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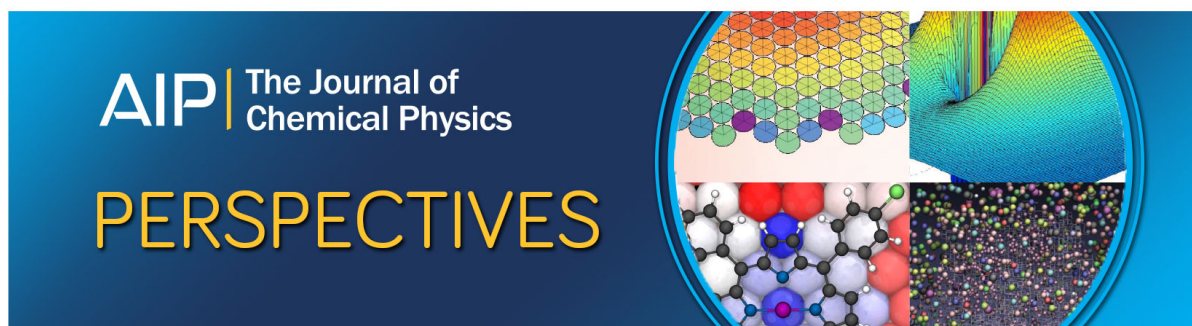
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Viscosity calculations of *n*-alkanes by equilibrium molecular dynamics

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We report shear viscosity results obtained using extensive equilibrium molecular dynamics simulations. By direct numerical comparison, we show the equivalence of the Green-Kubo and Einstein approach to the calculation of viscosity in both the atomic and molecular representations. Comparing the results for two models of linear alkanes, we discuss the molecular factors determining their low-temperature liquid-state transport properties. In the mass range considered here ($\leq C_{16}$), large corrections to Rouse-dynamics scaling are observed, as expected. We indicate, however, how the scaling relation between rotational-diffusion-time and shear-viscosity still provides a semi-quantitative way of estimating the latter, using simulations which are at least one order of magnitude shorter than required for direct determination of viscosity for *n*-alkanes.

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I. INTRODUCTION

The study of the transport properties of alkanes is of considerable practical and theoretical interest. In the petrochemical industry, the ability to predict and control the viscosity of alkanes and their mixtures is critical for rational product design and process optimization. The study of the rheology of alkanes can also offer valuable insight into the short-range, short-time aspects of polymer viscoelasticity. It also provides a direct bridge between the liquid-state theory of simple molecular fluids and the Rouse regime of polymer dynamics. In this paper we discuss the use of equilibrium molecular dynamics (EMD) for the calculation of viscosity in neat linear-alkane systems, stressing both general methodological issues and the limitations of presently available *n*-alkane models.

In two previous publications,^{1,2} referred to in the following as papers I and II, we investigated by EMD simulations the static and diffusion properties of several linear and branched alkanes. Two models of *n*-alkanes from the literature, that of Siepman *et al.*,³ designated as model A, and Padilla and Toxvaerd⁴ (model B) were studied. Model A was shown to quantitatively describe the liquid-gas coexistence curve of the *n*-alkane phase diagram,³ while model B was optimized to describe the static and dynamic behavior of short *n*-alkanes (C_5H_{12} - $C_{10}H_{22}$) at moderately high pressures and high temperatures.⁴ Both models use a spherical united atom (UA) potential, but model B⁴ introduces a displacement between the centers of force of non-bonded interaction and the centers of mass of the united atoms [Asymmetric United Atom (AUA)]. We used simple extensions of the two models to study the branched alkanes. In I and II, the calculated diffusion constants were compared with those obtained from new pulsed-field-gradient NMR measurements. Our study showed that, for a wide range of temperatures at atmospheric pressure, model B works better than model A in describing the diffusion constant of *n*-alkanes. Equilibrium molecular geometries were also significantly different between the two

models, although no direct comparison with experiment was available.

