Journal of Molecular Liquids 222 (2016) 520–534

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Scaling the transport properties of molecular and ionic liquids☆,☆☆

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ARTICLE INFO

Article history:
Received 24 February 2016
Received in revised form 4 July 2016
Accepted 11 July 2016
Available online 19 July 2016

Keywords:
Liquids
Transport properties
Hard-sphere theory
Stokes-Einstein-Sutherland
Density scaling

ABSTRACT

There are many forms of scaling for the transport properties of liquids and liquid solutions. This review concentrates on the application of models based on (a) hard-sphere molecular dynamics results for dense molecular fluids, (b) Stokes-Einstein-Sutherland (SES) scaling of experimental transport properties with the viscosity for both molecular and ionic liquids, and (c) thermodynamic or density scaling, again for both types. An alternative, but similar, approach to SES scaling for ionic liquids employs so-called "distinct diffusion coefficients" incorporating both conductivity and self-diffusion terms in Walden-type plots. In ionic liquid families, related compounds are found to scale on to common curves in some cases. Recently thermodynamic scaling, using (TV^{γ}) as the scaling function has been introduced. For molecular liquids, γ can be related to the exponent of the repulsive part of the potential, but its meaning is less clear for ionic liquids that consist of large charged ions and have both significant van der Waals and Coulombic interactions. The further development of scaling offers promise for the future in relating the behaviour of ionic liquids to those of other liquid classes.

1. Introduction

The determination of the transport properties of fluids has a long history in science dating back to Newton and Fourier who derived linear response laws for viscosity (1687) [1] and thermal conductivity (1822) [2] respectively. The equivalent for inter-diffusion (diffusion due to composition gradients) is due to Berthollet [3] in a qualitative sense and to Fick [4,5] in a quantitative one. The concept of self-diffusion (molecular Brownian motion or intra-diffusion [6,7]) was first described theoretically by Maxwell for gases (1871) [8] and first determined experimentally in a liquid by Gróh and von Hevesy somewhat later (1920) [9] (molten lead: as the tracer diffusion of a radioactively labelled isotope). The phenomenological relations for such irreversible processes due to Onsager [10–12], who built on earlier work by Nernst [13–15] and others [10], are generalisations of these linear response laws for the whole range of transport properties, including electrical conduction, interacting flows in the isothermal diffusion of multicomponent systems [16], thermal diffusion and other non-isothermal phenomena. A useful, straightforward summary of non-equilibrium thermodynamics and transport processes has been given by Haase [17].

Why measure the transport properties? For a scientist it is route to the understanding of molecular motion, mass, momentum, charge and energy transfer and the molecular interactions that govern these processes. Moreover, industrial chemical processes are not equilibrium processes: things happen and transport as well as kinetic information is required for their proper understanding. Industrial applications involving fluid systems particularly require accurate viscosity data, together with heat capacities and thermal conductivity, if the capital cost of plant and running costs are to be optimized and the most economic choice of materials to be made [18]. Chemical reactors employing porous catalysts and separation processes may require knowledge of diffusion coefficients, though usually rationalisation and simplification is necessary due to the complexity of describing multicomponent systems [19,20]. In the words of Wakeham and Assael [21], "the thermodynamic properties of a fluid often determine the feasibility of what is proposed, whereas the transport properties essentially determine how large the equipment or process unit must be or the time scale of the operation. This essential difference is responsible for the fact that the transport properties have, traditionally, been less emphasized in process design activities. However, as the needs for process integration and energy minimization grow, there is a tendency to examine more carefully the effects of the transport properties on the process design."

Applications for ionic liquids that involve the exploitation of ionic charge rather than just their properties as solvents [22] (e.g. batteries, [23,24] fuel cells, energy storage, [25] electroplating and electro-winning of metals [26]) usually require electrical conductivities and, in principle, transport numbers, though the latter are particularly difficult to determine accurately [17,27,28].

In this invited lecture, three systems in current use for the scaling of the transport properties of molecular and ionic liquids, either with one another, or with temperature and density, are reviewed. This is a somewhat personal account as I have used all three at one time or another, but such is the nature of this lecture.

☆ Invited lecture, Joint EMLG/JMLG Meeting, *Molecular Liquids Meet Ionic Liquids*, Universität Rostock, Rostock, Germany, 6–10 Sept 2015

☆☆ Dedicated to the late Pierre Turq, 1944–2015.

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http://dx.doi.org/10.1016/j.molliq.2016.07.029
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Scaling analyses require high pressure experimental measurements that allow the separation of the effect of temperature from that of density. There are other scaling systems in the literature than the three discussed here. Some with a long provenance, such as the use of the corresponding states principle [29–32], or the correlation of "excess" properties based on a modified Enskog theory of simple dense fluids [33]. However the scaling systems selected here are currently the more successful for the rationalisation of the transport properties of a broad range of liquids. They illustrate the "quasi-universality" of liquid dynamics [34,35] despite the wide variety of liquid types and the different length scales of molecular and ionic interactions.

2. Theoretical considerations

We first consider how gradients of concentration, temperature, and molecular or ion velocity are relieved in a fluid. According to Enskog [36, 37], kinetic transfer – molecular movement – dominates in dilute gases so inter-diffusion (D_{12}), self-diffusion (D_{si}), viscosity (η), thermal conductivity (λ) all increase with temperature and the density (ρ) – diffusion coefficient products, (ρD_{12}, ρD_{si}), viscosity and thermal conductivity are independent of density to a first approximation. With the development of precise methods in the later decades of the 20th century for the measurement of the transport properties of gases, particularly for inter-diffusion (concentration dependence [38]), thermal diffusion (D_{Th}) [39] and viscosity [40,41], in addition to those for thermodynamic properties such as second virial coefficients for mixtures [42,43], and molecular beam and high-resolution spectroscopic studies [44,45] it has become possible to determine accurate intermolecular pair potentials for atomic and polyatomic gases and their combinations [46–48].

