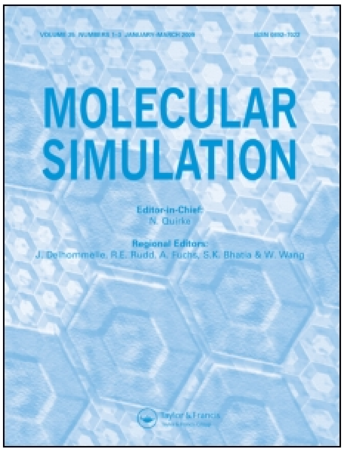

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

# Molecular simulation of the thermophysical properties of fluids: phase behaviour and transport properties

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**To cite this Article** Sadus, R. J.(2006) 'Molecular simulation of the thermophysical properties of fluids: phase behaviour and transport properties', Molecular Simulation, 32: 3, 185 — 189

**To link to this Article: DOI:** 10.1080/08927020600592977

**URL:** http://dx.doi.org/10.1080/08927020600592977

*Molecular Simulation*, Vol. 32, Nos. 3–4, 15 March–April 2006, 185–189

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# Molecular simulation of the thermophysical properties of fluids: phase behaviour and transport properties

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*(Received November 2005; in final form January 2006)*

Historically, reliable data for the thermophysical properties of fluids could only be obtained from accurate experimental measurement. The input from theory was, at best, limited to a supporting role by providing correlations. The large number of assumptions and approximations involved in theoretical tools such as equations of state meant that it was unrealistic to expect genuinely reliable predictions. More recently, the advent of powerful molecular simulation techniques has greatly enhanced the usefulness of thermophysical calculations, particularly in chemical engineering. Unlike conventional calculations, molecular simulation determines the properties of a fluid directly by evolving molecular coordinates in accordance with a rigorous calculation of intermolecular energies or forces. In this work, the application of molecular simulation to the prediction of the thermophysical properties of fluids relevant to chemical engineering applications is examined. In particular, the role of three-body interactions on the vapour-liquid coexistence of fluids is illustrated and compared with experimental data. Molecular simulation is also used to compare the viscosities of dendrimer fluids with linear polymers of equivalent molecular weight.

*Keywords*: Molecular simulation; Dendrimer; Viscosity; Phase behaviour

## 1. Introduction

Until recently, progress in understanding the thermophysical properties of fluids has been overwhelmingly dominated by experimental observations or measurements. In general, theory and calculations have played a supporting role by helping to rationalize experimental phenomena or guiding experimental work via predictions. Except for relatively simple cases, traditional theoretical approaches are often severely disadvantaged by too many simplifying assumptions resulting in considerable inaccuracy. A good example of the inaccuracy of theory is the large number of equations of state [1] that often need to be individually adjusted to give optimal agreement for even a relatively narrow range of substances and conditions.

In contrast, molecular simulation [2] provides a theoretical tool, which is free from most of these traditional limitations. The results of a molecular simulation are essentially exact with very few assumptions. Therefore, molecular simulation can be potentially used to improve our understanding of the thermophysical properties of fluids. For example, until recently three-body interactions were thought to have a minor role on vapour-liquid equilibria whereas molecular simulation indicates [3] that the effect is quite profound. The shear viscosity of fluids as a function of strain rate was previously believed to conform to a widely used relationship from mode-coupling theory. However, this belief is not supported by recent non-equilibrium molecular simulation results [4]. Increasingly, molecular simulation is being applied to bioactive molecules such as adenosine triphosphate (ATP) and used to model molecular motors [5].

