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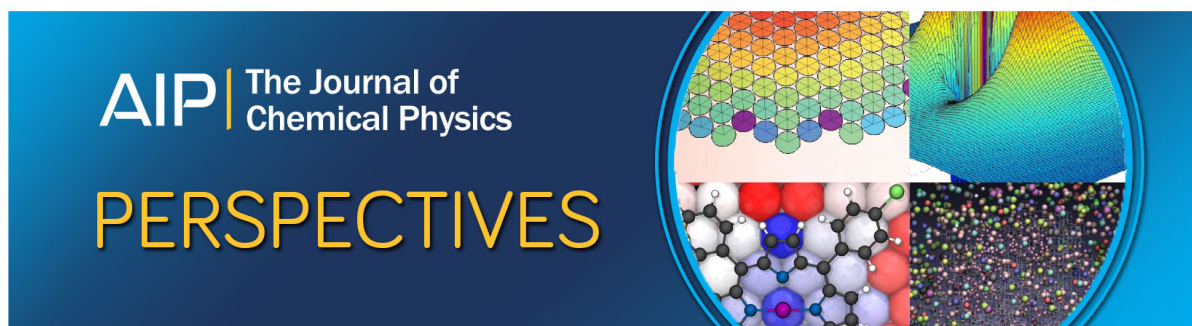
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Transport coefficients of liquid butane near the boiling point by equilibrium molecular dynamics

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We present very precise results for the linear viscosity, thermal conductivity, and self-diffusion coefficient of the Ryckaert–Bellemans model of liquid butane near the boiling point, calculated from their respective Green–Kubo formulas using equilibrium molecular dynamics simulations. These results are used as a basis for the appraisal of previous calculations of these transport coefficients, which vary considerably. We find excellent agreement between our results and the results of the most precise nonequilibrium molecular dynamics simulations. We directly examine the system-size dependence of these transport coefficients for system sizes between 64 and 864 molecules and find that it is negligible, within experimental errors, for the viscosity and the thermal conductivity. The self-diffusion coefficient increases with increasing system size. The long-time decay of the shear stress, heat flux, and velocity autocorrelation function is also discussed quantitatively. © 1995 American Institute of Physics.

I. INTRODUCTION

The Ryckaert–Bellemans (RB) model of butane^{1,2} is now a commonly used starting point for computer simulation studies of the thermodynamic and transport properties of liquids of nonrigid molecules. In particular, the self-diffusion coefficient and the viscosity of butane have been studied by several different groups. However the reported results, especially for the viscosity (see Table I), differ considerably. These discrepancies have never been fully explained, but system size dependence has been suggested as a possible reason for the disagreement. One of the purposes of this paper is to resolve this question by directly calculating the system size dependence of the viscosity, self-diffusion coefficient, and thermal conductivity of liquid butane at the state point at which the discrepancies were found.

Both equilibrium molecular dynamics (EMD) calculations with the Green–Kubo (GK) formula and nonequilibrium molecular dynamics (NEMD) simulations have previously been used to calculate the viscosity of liquid butane. However, no direct comparison of the two methods using reliable data for identical models and state points has yet been published. We present such a comparison in this paper.

The behavior of the velocity, stress, and heat flux autocorrelation functions (ACFs) at long times for molecular liquids is very difficult to discern, due to the difficulty of obtaining high precision data for these quantities. In this paper, we present very precise correlation functions whose long time decays can be discussed quantitatively.

It is hoped that the critical review of previous work and the new results presented here will remove doubts created by the disparities in some of the older data and establish a definitive set of results that can be used as benchmarks for future work.

II. EQUILIBRIUM SIMULATIONS

We used the Edberg, Evans, and Morriss (EEM) algorithm^{3,4,5} to perform equilibrium simulations of the Ryckaert–Bellemans model of butane at two state points

with the same density, but different temperatures. The details of the EEM algorithm have been published before.^{3,4,5} The Ryckaert–Bellemans potential parameters were the same as described previously and the Lennard-Jones potential for site–site interactions was truncated at 2.5σ and shifted to zero at the truncation point as usual. All simulations were performed with a timestep of 0.002 in reduced units (3.865 fs) and used Gauss' principle of least constraint to maintain a constant temperature.

