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# Relationship between structure, entropy, and mobility in network-forming ionic melts

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Diffusivity, ionic conductivity, and viscosity of network-forming ionic melts are examined using molecular dynamics simulations of $BeF_2$ and $SiO_2$ melts. These tetrahedral, network-forming ionic melts are shown to possess a conductivity anomaly, in addition to waterlike viscosity and diffusivity anomalies, corresponding to a striking breakdown of the Nernst-Einstein relation. The contrasting scaling behavior of the different mobility measures with different structural contributions to the excess entropy is demonstrated.

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Quantitative relationships between structure and transport properties are valuable for predicting properties of complex liquids. A recent development is the demonstration that a semiquantitative connection between mobility and structure can be established by focusing on the excess entropy ($S_e$), defined as the difference between the total thermodynamic entropy ($S$) and the corresponding ideal gas entropy ($S_{id}$) at the same temperature and density. Scaling relationships between the excess entropy and transport properties were originally formulated by Rosenfeld [1–4] and, in conjunction with multiparticle correlation expansions of the excess entropy [5–7], provide a means of relating entropy, mobility, and structure of fluids [8–14].

Structural correlations lower the entropy of a fluid relative to the ideal gas which is expressed as a multiparticle correlation expansion, $S_e=S_2+S_3+\cdots$, where $S_n$ is the entropy contribution due to $n$-particle spatial correlations [5–7]. The entropy contribution due to pair correlations between atoms of type $\alpha$ and $\beta$ can be written as

$$S_{\alpha\beta}=\int_0^\infty \{g_{\alpha\beta}(r)\ln g_{\alpha\beta}(r)-[g_{\alpha\beta}(r)-1]\}r^2dr, \qquad (1)$$

where $g_{\alpha\beta}(r)$ is the atom-atom radial distribution function. The overall pair correlation entropy $S_2$ is $S_2/Nk_B=-2\pi\rho\Sigma_{\alpha,\beta}x_\alpha x_\beta S_{\alpha\beta}$ where $N$ is the number of particles and $x_\alpha$ is the mole fraction of component $\alpha$ in the mixture. In simple liquids, $S_e$ is dominated by the $S_2$ contribution and the residual multiparticle entropy (RMPE), $\Delta S=S_e-S_2$, is relatively small [6].

Excess entropy scaling relationships are of the form $X^*=A\exp(\alpha S_e)$ where $X^*$ are dimensionless transport properties with either macroscopic (Rosenfeld) or microscopic (Dzugutov) reduction parameters [1–3]. The scaling form may be justified using corresponding states arguments or mode-coupling theory [2,4]. Intuitively, it can be understood as reflecting the fact that structural correlations lower the excess entropy as well as the diffusivity by enhancing cage effects due to nearest neighbor shells. An alternative view is that since the liquid state is characterized by a very high degree of connectivity of configurational space, the probability that a particle will make a successful move from its current position will be proportional to to the number of accessible configurational states relative to the ideal gas, given by $\exp(\alpha S_e)$. In keeping with the corresponding states character of the relation, $\alpha$ depends on the functional form of the interaction potential. Entropy scaling relationships have been used to connect structure, mobility, and entropy in liquids with waterlike anomalies [8–12], confined fluids [13], and polymeric melts [14]. These studies have been largely restricted to fluids of structureless particle with spherically symmetric pairwise-additive interactions, except for a few studies on water and silica [8,11].

This study considers the effect of multiparticle and pair correlations on single-particle as well as collective transport properties. Entropy scaling ideas are extended to complex, inorganic network-forming ionic melts with significant multiparticle correlations, using simulations of liquid $SiO_2$ and $BeF_2$. Such an ionic melt can be treated as a multicomponent mixture of atoms with very different electronegativities. If the electronegativity difference is large, Coulombic interactions dominate the structure, as in alkali halides. As the electronegativity difference decreases, local anisotropic or "covalent" interactions result in formation of liquid state networks; e.g., molten $BeF_2$, $SiO_2$, or $AlCl_3$. The complex interplay of relative electronegativities and polarizabilities results in a diversity of liquid state structures, anomalous properties, and polyamorphic phases [15,16]. Extending entropy scaling ideas to ionic melts is interesting because the RMPE contribution will be sensitive to network formation, though the pair correlation term $S_2$ will typically be the dominant contribution to $S_e$. Ionic melts possess an additional transport property, ionic conductivity ($\sigma$), that has so far not been considered in the excess entropy scaling literature. The two $AB_2$ ionic melts, $SiO_2$ and $BeF_2$, are known to form three-dimensional, locally tetrahedral networks similar to the hydrogen-bonded network of water [17–22]. Like water and mesoscopic liquids with core-softened potentials, they show a density anomaly, where density increases on isobaric heating, and a diffusional anomaly, where diffusivity increases on isothermal compression. The entropy scaling approach shows that the common feature of these systems underlying both thermodynamic and kinetic anomalies is an excess entropy anomaly $[(\partial S_e/\partial\rho)_T>0]$, originating in the competition between two different length scales or order metrics [8–12,23–25].