## 2. Results and discussion

### 2.1 Role of three-body interaction on phase equilibria

The main assumptions in a molecular simulation [2] are the choice of intermolecular potential and how many atoms or molecules are involved in each interaction. The heart of a molecular simulation is the evaluation of intermolecular energy (MC simulation) or forces (MD simulation). For example, in the absence of external influences, the potential energy of $N$ interacting particles

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*Molecular Simulation*
ISSN 0892-7022 print/ISSN 1029-0435 online
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020600592977

can be obtained from:

$$E_{\text{pot}} = \sum_i \sum_{j>i} u_2(r_i, r_j) + \sum_i \sum_{j>i} \sum_{k>j>i} u_3(r_i, r_j, r_k) + \ldots, \quad (1)$$

where the summations are performed for all distinct particle interactions, $u_2$ is the potential between pairs of particles, $u_3$ is the potential between particle triplets, etc.

The point of truncation of equation (1) determines the overall order of the algorithm. Including pair, three-body or four-body interactions result in algorithms of $O\mathrm{N}^2$, $O\mathrm{N}^3$ and $O\mathrm{N}^4$, respectively. In a molecular simulation equation (1) is typically truncated after the first term and the two-body potential is replaced by an effective potential:

$$E_{\text{pot}} = \sum_i \sum_{j>i} u_{\text{eff}}(r_i, r_j). \quad (2)$$

Therefore, only pairwise interactions are calculated and the effects of three or more body interactions are crudely incorporated in the effective intermolecular potential such as the widely used Lennard-Jones potential.

The use of effective intermolecular potentials and confining the calculations to pairwise interactions makes molecular simulation computationally feasible for a diverse range of molecules. Effective intermolecular potentials generally yield good results. However, the use of effective intermolecular potentials also means that the effects of three-body interactions remain hidden.

It has recently [4,6,7] become computationally feasible to perform molecular simulations involving three-body interactions. These simulations indicate that three-body interactions significantly affect the observed phase behaviour. This is exemplified by calculations for the noble gases, which involve the Barker–Fisher–Watts (BFW) [8] potential in combination with the [9] three-body potential. The BFW potential has the following functional form:

$$u_2 = \varepsilon \left[ \sum_{i=0}^{5} A_i (x-1)^i \exp\left[\alpha(1-x)\right] - \sum_{j=0}^{2} \frac{C_{2j+6}}{\delta + x^{2j+6}} \right]. \quad (3)$$

In equation (3), $x = r/r_m$ and the other parameters are obtained by fitting the potential to experimental data for molecular beam scattering, second virial coefficients, and long-range interaction coefficients. The contribution from repulsion has an exponential-dependence on intermolecular separation and the contribution to dispersion of the $C_6$, $C_8$ and $C_{10}$ coefficients are included.

The main contribution to three-body dispersion can be obtained from the triple-dipole term determined by [9]:

$$u_3 = \frac{v(1 + 3\cos\theta_i \cos\theta_j \cos\theta_k)}{(r_{ij} r_{ik} r_{jk})^3}, \quad (4)$$

where $v$ is the non-additive coefficient, and the angles and intermolecular separations refer to a triangular configuration of atoms.