The first state point (which we will call state point A) had a reduced temperature of 3.7889 (272.8 K) and a reduced site number density of 1.46 (583 kg m⁻³), and was used for a study of the system size dependence of the self-diffusion coefficient, the viscosity, and the thermal conductivity. Simulations (7.7 ns averaging time) of a 108 molecule system at a nearby state point (state point B) with a reduced temperature of 4.05 (291.6 K) and reduced site number density of 1.46 (583 kg m⁻³) were also performed to enable us to make direct comparisons with previously published work.

The self-diffusion coefficient, viscosity, and thermal conductivity were determined for systems of 64, 108, and 864 molecules in the number dependence study. The standard Green–Kubo relations using molecular localization of the observables were used to evaluate the transport coefficients⁶ and averages over all symmetry related correlation functions⁷ were taken in order to reduce the noise in the results.

Uncertainties quoted in Tables I–III and Figs. 4–6 were calculated in the following way. A number of independent simulations were performed for each value N in the case of the number dependence studies. Each simulation was at least ten times longer than the interval over which the correlation functions were determined (8 ps). The transport coefficients were determined for each of these shorter runs, the results averaged, and the uncertainty calculated from the standard error in the mean. When the results of less than five runs were averaged, the standard deviation was used rather than the standard error in the mean, giving a more conservative error estimate. The uncertainties for the results at state point

TABLE I. Calculated values of the viscosity of liquid butane at state point B (experimental value, 0.173 mPa s). The various versions of the RB model used in the calculations are as follows: RB-1 simple RB model; RB-2 different masses and LJ parameters for sites representing CH₂ and CH₃ groups; RB-3 same as RB-1 but with bond length and angle potentials; S rigid body (all *gauche*) model. Results of both equilibrium (GK) and nonequilibrium simulations (NEMD) are included. Values with asterisks are estimated.

Reference	Temp/K	Density /kg m ⁻³	<i>N</i>	Model	Method	Viscosity /mPa s
6	272.6	603.4	192	RB-2	GK, 0.0513 ns	0.26±0.06
11	293	601	128	RB-2	GK, 1.064 ns	0.38±0.05
4	291.6	583	64	RB-1	NEMD, 1.5* ns	0.24±0.02
15	291.6	584.4	486	RB-3	NEMD, 2* ns	0.165±0.01*
10	283	601	108	S	GK, 1* ns	0.17±0.02
19	291.6	583	64	RB-1	NEMD, 5 ns	0.152±0.001
This work	291.6	583	108	RB-1	GK, 7.7 ns	0.154±0.004

B were calculated from the uncertainties for the 108 molecule results for state point A, assuming that the standard error in the mean is proportional to the inverse square root of the number of time steps in the run, since the simulation conditions were almost identical.

III. RESULTS AND DISCUSSION

Averaged correlation functions calculated at state point A (108 molecule simulations) are shown in Figs. 1–3. The precision of these correlation functions allows us to quantitatively discuss several points which have received little attention in previous work.

Considering the velocity autocorrelation function (Fig. 1) first, we see that it displays a clear negative region corresponding to a “cage effect” between 0.8 and 4.5 ps. This was not clearly observed in the results of Ryckaert and Bellemans,^{1,2} because of the relatively large statistical errors that resulted from their short simulation times. Although it has a small amplitude, the negative peak is quite broad, and thus is still relatively important, making a (negative) contribution of about 9% to the final value of the self-diffusion coefficient. After this negative “backscatter” peak, we see a long, approximately exponential decay of the velocity ACF: The absence of systematic deviations in the plot of the residuals for a single exponential fit to the velocity ACF beyond a correlation time of 2.5 ps suggests that the tail of the velocity ACF is well described by a single exponential with a time constant of 0.9 ps. The estimated uncertainty in this decay constant is ±10%, obtained by fitting a single exponential to the velocity ACF in the ranges 1.5–8.0 ps up to 4.0–8.0 ps, increasing the starting time in 0.5 ps increments.

Mode-coupling theory and generalized hydrodynamics predict that the velocity ACFs of all fluids that exhibit “hydrodynamic” behavior should decay with a positive power law ($t^{-3/2}$) tail at very long times.⁸ This has been observed in simulations of simple liquids, most definitively in hard sphere simulations at low and moderate densities,⁹ but it has been difficult to observe (even in hard sphere systems) at high densities. Our simulations provide no evidence for its existence in dense liquid butane.