In this work, we compute the behavior of ionic conductivity ($\sigma$), viscosity ($\eta$), and diffusivity ($D$) as a function of

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temperature and pressure for liquid $SiO_2$ and $BeF_2$. The validity of the Stokes-Einstein (SE) and Nernst-Einstein (NE) equations which relate ionic diffusivities to viscosity and conductivity, respectively, are then examined. We then consider the excess entropy scaling relationships for the different mobility measures.

We performed molecular dynamics simulations of a rigid-ion (TRIM) model of $BeF_2$ and a van Beest–Kramer–van Santen (BKS) model of silica using the DL_POLY code [19,21,27,28]. Diffusivities were evaluated using the Einstein relation and the shear viscosity and ionic conductivity were evaluated using the Green-Kubo route [26,29]. Thermodynamic integration was used to estimate the excess entropy [25]. Computational details are given elsewhere [23–25,29]. Thermodynamic and structural anomalies of both systems have been mapped out previously. The maximum temperature along the locus of state points corresponding to temperatures of maximum density (TMD) along isobars occurs at 4940 K, 2.3 g $cm^{-3}$ for $SiO_2$ and 2310 K, 1.8 g $cm^{-3}$ for $BeF_2$ [19,23].

$BeF_2$ and $SiO_2$ melts show viscosity ($\eta$) and diffusivity ($D_{\pm}$) anomalies, as expected on the basis of earlier studies [17–25]. For example, Fig. 1(a) shows the anomalous decrease in $\eta$ with increasing $\rho$ for temperatures below 2250 K. The SE relation connects ionic diffusivities ($D_{\pm}$) with the viscosity ($\eta$):

$$D_{\pm} = k_B T/4\pi\eta r_{\pm}, \tag{2}$$

where $r_+$ and $r_-$ are the cationic and anionic radii, respectively, and the factor of 4 originates from the use of "slip" boundary conditions [26]. Validity of the Stokes-Einstein relation for $BeF_2$ melt is demonstrated by the fitting of all the diffusivity data by the equations $D_+ = 0.78D_-$ and $\ln D_+ = 0.95\ln(T/\eta) - \ln(4\pi r_+)$. There are small variations in the hydrodynamic radius with density and temperature which reflect the overall network dynamics [30].

The Nernst-Einstein equation relates the ionic diffusivities ($D_{\pm}$) to the ionic conductivity ($\sigma$):

$$\sigma = (e^2\rho/k_B T)(x_+ z_+^2 D_+ + x_- z_-^2 D_-)(1-\Delta), \tag{3}$$

where $e$ is the electronic charge, $x_{\pm}$ and $z_{\pm}$ are the ionic mole fractions and charges, respectively, and $\Delta$ is the Nernst-Einstein deviation factor [26]. The ionic conductivity should mirror the behavior of $1/\eta$ if $\Delta \approx 0$. The $\sigma(\rho)$ isotherms in Fig. 1(b), however, show a dramatic deviation from Nernst-Einstein predictions with a monotonic rise in $\sigma$ over the entire range of density studied. The Nernst-Einstein deviation parameter is $\approx 0.5$ in the normal regime, comparable with that of alkali halides [26]. In the structurally anomalous regime, however, $\Delta$ decreases sharply with a decrease in density. We identify the conductivity anomaly as the increasing negative value of the NE deviation parameter with decreasing density suggesting that in the diffusionally anomalous regime, collective effects enhance conductivity relative to the NE value. The parameter $\Delta$ does not show a simple correlation with static tetrahedral order due to the $BeF_4^{2-}$ moiety or to the hydrodynamic radius.