In this paper we expand our comparative study investigating the ability of model A and B to predict the viscosity of linear alkanes, concentrating on *n*-decane and *n*-hexadecane as test cases. Some results for the viscosity of these two molecules using model A have already appeared in the literature,⁵ while the results for model B are new. All of the previous numerical results for the viscosity of alkanes were obtained using non-equilibrium molecular dynamics (NEMD)⁵⁻¹² or, for short alkanes ($\leq C_{10}$), the Green-Kubo (G-K) relation.^{6,13-15} Here we perform all calculations using both G-K and Einstein relations and numerically show the equivalence of the two procedures. For model A, we compare our results with those obtained by NEMD.⁵ For currently typical system sizes and a given statistical accuracy, we find that the calculation of viscosity by equilibrium and non-equilibrium methods has comparable CPU time requirements. EMD results can also be effectively used as a test for the NEMD viscosity calculations, given the difficulties to obtain homogeneous and unbiased thermostating of systems of flexible molecules under shear.¹⁶

The transport properties of linear alkanes have often been rationalized in terms of hard-sphere type models^{17,18} emphasizing the connection with the theory of simple (molecular) liquids. Here we offer a complementary approach, stressing the connection with (unentangled) polymer dynamics. In particular, we show how the Rouse formula for the rotational diffusion time of polymers can actually provide an effective way to estimate the viscosity of linear alkanes. This has both practical and theoretical interest. From a theoretical standpoint, it shows how medium-size (linear) alkanes can be used to investigate the relation between the liquid-state theory of simple fluids and the Rouse dynamics of polymers. From a practical standpoint, the slower statistical convergence of viscosity calculations, compared to diffusion calculations, makes it useful to be able to estimate viscosity from diffusion results.

In Sec. II we briefly summarize models parameters and

TABLE I. Lennard-Jones potential parameters.

Model	Group	σ (Å)	ϵ (kcal/mol)	d (Å)
A (UA ^a)	CH ₃	3.930	0.227	
	CH ₂	3.930	0.093	
B (AUA ^b)	CH ₃	3.527	0.238	0.275
	CH ₂	3.527	0.159	0.370 ^c

^aFrom Reference 3.

^bThis is model AUA₍₂₎ from Ref. 19.

^cIn Table I of Ref. 1, d of CH₂ was incorrectly reported as 0.159. The correct value (0.370) was used in the simulations.

simulation methodology. The equilibrium results for static properties are presented in Sec. III. The methodology of the viscosity calculation is reviewed in Sec. IV, while the diffusion and viscosity results are presented in Sec. V. The connection with the Rouse dynamics of polymers is discussed in Sec. VI. We compare EMD and NEMD approaches to the calculation of viscosity in Sec. VII and summarize our conclusions in Sec. VIII. Some technical details of the computation of the AUA stress tensor in the atomic representation are confined to an Appendix.

II. SIMULATION MODELS AND METHODOLOGY

For a comparative description of models A (UA) and B (AUA) we refer the reader to paper I.¹ However, for ease of reference and to point out previous misprints and a minor difference with Ref. 1, we list again, in Tables I and II, the non-bonded and bonded interaction parameters for the two models investigated. Bond lengths are kept constant using the RATTLE algorithm²⁰ and we used a 10 Å cut-off for the (shifted) Lennard-Jones (LJ) potential.

As for the diffusion studies,^{1,2} all the results presented here were obtained by constant volume simulations, using, with one exception, experimental densities at 0.1 MPa. The velocity rescaling algorithm of Berendsen *et al.*²¹ was used to control the temperature. The equation of motion was integrated using the velocity Verlet algorithm with a 5 fs time-step. The molecules and state points specifically investigated for this paper are collected in Table III. In the Sec. VI, where

TABLE II. Intramolecular interaction parameters.

	Model A (UA ^a)	Model B (AUA ^b)	Units
Bond length	1.54	1.54 ^c	Å
k_b (bending)	124.18	124.18	kcal/(mol rad ²)
θ_b	114.0°	114.6°	deg.
a_0 (torsion)	2.007	2.062	kcal/mol
a_1	4.012	4.821	
a_2	0.271	0.162	
a_3	-6.290	-6.218	
a_4		-0.324	
a_5		-0.502	

^aIntramolecular parameters for *n*-alkanes from Ref. 3. Torsional potentials are taken from Ref. 22.