Next, we consider the shear stress autocorrelation function, shown in Fig. 2. We observe that it decays rapidly to a minimum, and then rises to a low, broad peak at about 0.5 ps which decays, approximately exponentially, until it reaches the noise level in our simulations at about 5 ps. The general features of this correlation function are similar to those that we observed previously for a model decane with purely repulsive Lennard-Jones site–site forces.⁷ Luo and Hoheisel¹⁰ and Maréchal, Ryckaert, and Bellemans¹¹ also observed similar features, although less clearly due to the poorer statistics of their data. In these studies, the slowly relaxing tail of the stress ACF was attributed to the coupling of shear stress fluctuations to the collective orientational motions found in dense liquids of anisotropic molecules. The relaxation time obtained by fitting our stress ACF at times greater than 0.75 ps with a single exponential decay was 1.0 ps ± 10%. The uncertainty was determined in the same way as the corresponding uncertainty in the velocity ACF long time decay constant. This is similar to the values of the reorientational relaxation times for short alkanes at atmospheric pressure and a temperature of 25 °C given by Volterra *et al.*¹² Note that the long-time exponential relaxation time of the

TABLE II. Calculated values of self-diffusion coefficient (experimental value, $6.4 \pm 0.6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$). All results quoted were calculated by either mean square displacement (MSD) or Green–Kubo (GK) methods in equilibrium simulations.

Reference	Temp/K	Density /kg m ⁻³	<i>N</i>	Model	Method	D_s /10 ⁻⁹ m ² s ⁻¹
2	291.5	583	64	RB-1	MSD/GK, 0.014 ns	6.5±0.4
3	291.6	583	64	RB-1	MSD, 0.333 ns	6.14
23	291.2	582	64	RB-5	MSD, 0.29 ns	7.2±0.7
19	291.6	583	125	RB-1	MSD, 1 ns	6.7±0.4
This work	291.6	583	108	RB-1	GK, 7.7 ns	6.96±0.04

TABLE III. Calculated values of thermal conductivity (experimental value, $0.110 \text{ W m}^{-1} \text{ K}^{-1}$).

Reference	Temp/K	Density /kg m ⁻³	<i>N</i>	Model	Method	$\lambda/\text{W m}^{-1} \text{ K}^{-1}$
6	272.6	603.4	192	RB-2	GK, 0.0513 ns	0.22 ± 0.03
18	291.6	583	108	RB-1	NEMD, 3 ns	0.093 ± 0.004
This work	291.6	583	108	RB-1	GK, 7.7 ns	0.097 ± 0.004

stress ACF is equal, within experimental uncertainties, to that of the velocity autocorrelation function, indicating that similar molecular processes govern the long time behavior in both cases. Hoheisel¹³ has demonstrated the usefulness of the single-particle orientational relaxation time as an indicator of the decay time of the stress ACF. Berne and Pecora note that the single particle and collective orientational relaxation times are, in general, not identical.¹⁴ More work would be required to definitively answer the question of how they are related to the long time decay constants of the velocity and stress ACFs that we have calculated.

Figure 3 shows that the heat flux vector ACF decays rapidly and monotonically to zero, with no remarkable features in contrast to the velocity and stress ACFs. Once again, we find that the correlation function is well described by a single exponential beyond a certain point. In this case, we find a relaxation time of 0.25 ps for times greater than 0.3 ps.

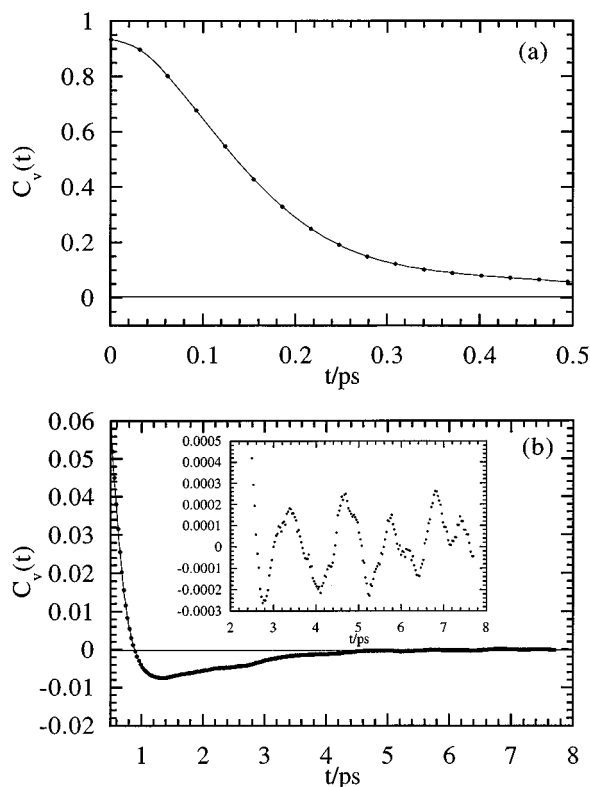


FIG. 1. Velocity autocorrelation function C_v as a function of time at short (a) and long (b) times for a 108 molecule RB model butane system at $T=272.8 \text{ K}$ and $\rho=583 \text{ kg m}^{-3}$. The total averaging time was 27 ns. The inset on (b) shows the residuals for an exponential fit at times $t > 2.5 \text{ ps}$, demonstrating that there are no systematic deviations from the single exponential form.