We now consider the excess entropy scaling of the diffusivities. Validity of the Stokes-Einstein relation implies that viscosity scaling can be predicted from diffusivities. Dzugutov scaling of diffusivities in silica melt with $\exp(\alpha S_2)$ was demonstrated earlier [8]. Figure 2(a) shows the Rosenfeld-scaled diffusivity $D_+^*$ as a function of $S_e$ for $SiO_2$ and $BeF_2$. Both melts show similar behavior though the curves do not overlap. A linear relationship between $\ln D_+^*$ and $S_e$ is observed for both ionic melts with a very similar value of the slope (1.42 for $BeF_2$ and 1.31 for $SiO_2$) at moderate and high temperatures. A distinct change in $\alpha$ is observed for the lowest temperature isotherms, especially at low densities.

To highlight the generic similarities between $AB_2$ melts with waterlike anomalies, we scale the entropy contributions ($S_e$, $S_2$, $\Delta S$, and $S_{AB}$) in terms of the magnitudes of the corresponding quantities at $(T_m, \rho_m)$, which is the state point

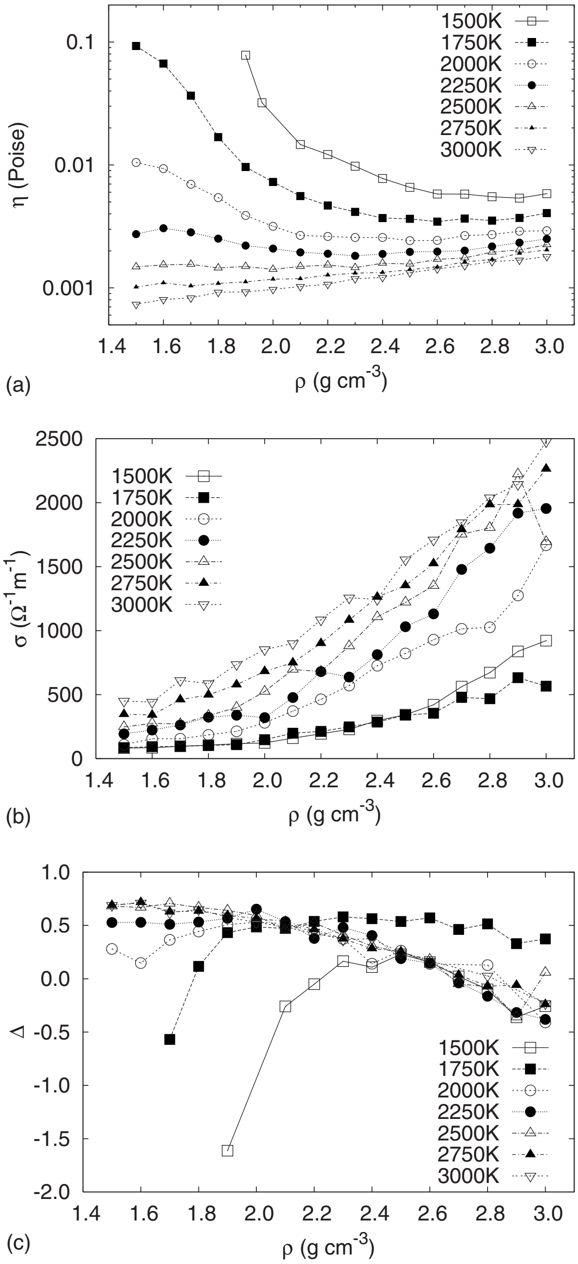

FIG. 1. Variation with density ($\rho$) of (a) shear viscosity $\eta$, (b) ionic conductivity $\sigma$, and (c) Nernst-Einstein deviation parameter ($\Delta$).