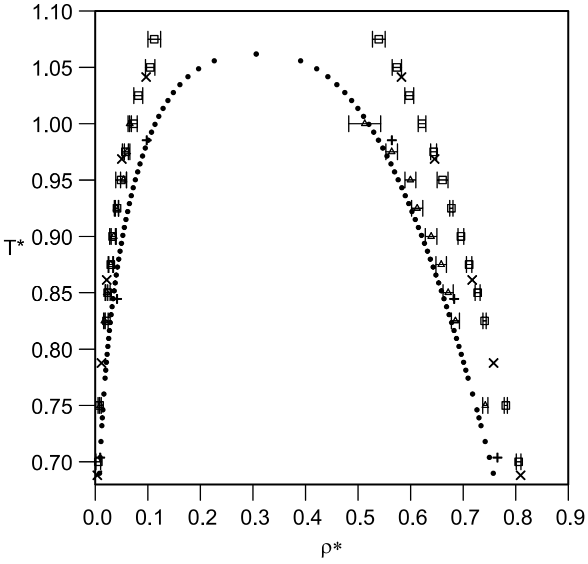

Figure 1. Comparison of experiment (·) ([16]) with Gibbs ensemble simulations ([17]) using the BFW potential (equation (3)) ( ), the Aziz-Slaman potential ( × ) ([6]), the Aziz-Slaman + Axilrod-Teller (+) ([6]) and the BFW + three-body interactions (+) for the vapour-liquid coexistence of argon ([3]). The temperature ($T^* = kT/\epsilon$) and densities ($\rho^* = \rho\sigma^3$) are in reduced units with respect to the characteristic intermolecular potential parameters ($\epsilon$, $\sigma$).

The effect of three-body interaction on vapour-liquid equilibria is shown in figure 1. It is apparent from figure 1, that two-body only interactions over-predict the phase envelope whereas the addition of three-body interactions results in near perfect agreement with experiment, particularly for the liquid phase. It is also apparent that the approach to the critical point is not over-predicted when three-body interactions are included.

### *2.2 Rheological properties of fluids*

An area of growing interest is the properties of fluids under some sort of external force, which prevents the attainment of thermodynamic equilibrium. An important example of such a property is shear viscosity, which occurs as the result of an applied strain rate ($\gamma$). To deal with such a situation, Newton's laws of motion must be modified. This can be achieved by implementing the sllod [10] algorithm with the following equations of motion:

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i \cdot \nabla \mathbf{u} \quad (5)$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{u} - \alpha \mathbf{p}_i \quad (6)$$

where $\mathbf{u} = (u_x, 0, 0)$ and $u_x = \gamma y$ is the velocity field corresponding to planar Couette flow with a strain rate $\gamma$. In equation (6), $\alpha$ is a thermostating constant. Simulation results [11] for linear chains of different length are shown in figure 2. The results show two different regions. At low strain rate (Newtonian region), the shear viscosity is independent of strain rate whereas at higher stain rates (non-Newtonian region) the fluid begins to 'shear thin' and its viscosity is highly dependent on the strain rate.

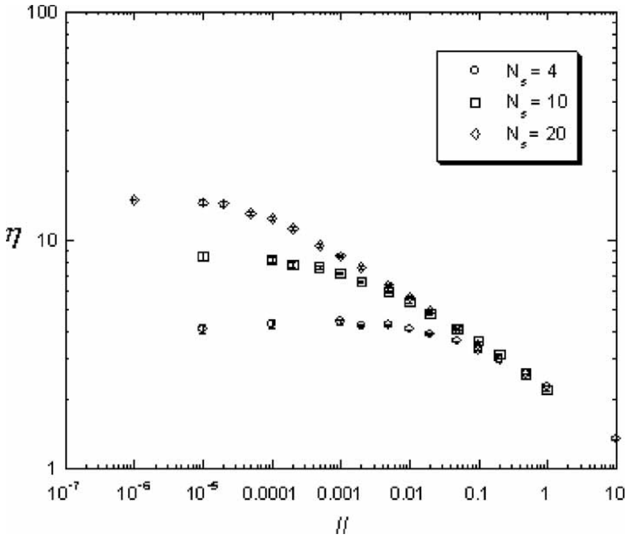

Figure 2. Comparison of the reduced shear viscosity as a function of reduced strain rate for linear chains containing 4, 10 and 20 monomers at $T^* = 1.0$ and $\rho^* = 0.84$ ([11]).

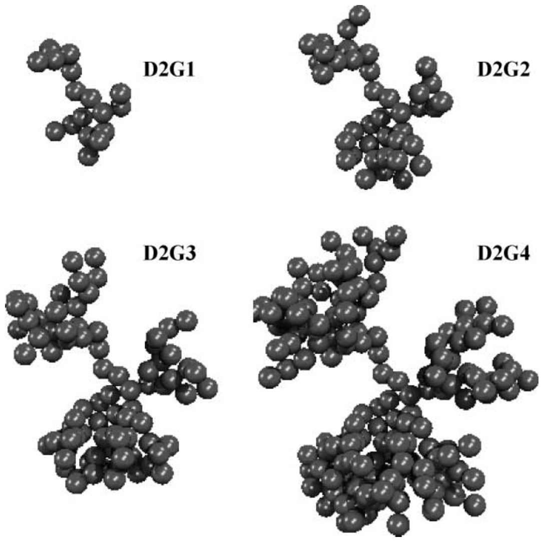

Figure 3. Illustration of dendrimers of different generations.