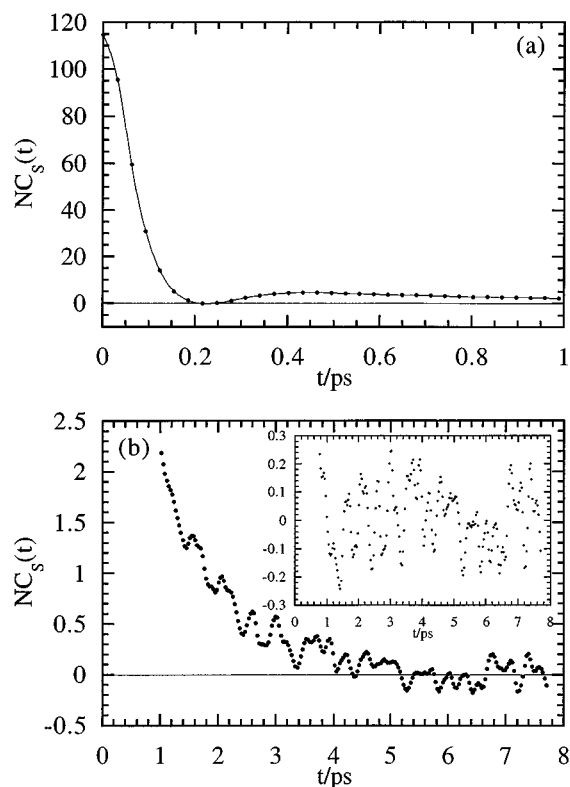


FIG. 2. Shear stress autocorrelation function multiplied by the system size, NC_s as a function of time at short (a) and long (b) times for the same system as in Fig. 1. This quantity is expected to be independent of system size. The inset of (b) is a plot of the residuals for an exponential fit to the stress ACF at times $t > 0.75 \text{ ps}$. The absence of any systematic trends in the residuals indicates that the function chosen for the fit is adequate.

Clearly, the molecular processes contributing to the relaxation of heat flux fluctuations in the long time limit are different from those responsible for the decay of the shear stress and molecular velocity ACFs.

The system size dependence of the calculated values of the transport coefficients is shown in Figs. 4–6. There is negligible system size dependence for the viscosity. The thermal conductivity also appears to be insensitive to the system

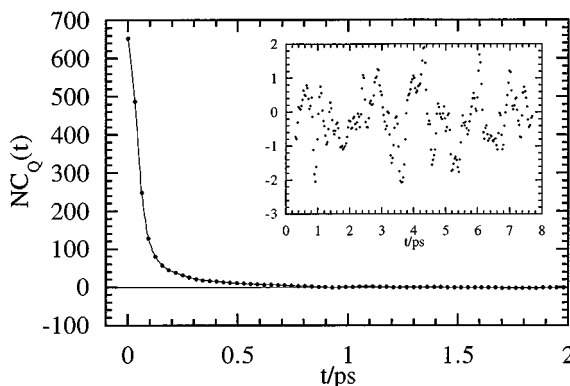


FIG. 3. Heat flux autocorrelation function multiplied by the system size, NC_Q as a function of time for the same system as in Fig. 1. This quantity is expected to be independent of system size. The residuals for an exponential fit at times $t > 0.3 \text{ ps}$ are shown in the inset.

