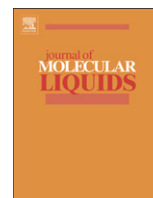




ELSEVIER

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Thermodynamic regimes over which homologous alkane fluids can be treated as simple liquids

Gourav Shrivastav, Manish Agarwal¹, Charusita Chakravarty², Hemant K. Kashyap*

Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, Delhi, India

ARTICLE INFO

Article history:

Received 19 November 2016
 Received in revised form 8 January 2017
 Accepted 24 January 2017
 Available online 27 January 2017

Keywords:

Simulation
 Alkanes
 Rosenfeld scaling
 Simple liquid

ABSTRACT

We compare the extent to which the properties of simple liquids are pertinent to short to moderate chain *n*-alkanes ranging from ethane (C₂) to dodecane (C₁₂). Explicit geometric features such as bonds, angles and dihedral potentials in currently available models of *n*-alkanes make these systems more realistic, and distinct from the generalized Lennard-Jones chain fluids. Our study confirms that the presence of these flexible geometric constraints completely suppresses the energy–virial correlation in these systems. However, they are found to have a strong energy–virial correlation in high density region of their phase diagram when the contribution from these geometric constraints are excluded. For fluids having simple liquid like behavior, semi-quantitative relationships between structure, dynamics, and thermodynamics are well established. Range of state points is explored to test the applicability of such relationships for *n*-alkanes. Considering the collection of monomer beads as the reference state, thermodynamic and structural entropic measures are systematically compared with and without intramolecular contributions. We show that the pair entropy computed with explicit intramolecular geometric constraints correlates well with thermodynamic excess entropy. Both the thermodynamic and pair entropy have strong isochore dependence with reduced diffusivity. Intermolecular pair entropy correlates well with reduced diffusivity. The role of multiparticle correlations is highlighted for predicting thermodynamic and transport properties in these chain systems. Triplet correlations in addition to pair correlations are used as an attempt to improve the structural contribution to excess entropy. We show that if the three particle contribution is included in the computation of structural entropy, the resulting value overestimates the excess entropy.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Simple liquids exhibit isotropic interparticle interactions involving strong short-range repulsions and weak long-range attractions. The liquid structure is characterized by a single length scale associated with the particle size, implying that the phase diagram of such systems is a function of a single thermodynamic variable, the reduced number density $((\rho^*)^{1/3})$ [1–3]. The ρ^* is defined here as $N\sigma^3/V$, where N , V , and σ denote the number of atoms, volume, and the finite distance at which inter-particle potential is zero, respectively. Approximate mapping to the hard-sphere model explains many characteristic behaviors of simple liquids, such as the rise in molar volume and thermodynamic response functions on heating, crystallization to close-packed structures, and a positive molar volume of fusion.

Obvious limitations of the hard-sphere model stem from the fact that for all liquids, reduced temperature (T^*) is a relevant thermodynamic variable and that atoms are best represented as spheres of variable softness. Recent work by Dyre and co-workers [4] overcomes these limitations by redefining simple liquids as “strongly correlating” or “Roskilde-simple” liquids, where equilibrium fluctuations in potential energy (U) and the virial (W) are strongly correlated, with a correlation coefficient R of about 90% or better, resulting in a number of useful insights. The phase diagram of the fluid is still a function of a single variable defined as $(\rho^*)^{\gamma_{UW}}/T^*$, where density scaling exponent, γ_{UW} depends on the interparticle interactions and may depend on the state-point. Isomorphs in the phase diagrams correspond to curves along which static and dynamic correlations are constant. The single variable phase diagram provides an explanation of two important relationships between thermodynamic and transport properties observed in simple liquids. Firstly, thermodynamic scaling corresponding to extensive data that relaxation times are a unique functions of $(\rho^*)^{\gamma_{UW}}/T^*$. Secondly, the transport properties from a range of state points collapse onto unique curve as a function of the excess entropy, defined as the difference in entropy

* Corresponding author.

E-mail address: hkashyap@chemistry.iitd.ac.in (H.K. Kashyap).¹ Present address: Computer Services Centre, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, Delhi, India.² Deceased.

between the liquid and the monatomic ideal gas at the same reduced number density and temperature.