The phenomena shown in figure 2 agree qualitatively with experimental observations.

### *2.3 Detecting differences in physical properties—dendrimers versus conventional polymers*

Molecular simulation is particularly useful in determining the difference between the physical properties of fluids. As an example, we have examined the rheological behaviour of dendrimers in the melt compared with linear chain molecules of similar size.

Dendrimers constitute a novel class of highly branched synthetic polymer. Developments in the synthesis of dendrimers over the last decade [12] allow the creation of dendrimers with almost full control over their structure and functionality. The unique molecular architecture of dendrimers makes their use for the design of novel materials very promising. For example, controlling surface reactivity can be used to make chemical sensors, and the ability of dendrimers to encapsulate other molecules means that they might be used as molecular delivery vehicles. Encapsulation in combination with the self-assembling behavior of dendrimers makes them a candidate for the fabrication of novel nanoscale materials.

The distinctive transport property of dendrimers is a source of potentially useful applications. The high degree of symmetry of high-generation dendrimers and the decreased entanglement in the melt causes significantly different flow properties compared with the behaviour of traditional polymer fluids such as linear polymers. Understanding the structure-property relationships for dendrimers in the melt or in solution would enable full application of these materials as rheological modifiers, processing aids, or nanoscale lubricants. Here, we discuss viscosity simulations using the sllod algorithm described above.

Bosko *et al.* [13] modeled dendrimers with tri-functional cores and 2 beads separating the branching points. As shown in figure 3, this model results in 19, 43, 91 and 187 beads per single dendrimer of generation 1, 2, 3 and 4, respectively. Henceforth, the model dendrimers will be referred to as D2G1, D2G2, D2G3, and D2G4. The length of the linear polymers studied corresponded exactly to the mass (i.e. the number of beads) of the dendrimers. Therefore, the properties of D2G1, D2G2, D2G3 and D2G4 were compared to linear chains of 19-mers, 43-mers, 91-mers and 187-mers, respectively. For simulations involving either D2G1 or 19-mers, a system of 256 molecules was used, whereas in all other cases 125 molecules were used. As detailed elsewhere [12,13], the inter- and intra-molecular interactions were obtained using a Weeks-Chandler-Anderson [2] and finitely extensible nonlinear elastic potentials, respectively.

A direct comparison of the viscosity-strain rate curves for dendrimers with those of traditional linear chain polymers of the same size (at the same density and temperature) is shown in figure 4. In all cases, when the fluid is in the Newtonian regime the viscosity of dendrimer melts is lower than that of the linear molecules. Internal branching and the compact globular structure of dendrimers, resulting in suppression of intermolecular entanglement, are responsible for this decrease in viscosity. Analysis of the structural changes of dendrimers under shear [12] indicates that the outermost branches, which might participate in entanglement, often fold back and can be found inside the molecule. Therefore they cannot interact with branches of other molecules, consequently reducing intermolecular entanglement and hence the shear viscosity. In the non-Newtonian regime the exponent in the power law region is always smaller for dendrimer melts in comparison to linear chain polymers, leading to lower viscosities for linear chains in comparison to dendrimers of the same molecular weight. In this case the branching of dendrimers prevents shear-induced alignment of molecules, which therefore slows shear thinning. Similar behaviour has been reported for

