamics simulations based on quantum forces. The structure factor agrees well with experiment. The values of the diffusion constants calculated from the mean square displacements and velocity autocorrelation functions are mutually consistent. The variation of the viscosity with temperature follows an Arrhenius-type behavior with an activation energy in good agreement with that extracted from experiments. Our results resolve a recent controversy that arise from disparate experimental results on the viscosity near the melting point of this important liquid alloy.

Acknowledgments

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FIG. 1: Total structure factor of *l*-CdTe near the melting point. The continuous curve represents our *ab initio* results at $T = 1411$ K, the dashed curve experimental data at $T = 1390$ K from Ref. 13.

FIG. 2: Normalized velocity autocorrelation functions and mean-square displacements (inset) of *l*-CdTe at $T = 1411$ K as obtained from our *ab initio* molecular dynamics simulation. The continuous curve corresponds to Cd, the dashed curve to Te.

FIG. 3: Diffusion constants of *l*-CdTe at different temperatures near the melting point as obtained from our *ab initio* molecular dynamics simulation. The circles correspond to Cd, the squares to Te. Diffusion constants calculated from the mean square displacements and velocity autocorrelation funtions are represented by solid and open symbols, respectively.

FIG. 4: Kinematic viscosity of *l*-CdTe at different temperatures near the melting point. The diamonds correspond to theoretical data as obtained from our *ab initio* molecular dynamics simulation, the squares and circles correspond to experimental data from Ref 4 and Ref 5, respectively. The solid and dashed lines represent the Arrhenius fit (see text) to theoretical and experimental data (Ref 4).

TABLE I: Values of the diffusion constant (in 10^{-5} cm^2/s), shear viscosity (in mPa s) and kinematic viscosity (in cS) at different temperatures (in K), as obtained from our *ab initio* molecular dynamics simulation of l-CdTe near the melting point. MSD stands for the diffusion constant calculated from the mean square displacement, and VAF from the velocity autocorrelation function.

T	D_{Cd}		D_{Te}		η	ν
	MSD	VAF	MSD	VAF		
1554	15.9	17.5	7.7	8.5	1.02	0.18
1468	13.6	14.4	7.4	7.7	1.06	0.19
1411	11.3	11.5	5.8	6.5	1.26	0.22
1349	10.6	10.9	5.4	5.7	1.30	0.23
1324	9.1	10.0	4.7	4.8	1.50	0.27