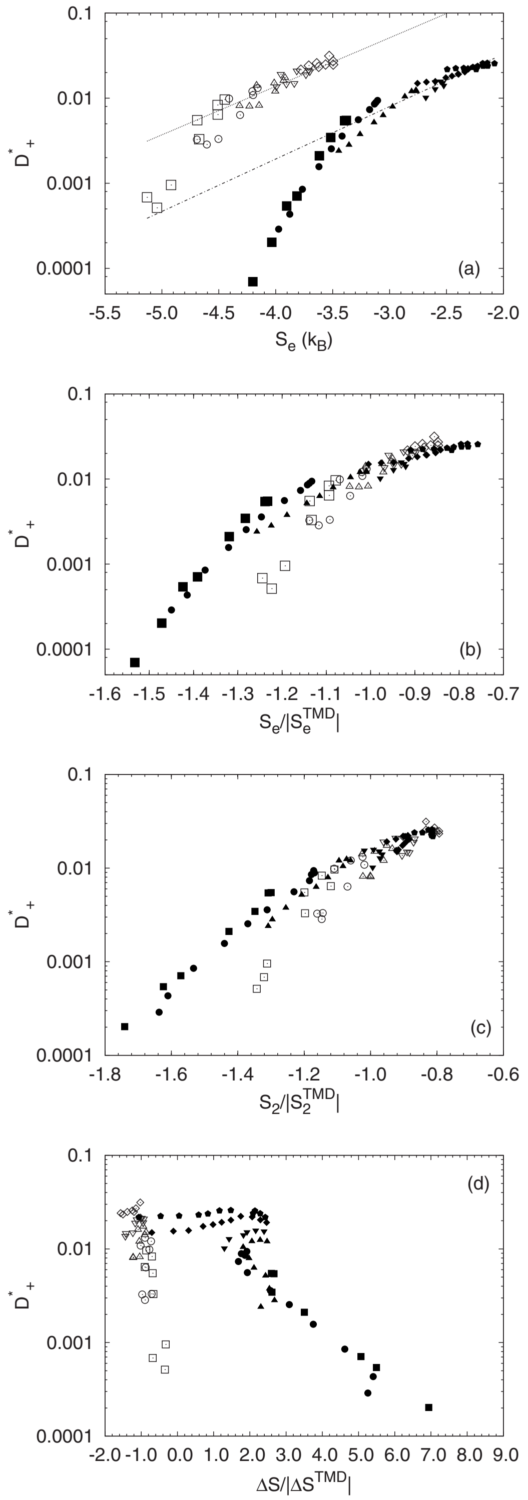

FIG. 2. Correlation of reduced diffusivities ($D_+^*$) in $BeF_2$ and $SiO_2$ melts with (a) $S_e$, (b) $S_e/S_e^{TMD}$, (c) $S_2/S_2^{TMD}$, and (d) $\Delta S/\Delta S^{TMD}$. $D_+^*=D_+\rho^{1/3}/(k_BT/m_+)^{1/2}$ where $m_+$ is the cation mass. Data for $SiO_2$ and $BeF_2$ are shown by open and closed symbols, respectively.

corresponding to the maximum temperature along the TMD locus. Figure 2(b) shows the correlation between the Rosenfeld-scaled diffusivity, $D_+^*$ and $S_e/|S_e^{TMD}|$ for $SiO_2$ and $BeF_2$. The two sets of state points now overlap completely, except for the lowest temperature isotherms. Thus an appropriate choice of scaling makes the equivalent behavior of the two ionic melts evident. Figure 2(c) shows the scaling of diffusivity with the pair correlation $S_2/|S_2^{TMD}|$; the $BeF_2$ and $SiO_2$ state points overlap except at the lowest temperatures, as in Fig. 2(b). The similar scaling of $D_+^*$ with scaled $S_e$ and $S_2$ must be because $S_2$ is the dominant contribution to $S_e$. Differences in the behavior of the two ionic melts emerge only at low temperatures, suggesting sensitivity to the detailed behavior of the interaction potential. Figure 2(d) plots $D_+^*$ vs $\Delta S/|\Delta S^{TMD}|$. The variation of diffusivity with the RMPE is very different for the two ionic melts. In the case of silica, $D^*$ is essentially independent of $\Delta S$ which is consistent with the low magnitude and variation of the RMPE. In the case of $BeF_2$, $D_+^*$ is relatively insensitive to variations in $\Delta S$ in the normal regime while in the anomalous regime, it shows a strong negative correlation. These results, along with previous studies, suggest that local tetrahedrality constraints are weaker in $SiO_2$ than $BeF_2$ [19,24,25]. Our overall conclusion is that the pair correlation contribution $S_2$ will dominate the diffusivity or viscosity scaling behavior when the diffusional mechanism is dominated by collisions and cage relaxations, as in simple liquids. At low temperatures or in strongly anisotropic systems, the diffusional mechanism is likely to require specific changes in local geometry. Excess entropy scaling will then show significant changes as the RMPE contribution will become important.