The theory of simple liquids was initially formulated for monatomic fluids. A large body of simulation and experimental studies, [5–11] however, indicate that thermodynamic and excess entropy scaling applies to a fair degree for a very large number of molecular and complex fluids, indicating that further generalization of concepts of strongly correlating liquids to such systems would be useful. The relationships between structure, thermodynamics and transport properties of simple liquids summarized above can then be effectively used to design liquid state properties, solvation and self-assembly behavior in a number of systems. In a monatomic fluid strong bond constraints, typical of molecular fluids, do not exist. Consequently, all interatomic distances ($(\rho^*)^{-1/3}$) scale with density. In contrast to the weak, isotropic intermolecular interactions, intramolecular bonds are strongly directional. They exhibit high-frequency vibrational modes associated with very small displacements; as a result, they do not scale with density. So, the tests for simple liquid behavior, alternative means of evaluating excess entropy and the corresponding scaling relationships for transport properties, need to be examined carefully. In this context, it is worth considering the range of systems for which the supporting data of thermodynamic and excess entropy scaling of transport properties is available. Thermodynamic scaling, corresponding to proportionality of relaxation times τ to $(\rho^*)^{\gamma_{UV}}/T^*$, is supported extensively by experimental data on hydrocarbons, sorbitols, room-temperature ionic liquids, and polymers. Many of these materials have a significant contribution from hydrogen-bonding or electrostatic interactions to the cohesive energy. The material specific exponent suggests that these are Roskilde-simple liquids. Simulations including tangential Lennard-Jones (LJ) chains with flexible [10,11] and rigid bond [12,13] stretches, octane [8,9], and glass-forming liquids are also reported [5–7,14,15]. The scaling of transport properties with the excess entropy was originally suggested by Rosenfeld for simple liquids in the thermodynamically stable regime with the functional form $X^* = A \exp(\alpha S_e)$. Here X^* may be any reduced transport property and S_e is the excess entropy of the fluid relative to the ideal gas at the same temperature and density [16–19]. The scaling parameters A and α , both depend on the nature of the interactions as well as the transport property. As cooperative effects emerge, e.g. because of supercooling or network formation, deviations from the simple exponential behavior are observed. Both experiments and simulations show approximate Rosenfeld-type excess entropy scaling in van der Waals liquids [9,20], polymers, non-associated liquids, liquid metals [19,21–23], molecular fluids [24–28], Lennard-Jones chain fluids [11–13,29], ionic liquids [30], confined fluids [31–33], colloidal dispersions [34,35] and liquid crystals, [36] even though the exact scaling parameters may vary considerably. It is important to note that the studies on water-like anomalous liquids [37,38] such as model core-softened fluids [39–41] suggest a weak degree of the collapse of transport properties like diffusivity and viscosity, and show significant deviation from Rosenfeld scaling along isotherm.

Our motivation for the current work is to study the extent and thermodynamic regimes of conformity of short to moderate chain alkane fluids ($\leq C_{12}$) to Roskilde-type simple liquid behavior. Alkanes are canonical examples of homologous chain fluids, widely used as fuel blends as well as solvents. Recent synthetic and simulation studies show that our understanding of structure and dynamics of liquids can be used to design synthetic strategies that exploit solvation forces to create temperature-independent solvation environments for nanoscale self-assembly [42,43]. In the context of mapping onto the behavior of Roskilde-simple liquids, they also illustrate a number of conceptual issues that arise when molecular fluids, particularly homologous chain fluids are considered, in contrast to monatomic fluids. While computational details are addressed in detail in Section 2, here we give a brief overview of the conceptual issues underlying the key methods used in the present article.

As discussed above, the key difference lies in the large time and length scale separation between intra- and intermolecular motion. The first problem is therefore to design a stable, efficient sampling algorithm for molecular dynamics simulations, which necessitates decoupling of intra- and inter-molecular modes of motion. One standard decoupling technique is to treat intramolecular bonds as rigid constraints which results in removal of the associated degrees of freedom from the phase space. An alternative approach is to use suitably realistic parameterised functional forms for the intramolecular bonds which retains those degrees of freedom in the phase space. The closest model to alkanes studied so far have been tangential Lennard-Jones chain fluids with rigid and flexible bond stretches for which the consequences of the two decoupling strategies have been recently compared [10]. If the rigid bond approach is used and the configurational energy-virial fluctuation correlations are computed on the basis of the isotropic, repulsion-dispersion interactions, then isomorphs in the phase diagram can be traced along which the structural properties, excess entropy, and transport properties are constant [12,29]. If, however, the second strategy is used then the positions do not scale automatically with density, and the phase diagram has no true isomorphs [10]. Instead, they have pseudoisomorphs in their phase diagram along which only transport properties and intermolecular structure remains invariant, but not the excess entropy. In comparison to Lennard-Jones chains, alkanes have additional intramolecular modes, including bond angles and torsional modes which impose additional constraints in the phase space. Even so, by computing the configurational energy-virial correlation using only non-bonded contribution for intra- and intermolecular interactions, we show that over a substantial range of temperature and density, alkanes exhibit strong correlations, Roskilde-simple fluids composed of packing of monomeric methyl/methylene pseudoatomic units.

We then consider the computation of the total entropy (S) of the alkane liquids, which is a well-defined thermodynamic quantity. In simulations, for a given potential model, it may be estimated by thermodynamic integration with respect to a given reference state. For single or multiple component atomic fluids, the obvious reference state is the corresponding ideal gas. In the case of molecular liquids, the corresponding ideal gas of non-interacting molecules can be used. In the case of alkanes, we estimate the total entropy S following the method outlined by Polson and Frenkel [44]. The definition of excess entropy, however, requires the definition of an ideal reference state, where physical intuition can be used to provide some useful structural insight. The entropy of the ideal chain fluid as used in estimating S (see Section 2.4) is logically correct but provides no additional physical insight. Instead, the mapping to a strongly correlating, Roskilde-simple fluids composed of packing of monomeric methyl/methylene pseudoatomic units, suggests that an appropriate reference state is an ideal gas of CH_x monomers. Using multiparticle correlation entropy, one can then estimate the contribution of higher-order correlations, particularly at the pair and triplet level [45–47] to the entropy. The consequences for excess entropy scaling of transport properties are then explored.

The paper is organized as follows. Section 2 contains computational details, including those associated with the estimation of various simulation observable. Section 3 contains the results. Section 4 discusses the conclusions.

2. Computational details

2.1. Potential model for alkanes

We have modeled alkane chains using the united atom approach of TraPPE-UA (Transferable Potentials for Phase Equilibria, united atom) force field [48]. In this approach, carbon and its bonded hydrogens are represented as a single interaction site using a pseudoatom.

Download English Version:

<https://daneshyari.com/en/article/5408696>

Download Persian Version:

<https://daneshyari.com/article/5408696>

[Daneshyari.com](https://daneshyari.com)