Ionic melts with waterlike anomalies: Thermodynamic properties of liquid BeF_2

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Thermodynamic properties of liquid beryllium difluoride (BeF_2) are studied using canonical ensemble molecular dynamics simulations of the transferable rigid ion model potential. The negative slope of the locus of points of maximum density in the temperature-pressure plane is mapped out. The excess entropy, computed within the pair correlation approximation, is found to show an anomalous increase with isothermal compression at low temperatures which will lead to diffusional as well as structural anomalies resembling those in water. The anomalous behavior of the entropy is largely connected with the behavior of the Be–F pair correlation function. The internal energy shows a $T^{3/5}$ temperature dependence. The pair correlation entropy shows a $T^{-2/5}$ temperature dependence only at high densities and temperatures. The correlation plots between internal energy and the pair correlation entropy for isothermal compression show the characteristic features expected of network-forming liquids with waterlike anomalies. The tagged particle potential energy distributions are shown to have a multimodal form at low temperatures and densities similar to those seen in other liquids with three-dimensional tetrahedral networks, such as water and silica. © 2007 *American Institute of Physics*. [DOI: 10.1063/1.2794766]

I. INTRODUCTION

Many network-forming liquids are characterized by strongly anisotropic short-range interactions which impose a preference for local tetrahedral symmetry, distinct from the random close-packing arrangements seen in simple liquids.[1] Examples of such systems include water, silicon, germanium, bismuth, and a number of ionic melts, such as SiO_2,[2-10] BeF_2,[11-17] $ZnCl_2$,[18] and GeO_2.[19-21] The presence of a random, three-dimensional, tetrahedral liquid-state network is associated in a number of these systems with waterlike thermodynamic and kinetic anomalies.[22-25] The most obvious signature of the thermodynamic anomalies is the existence of a region of anomalous density behavior where the thermal expansion coefficient $\alpha = (1/V_m)(\partial V_m/\partial T)_P$ is negative, implying that the molar volume V_m decreases with increasing temperature T along an isobar at pressure P. This region of anomalous density must be bounded by temperatures of maximum and minimum densities for which $\alpha=0$. While the temperature of maximum density (TMD) is well known experimentally for many systems (4 °C for H_2O), the temperature of minimum density has been observed only in simulations. The other thermodynamic waterlike anomalies are related to the behavior of the compressibility (κ_T) and the constant pressure heat capacity (C_P), both of which increase with decreasing temperature along an isobar in anomalous fluids. On thermodynamic grounds, it can be shown that a negatively sloped locus of TMD points on the TP plane should lead to such anomalous behavior of the compressibility.[26,27] Given that only C_P, and not the constant volume heat capacity (C_V), shows the anomalous behavior, one can surmise that the heat capacity anomaly must be connected to anomalies in α and κ_T. Thus, the presence of the density anomaly signals the presence of a set of connected thermodynamic anomalies. The waterlike kinetic anomalies are associated with an increase in various measures of molecular mobility with increasing density. For example, the diffusional anomaly corresponds to a regime in which the diffusivity increases as a function of density, in contrast to simple liquids where diffusivity decreases with density due to increasing steric hindrance. Qualitatively, this anomalous behavior of the mobility can be understood in terms of the disruption of the tetrahedral network by increasing pressure or density which facilitates translational motion. There is also increasing evidence that tetrahedral liquids can show polyamorphism, i.e., the existence of low- and high-density distinct liquid or glassy phases.[28-30]

A quantitative connection between the structure of the tetrahedral network and the thermodynamic and diffusional anomalies can be made by introducing two order metrics: (i) a local tetrahedral order parameter q_{tet} and (ii) a translational or pair correlation order parameter τ.[5,27] At a given temperature, q_{tet} will show a maximum and τ will show a minimum as a function of density; the loci of these extrema in order define a structurally anomalous region in the density-temperature (ρT) plane within which q_{tet} and τ are strongly correlated. The region of the density anomaly, where $(\partial\rho/\partial T)_P > 0$, is bounded by the structurally anomalous region. The diffusionally anomalous region ($(\partial D/\partial\rho)_T > 0$) closely follows the boundaries of the structurally anomalous region, specially at low temperatures. The connection between these structural, diffusional, and density anomalies can be understood in terms of the behavior of the excess entropy.

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