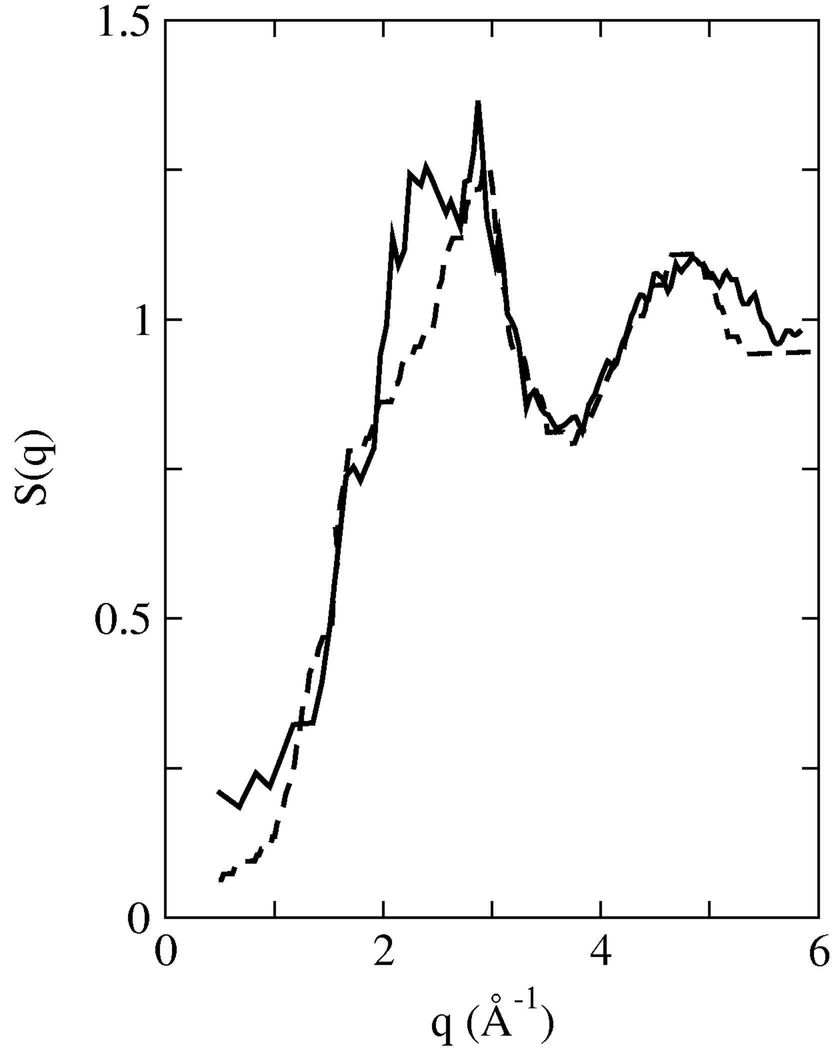


Figure 1

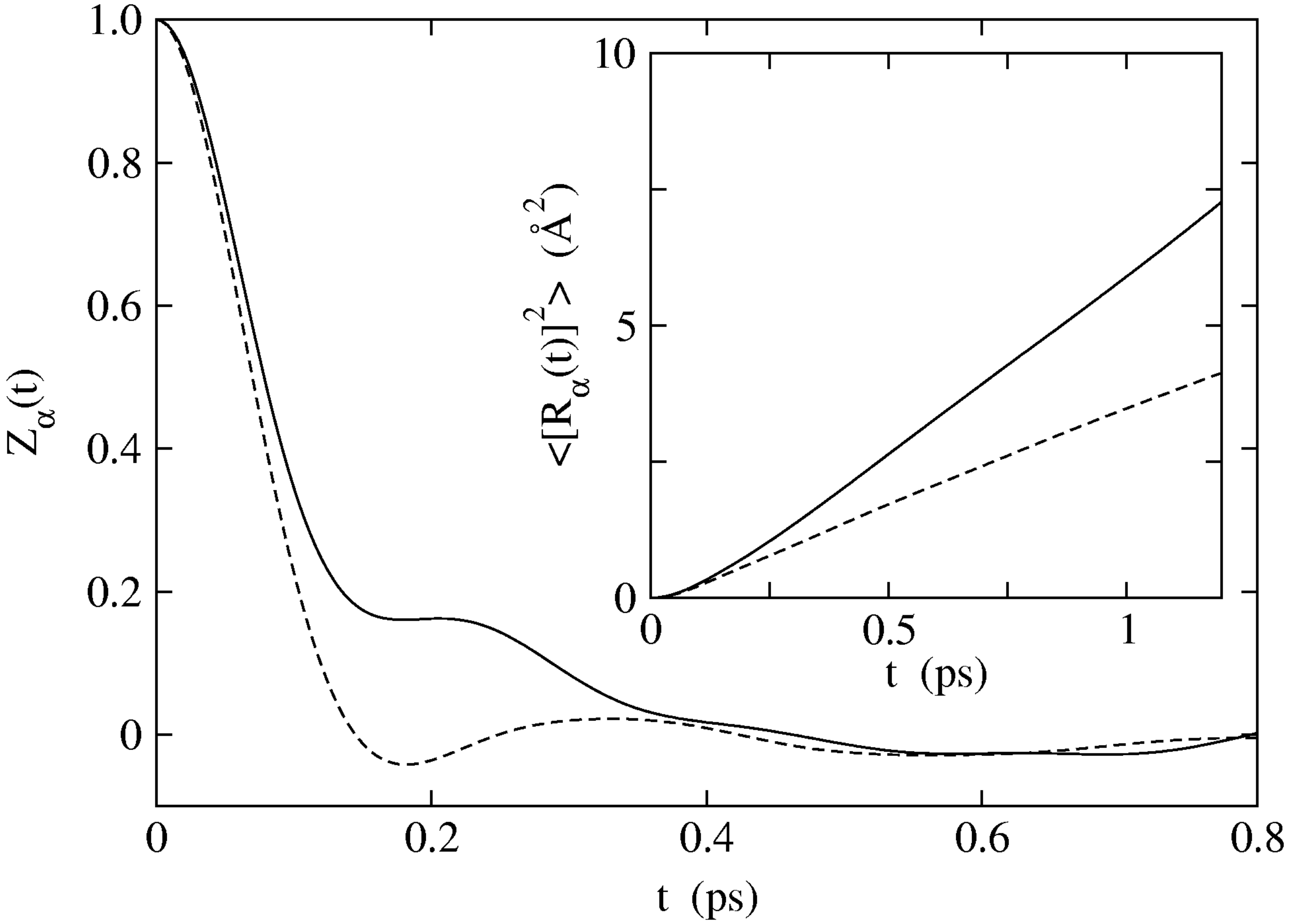

1.0
0.8
0.6
0.4
0.2
0
$Z_\alpha(t)$
0
0.2
0.4
0.6
0.8
t (ps)
10
5
0
$<[R_\alpha(t)]^2>$ (Å^2)
0
0.5
1
t (ps)