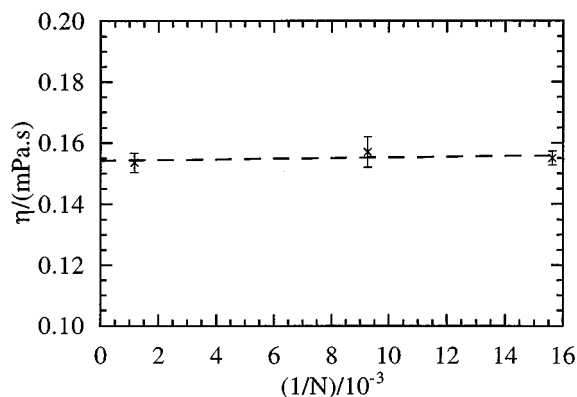


FIG. 4. System size dependence of the viscosity for Ryckaert–Bellemans model butane at $T=272.8$ K and $\rho=583$ kg m $^{-3}$. The viscosity is plotted against $1/N$, where N is the number of molecules in the primary simulation box. The equivalent simulation lengths were 7.4 ns ($N=64$), 27 ns ($N=108$), and 2.3 ns ($N=864$).

size in the range investigated, but the self-diffusion coefficient displays a significant number dependence. When the shear stress ACFs are multiplied by the system size N , and plotted on the same axes, we see that there are minor systematic differences in the region of the minimum of the ACF, but these differences are obscured by noise when the ACFs are integrated and the thermal conductivity is calculated. No systematic differences are observed in the heat flux ACFs. In contrast, the velocity ACFs (which do not need to be multiplied by the volume) display two systematic and significant changes. The zero-time intercept of the velocity ACF varies with the number of particles because it is assumed that all $3N$ correlation functions are independent. Because of the conservation of momentum, and the Gaussian constraint on the peculiar kinetic energy, in fact there are only $3N-4$ independent velocity ACFs. Multiplication of each velocity ACF by $3N/(3N-4)$ removes this variation. This correction has already been applied to the results given in Fig. 6. However, a systematic number dependence of the ACFs remains. As the number of particles is increased, the depth of the minimum in the velocity ACF decreases and the diffusion coefficient increases. Smaller system sizes apparently lead to a

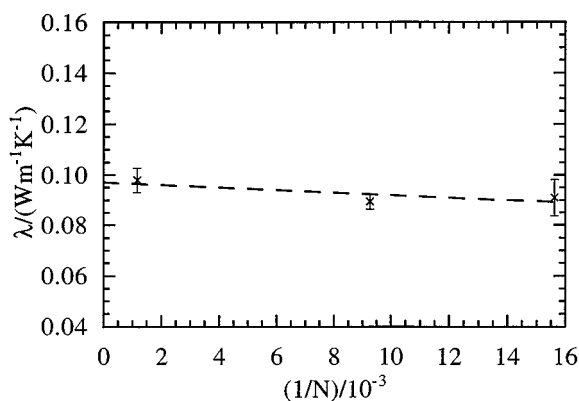


FIG. 5. System size dependence of the thermal conductivity for the system described in Fig. 4.

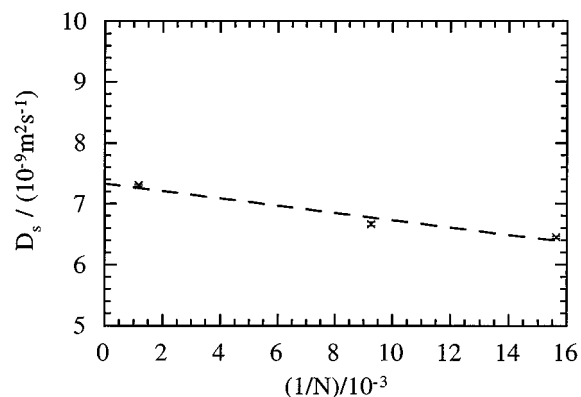


FIG. 6. System size dependence of the self-diffusion coefficient for the system described in Fig. 4.

more rigid nearest neighbor shell, and hence a stronger backscatter peak for dense liquid butane.

Chynoweth *et al.*¹⁵ suggested that system size dependence was responsible for the disparity between their results for the zero-shear viscosity of butane and those obtained by Edberg, Morriss, and Evans.⁴ This claim was later discussed by Rowley and Ely,¹⁶ who pointed out that the difference between the two sets of results could be accommodated within the large statistical uncertainty in the EEM results, which were obtained from relatively short simulations on a small (64 molecule) system. Rowley and Ely also performed a direct comparison between results obtained from NEMD simulations on a 125 molecule system and those obtained for a 512 molecule system, and found a small, but apparently significant difference between the two sets of results. Note that the state point used for the comparison by Rowley and Ely had a higher density and lower temperature than the one used by EEM and Chynoweth, raising the possibility that system size dependence may itself depend on the state point investigated. Our results provide no evidence for significant system size dependence of the viscosity at the EEM state point.