The Enskog theory of dense fluids neglects velocity correlations (discussed below) but retains spatial correlations arising from volume exclusion effects. This theory can be extended to take ternary and higher order collisions into account as density is increased, e.g. the theory of Rainwater and Friend and its variants [49,50], and the Modified Enskog Theory (MET) [33]. Such collisional transfer – energy and momentum exchanged in collisions between molecules due to the finite size of molecules – dominates in liquids. Consequently, the viscosity decreases and the thermal conductivity may decrease [51] with increasing temperature and both increase with increasing density. Diffusion slows non-linearly with increasing density.

The perfect gas and simple Enskog hard sphere models where collisions are binary, instantaneous and uncorrelated only consider elastic collisions. In real fluids, collisions are inelastic as the intermolecular potential varies with distance and momentum and energy can be exchanged between nearby molecules without a direct contact "collision". In the case of polyatomic molecules there can also be transfer of energy between rotational and vibrational states which contributes particularly to the thermal conductivity and between translational and rotational modes, effecting both diffusion and the viscosity [52,53].

The transport properties are governed by intermolecular collisions. Linear response theory [54] expresses transport properties in terms of time integrals of appropriate correlation functions. The simplest, a velocity auto-correlation function, gives the self-diffusion coefficient (D_{S}) of component or species *i* in terms of the randomization of the velocity of a given molecule (α) over time by collisions, averaged over the ensemble:

$$D_{si} = \frac{1}{3}\int_0^\infty \langle v_{i\alpha}(t) \cdot v_{i\alpha}(0)\rangle \mathrm{d}t. \tag{1}$$

For ionic melts, the electrical conductivity, κ, is similarly expressed in terms of a velocity *cross*-correlation function [55]:

$$\kappa = \frac{z_+ z_- (FcM)^2}{M_+ M_- RT}\frac{N_A V}{3}\int_0^\infty \langle v_{+\alpha}(0) v_{-\beta}(t)\rangle \mathrm{d}t \tag{2}$$

where the correlation is between the velocities of different (α and β) ions of opposite charge.

In the dense gas state and in liquids, collisions are highly correlated as shown in Fig. 1 [56] and the Enskog assumption of molecular chaos fails. Of particular interest are the vortex collisions shown in Fig. 1(e) and (f). These ring collisions allow correlations of momentum and energy over distances (times) large compared to the mean free path (time) in the fluid and result in a positive contribution to the self-diffusion coefficient relative to that predicted by simple Enskog theory at moderate densities. In other words there is a coupling of purely diffusive and viscous (momentum transfer) modes [56]. Caging, on the other hand, as in Fig. 1(d), dominates at higher densities, leading to a negative contribution, with D_{S} much slower than the Enskog prediction.

3. Behaviour of molecular liquids

The pressure dependence of the self-diffusion coefficient of liquid methane [57] is shown in Fig. 2. This is close to exponential and typical of liquids with small molecules.

$$D_{\mathrm{S}} = A\exp(a(T) + b(T)p + c(T)p^2 \ldots) \tag{3}$$

The viscosity shows the inverse behaviour, increasing with increasing pressure. Larger, more asymmetric molecules, with higher freezing pressures may require higher order polynomial terms within the argument of the exponential factor. For such substances at very high

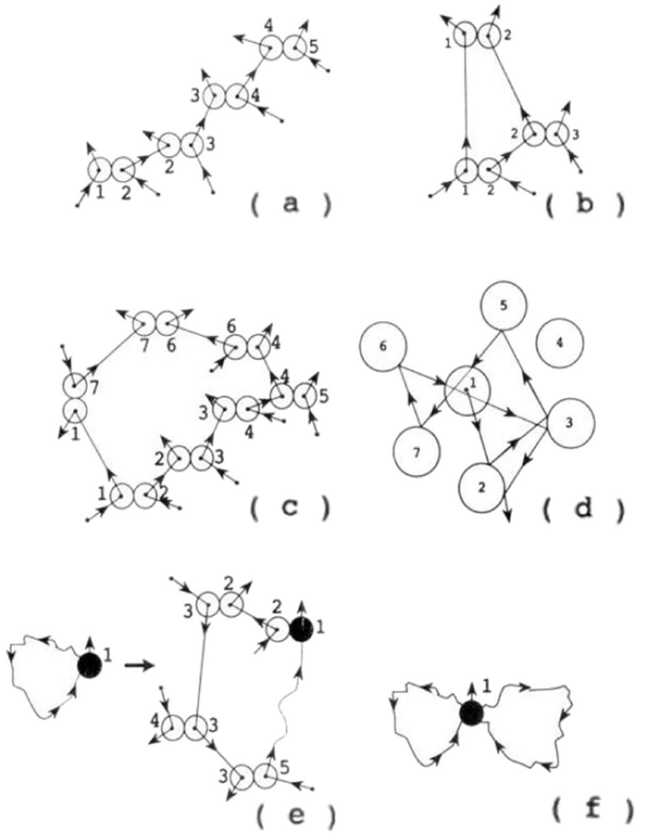

Fig. 1. Types of correlated molecular collisions, from ref. [56]. "Sequences of binary collisions starting with a (12) collision: (a) uncorrelated; (b) correlated (recollision: simplest ring collision); (c) correlated (ring collision: 7 and 6 trace back to 1 and 2, respectively); (d) cage-diffusion collisions of central particle 1 (motion of wall particles 2 to 7 not shown; distances between spheres have been enlarged for clarity); (e) part of ring collision sequence contributing to vortex-diffusion; (f) example of two ring collision sequences contributing to vortex diffusion."
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