Figure 2

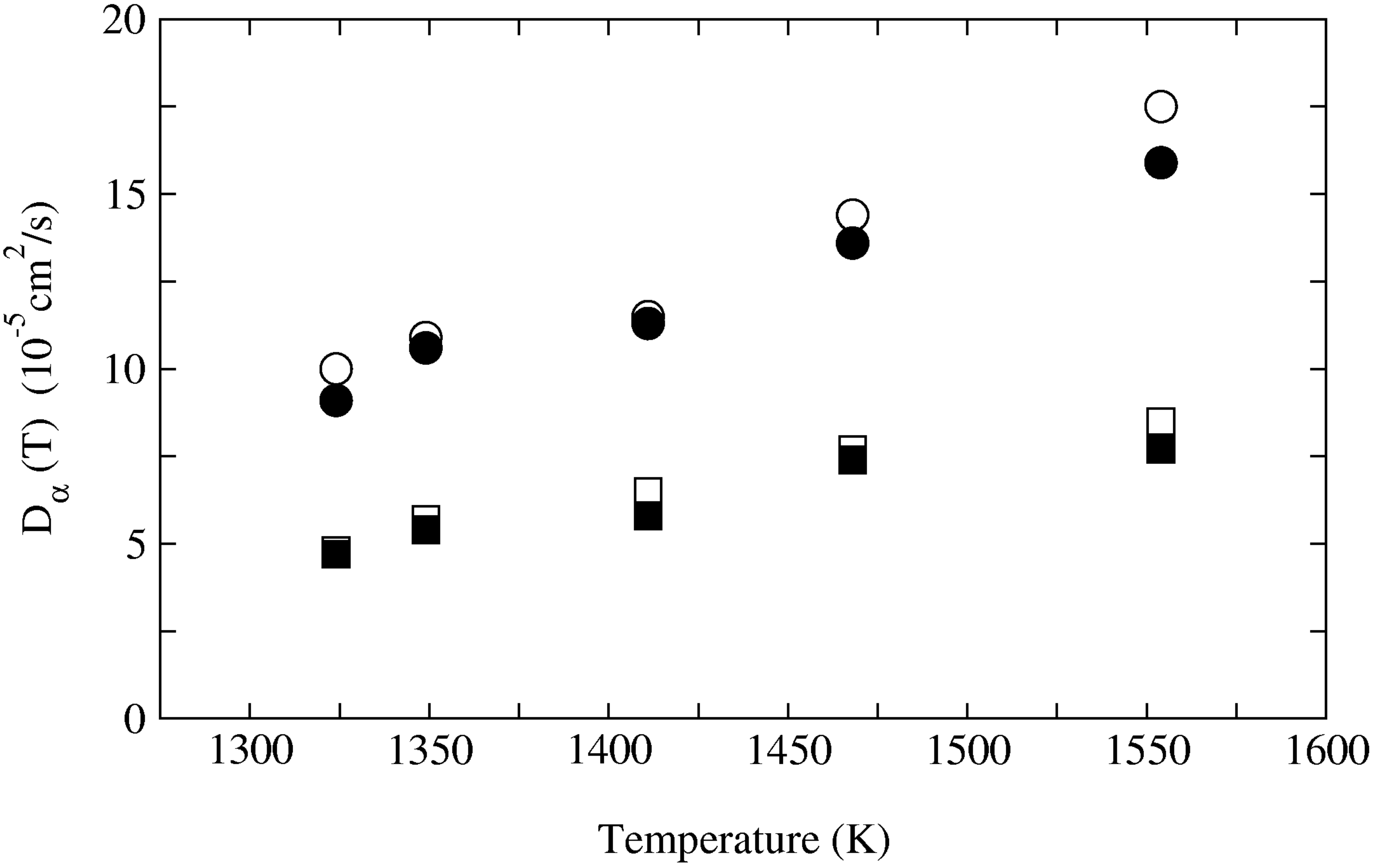
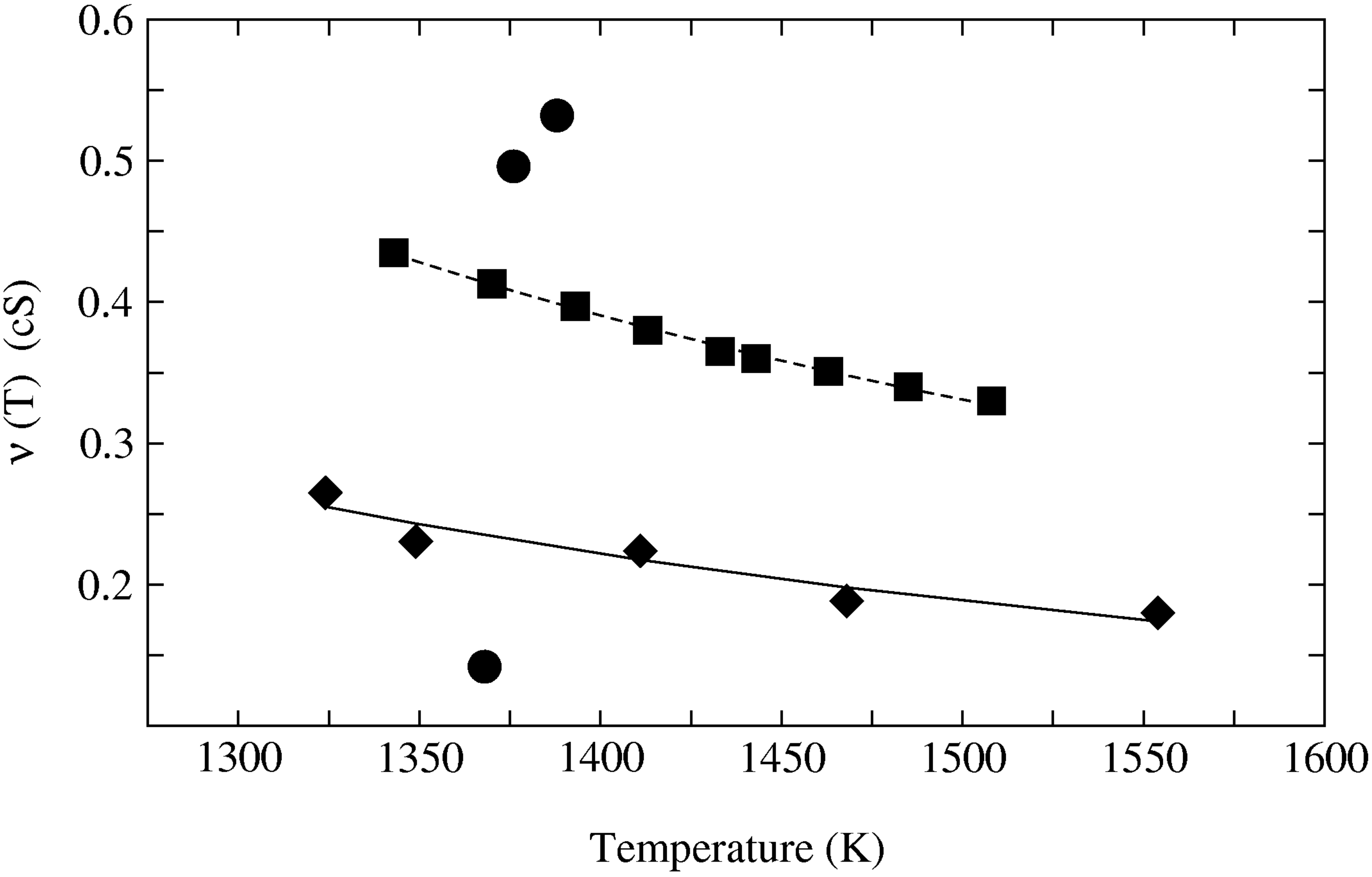

20
15
10
5
0
1300
1350
1400
1450
1500
1550
1600
D_α (T) (10^{-5}cm^2/s)
Temperature (K)

Figure 3



0.6
0.5
0.4
0.3
0.2
ν (T) (cS)
1300
1350
1400
1450
1500
1550
1600
Temperature (K)

Figure 4