Most of the reported results for the transport coefficients of liquid butane obtained by computer simulation are for state point B. This state point is often referred to as being near the boiling point. In fact, if we take the density and temperature as 582.8 kg m $^{-3}$ and 291.6 K and interpolate using the tables given by Younglove and Ely,¹⁷ we obtain a pressure of 1.85 MPa, which is far above atmospheric pressure (0.101 MPa) and a boiling point of approximately 380 K. (This interpolation is slightly more accurate than the one we used previously.¹⁸) However, since this state point has become a standard state point for simulations of liquid butane, we have used it as a reference point for the comparison of different sets of data.

Collections of simulation results from the literature for the viscosity, self-diffusion coefficient, and thermal conductivity of liquid butane at state point B are shown in Tables I, II, and III. First we will consider the results for the viscosity. It is clear that some of the results shown in Table I are very imprecise, due to extremely short simulation times. We note also that the quoted errors, where they have been given, are

often underestimated. It is gratifying, however, to find that the most precise of the equilibrium (this work) and nonequilibrium (Ref. 19) results agree very well, given that the calculations were performed independently, by different methods and with different numbers of molecules. Note that the NEMD value given here was obtained by extrapolation to zero strain rate with the three-parameter Cross fit. The experimental value (0.173 mPa s) quoted in Table I is an interpolated value taken from the tables of Ref. 17, at the state point $T=291.6$ K and $\rho=582.8$ kg m⁻³. It differs slightly from the values used in other comparisons of experiment with theory, which have generally been near the boiling point ($T=272.6$ K) at atmospheric pressure. The comparison of experiment with theory is now quite favorable, with a discrepancy of only 11%. Better alkane models, such as Toxvaerd's AUA(2) model²⁰ would presumably reduce this discrepancy still further, with only a modest increase in computational effort.

Next, we consider the results for the self-diffusion coefficient, shown in Table II. The experimental value (6.4×10^{-9} m² s⁻¹) was obtained by applying the curve fit parameters for the Speedy modification of the rough hard sphere model given by Vardag *et al.*²¹ This value is in good agreement with the result (6.6×10^{-9} m² s⁻¹) obtained by applying the correlation for *n*-alkanes developed by Assael *et al.*²² The agreement between independent calculations is much better for the self-diffusion coefficient than for any of the other transport properties, due to it being a single particle property which can be averaged over all particles as well as time averaged. The results agree quite well with the experimental value given in Table II, but the more precise calculations show that the model butane calculations overestimate the self diffusion coefficient by approximately 9%. This overestimation of D_s by the RB model is in agreement with the conclusions of Padilla and Toxvaerd²⁰ based on RB model simulations and self diffusion data for pentane and decane.

In Table III, we present a compilation of all the available calculations of the thermal conductivity of butane for this state point. The experimental value (0.110 W m⁻¹ K⁻¹) was interpolated from the tables of Younglove and Ely.¹⁷ The thermal conductivity is clearly a less commonly studied property than either the viscosity or the self-diffusion coefficient. The agreement between NEMD results and equilibrium MD results is excellent, and the results indicate that the RB model underestimates the thermal conductivity at this state point by 12%.

IV. CONCLUSION

Previous calculations of the transport properties of liquid butane have produced widely differing results and have led to many questions regarding the accuracy of the Ryckaert–Bellemans model, the agreement of transport coefficients calculated from NEMD with those of EMD, and the system size dependence of calculated values of the viscosity, thermal conductivity, and the self-diffusion coefficient. In this work, we have found that the disagreement of previous results is largely due to poor statistics resulting from short simulations.

Our much more precise calculations show that NEMD and EMD calculations give results for the viscosity, thermal conductivity, and the self-diffusion coefficient that are in very good agreement with each other. We find that the transport coefficients calculated by EMD methods display negligible system size dependence for between 64 and 864 molecules, except in the case of the self-diffusion coefficient, where a small but significant dependence is found. Our results, along with the most precise of the NEMD results, show that the RB model gives the viscosity, self-diffusion coefficient, and the thermal conductivity in reasonable agreement with experiment, with discrepancies of the order of 10% for the state point studied.

We find that the long time decays of our velocity, stress, and heat flux autocorrelation functions show no evidence of the hydrodynamic $t^{-3/2}$ long time tail. In all cases, the long time behavior of the ACF's is exponential. The velocity and stress ACF's decay with a time constant that is close to the collective molecular reorientational relaxation time, but the time constant for the long time decay of the heat flux ACF is much smaller.

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