

RESEARCH ARTICLE

Estimating the entropy of liquids from atom–atom radial distribution functions: silica, beryllium fluoride and water

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Molecular dynamics simulations of water, liquid beryllium fluoride and silica melt are used to study the accuracy with which the entropy of ionic and molecular liquids can be estimated from atom–atom radial distribution function data. The pair correlation entropy is demonstrated to be sufficiently accurate that the density–temperature regime of anomalous behaviour as well as the strength of the entropy anomaly can be predicted reliably for both ionic melts as well as different rigid-body pair potentials for water. Errors in the total thermodynamic entropy for water melt due to the pair correlation approximation are of the order of 10% or less for most state points, but can be significantly larger in the anomalous regime at very low temperatures. In the case of water, the rigid-body potentials result in larger errors in the pair correlation approximation, between 30 and 50%, for most state points. Comparison of the excess entropy, S_e of ionic melts with the pair correlation entropy, S_p , shows that the temperature dependence of S_e is well described by $T^{-1/2}$ scaling across both the normal and anomalous regimes, unlike in the case of S_p . The residual multiparticle entropy, $\Delta S = S_e - S_p$, shows a strong negative correlation with tetrahedral order in the anomalous regime.

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1. Introduction

The thermodynamic excess entropy of a fluid is defined as the difference in entropy between the fluid and the corresponding ideal gas under identical temperature and density conditions. In the case of a classical fluid, the excess entropy corresponds to the lowering of the entropy of the fluid, relative to the ideal gas, due to the presence of multiparticle positional correlations [1]. The total entropy of a classical fluid can be written as [2–10]

$$S = S_{\text{IG}} + S_1 + S_2 + \dots = S_{\text{IG}} + \sum_{n=2}^{\infty} S_n \quad (1)$$

where S_{IG} is the entropy of the ideal gas reference state, S_n is the entropy contribution due to n -particle spatial correlations and the excess entropy is defined as, $S_e = S - S_{\text{IG}}$. Such a multiparticle expansion of the entropy is interesting because it allows for the prediction of thermodynamic properties from structural correlation functions. Moreover, semi-quantitative excess-entropy-based scaling relationships of the form

$$\lambda = A \exp(-\alpha S_e) \quad (2)$$

where λ is a suitably scaled transport property [11–15], allow for the possibility of making interesting

connections between structural, thermodynamic and transport properties of fluids.

Neutron or X-ray scattering experiments can provide atom–atom radial distribution functions (PDFs), $\rho_{\alpha\beta}(r)$, associated with the probability of finding an atom of species β at a distance r from an atom of species α relative to the probability in the corresponding ideal gas [1]. In terms of the atom–atom radial distribution function, one can write an ensemble-invariant expression for the pair correlation contribution to the entropy of a multiscomponent fluid of N particles enclosed in a volume V at temperature T as [16,17]

$$S_p/Nk_B = -2\pi \sum_{\alpha\beta} x_{\alpha} x_{\beta} \int_0^{\infty} [\rho_{\alpha\beta}(r) \ln \rho_{\alpha\beta}(r) - \{\rho_{\alpha\beta}(r) - 1\} r^2 dr] \quad (3)$$

where x_{α} is the mole fraction of component α in the mixture and ρ is the number density of the fluid. Note that the excess entropy is measured in this case with respect to the entropy of an ideal gas consisting of a non-interacting mixture of spherical particles with entropy S_{IG} given by

$$S_{\text{IG}}/Nk_B = 1 + \sum_{\alpha} x_{\alpha} [\ln x_{\alpha} + \ln \rho_{\alpha} \Lambda_{\alpha}^3] \quad (4)$$

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