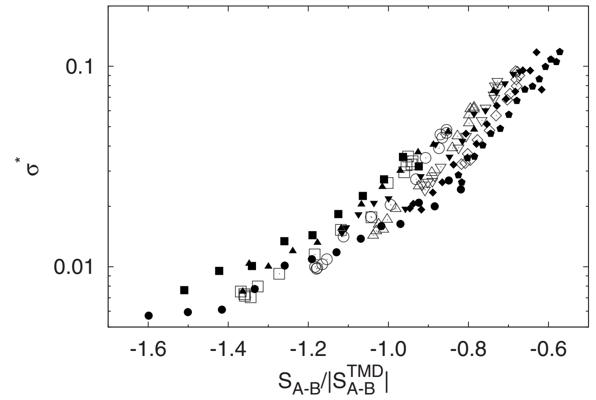

FIG. 3. Variation of reduced ionic conductivity [$\sigma^*=\sigma\rho^{-2/3}(k_BTm)^{1/2}e^{-2}$] with $S_{AB}$, where $m=x_Am_A+x_Bm_B$ and $x_i$ and $m_i$ are mole fractions and masses of ions of type $i$. The key is given in Fig. 2.

The dramatic breakdown of the Nernst-Einstein relation implies that the ionic conductivity cannot obey the entropy scaling relationships that hold for the diffusivity. We examined the correlation of the reduced conductivity, $\sigma^*=\sigma\rho^{-2/3}(k_BTm)^{1/2}e^{-2}$, with the different pair contributions to the entropy. Figure 3 shows the strong positive linear correlation of $\ln\sigma^*$ with the cation-anion contribution to the pair correlation entropy, $S_{AB}/|S_{AB}^{TMD}|$. In contrast, the dependence of $\ln\sigma^*$ on $S_{Be-Be}$ and on $S_{F-F}$ is highly nonmonotonic and is not shown here. This exponential scaling of the ionic conductivity with the cation-anion contribution to the excess entropy is unexpected since the Nernst-Einstein relation would predict a linear scaling with total pair correlation entropy.

To summarize, we use molecular dynamics simulations to study diffusivity, viscosity, and ionic conductivity of two network-forming ionic melts, $BeF_2$ and $SiO_2$. While the Stokes-Einstein relation is valid for both systems, there is a striking breakdown of the Nernst-Einstein relation within the structurally anomalous region. Except at the lowest temperatures, diffusivity as well as viscosity for both the ionic melts show similar Rosenfeld-scaling with both the excess entropy ($S_e$), as well as the dominant pair correlation contribution ($S_2$). The generic similarities in transport properties of these $AB_2$ ionic melts with waterlike anomalies are illustrated. The diffusivity is essentially unaffected by the residual multiparticle contribution to the entropy (RMPE), except at very low temperatures when the diffusional mechanism is strongly dependent on network connectivity and geometry. In contrast to the diffusivity and viscosity, the conductivity shows exponential scaling with only the cation-anion contribution to the pair correlation entropy, e.g., $\ln \sigma^* \propto S_{AB}$.

This study shows that different transport properties, such as conductivity and viscosity, may be sensitive to different types of structural correlations. The associated entropic contributions provide a convenient means of devising semiquantitative relationships between structure and transport properties. The contrasting scaling behavior of the diffusivity and entropy provides an unexpected extension of entropy scaling ideas for transport properties of liquids and further exploration should lead to interesting insights into the microscopic basis for excess entropy scaling behavior. While the present study looks at tetrahedral network-forming ionic melts with waterlike anomalies, this approach should prove useful for for many ionic melts. In particular, the entropy scaling of the ionic conductivity should be examined to understand the anomalous conductivity of lithium cations in lithium fluoroberyllates and $AB_2$ systems where variations in anion polarizability induce a transition from three-dimensional network connectivity to linear chains [31,32]. Possible extensions to mesoscopic fluids with mobile charge carriers or strong anisotropy, such as charged or patchy colloids, would also be of interest [33].

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