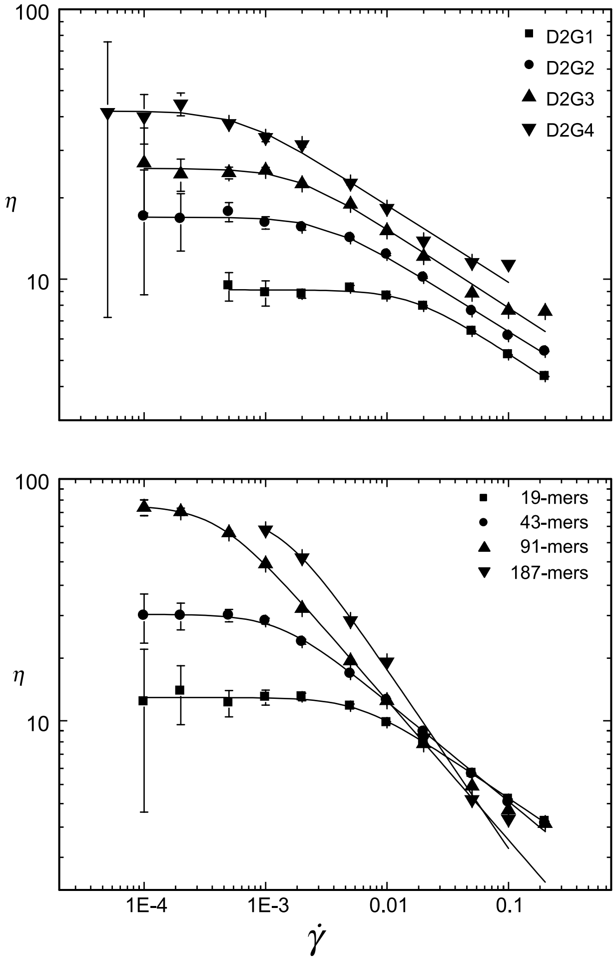

Figure 4. Comparison of shear viscosity vs. strain rate for dendrimers and linear chains of equivalent molecular weight (i.e. same number of beads in the molecule) at $T* = 1.25$ and $\rho* = 0.84$ ([13]).

star-shaped molecules compared to linear chain molecules of the same mass[15].

### 2.4 *Application to proteins*

Increasingly, molecular simulation can be used to determine the functioning of proteins. One important class of proteins is ATPase, which functions as a 'molecular motor' in cells. The viability of the atomistic approached proposed here has been recently demonstrated by Böckmann and Grunmüller [14] who used molecular dynamics to mimic the effect of the rotation of the $F_0$ part by inducing a forced rotation of the $\gamma$ unit. Ma *et al.* [15] proposed a 'targeted' molecular dynamics approach to span the different time frames involved between movement in the proteins (nanoseconds) and the rotation of the active domains (microseconds). These simulations provide insights into the structural changes of the active subunits but the changes triggered by ATP synthesis or hydrolysis were not considered. We are currently using molecular simulation coupled with quantum mechanical considerations to investigate the causes of rotary motion in this important system.

Despite these successes, it should be noted that the application of molecular simulation to proteins and very large molecular systems often remains computationally prohibitive. This is particularly the case for processes such as protein folding which occur on a time scale that is much longer than can be readily simulated with existing computational resources and techniques.

## 3. Conclusions

Molecular simulation techniques are poised to provide fundamental insights into the thermophysical properties of a diverse range of systems. The strength of these techniques stems fundamentally from the fact that they can be applied rigorously with very few limiting assumptions. Prior to the advent of robust molecular simulation techniques, reliable data for the thermophysical properties of fluids could only be obtained from accurate experimental measurement. The input from theory was, at best, limited to a supporting role by providing correlations. The large number of assumptions and approximations involved in theoretical tools such as equations of state meant that it was unrealistic to expect genuinely reliable predictions. In contrast, molecular simulation can be used to provide reliable data for important chemical engineering applications such as phase behaviour, rheology and protein systems.

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