^bIntramolecular parameters from Ref. 19. The torsional potential (d) from the same reference was used.

^cIn Ref. 1 we used 1.545 instead.

TABLE III. Substances and state points simulated.^a

Substance	T (K)	ρ^b (g/cm ³)
<i>n</i> -decane	298	0.7247 ^c
	480	0.6136 ^d
<i>n</i> -hexadecane	298	0.7703 ^e
	323	0.7531 ^e
	373	0.7187 ^e

^aDifferent system sizes and run lengths were used. See following tables.

^bNormal pressure density, except when otherwise specified.

^cFrom Ref. 23.

^dDensity corresponding to a system under moderately high pressure. From Ref. 14.

^eFrom Table VI of Ref. 24.

we discuss the use of the Rouse-dynamics model to connect diffusion and viscosity results, we have also reconsidered data from papers I and II and made comparisons with the results of Cui *et al.*⁵ Most of the simulations were performed using systems of 64 molecules. To gain some insight on possible finite-size effects and to establish a basis for estimating the error of the calculated transport properties, we also performed very long simulations using 32 *n*-decane and 128 *n*-hexadecane molecules.

III. EQUILIBRIUM PROPERTIES

The static equilibrium results are collected in Table IV. The very long runs required for viscosity calculations provide very accurate information about the average molecular shape. These results confirm the significant difference in thermodynamic flexibility between models A and B. Model B describes a more compact (more thermodynamically flexible) molecule than model A. There is also a difference in the expansion coefficient $k = d(\ln R_g^2)/dT$ between the two models, although not quite as large as that suggested by the less accurate measurements of paper I. This leads to a (very) slow convergence of molecular sizes for the two models with increasing temperatures. In this respect, note that the average radius of gyration of model A of *n*-decane at 480 K is still larger than the value for model B at 298 K. For both models, the molecular geometry seems to be essentially unaffected by the system size.

In Table IV we also report the calculated pressures (including long-tail corrections). Contrary to our previous papers,^{1,2} where the pressure in the molecular representation was reported, here we report the pressure in the atomic representation.²⁵ From test runs performed with smaller time-steps, we find that the “atomic” pressure is less sensitive to changes in the integration time-step. With the 5 fs time-step used here, the “molecular” pressure is 1 to 2 MPa higher than the “atomic” value (see paper I). Note that this discrepancy is significantly larger than the statistical errors reported in Table IV for the “atomic” pressure. To the reported accuracy, the statistical fluctuations of “atomic” and “molecular” values are identical.

TABLE IV. Equilibrium results. The square radius of gyration R_g^2 and the square end-to-end distances R_{ee}^2 are expressed in \AA^2 . Uncertainties in the last reported digit are given in parenthesis.^a The eigenvalues of the mass tensor (l_i^2) satisfy the equality $l_1^2 + l_2^2 + l_3^2 = R_g^2$, with $l_1^2 \geq l_2^2 \geq l_3^2$. Data for systems of 64 molecules, unless otherwise specified.

Substance	Model	T (K)	R_g^2	l_1^2/R_g^2	l_2^2/R_g^2	R_{ee}^2	P_{EMD} (MPa)	Run (ns)
<i>n</i> -decane	A	298	11.48(1)	0.919(1)	0.067(1)	96.8(1)	-0.3(2)	20
		298 ^b	11.48(1)	0.919(1)	0.067(1)	96.8(1)	-1.1(1)	110
		480	10.67(1)	0.896(1)	0.085(1)	86.4(1)	11.7(2)	10
<i>n</i> -decane	B	298	10.65(2)	0.894(1)	0.087(1)	85.9(2)	0.9(2)	20
		298 ^b	10.64(1)	0.894(1)	0.087(1)	85.9(1)	-0.1(1)	100
		480	9.96(1)	0.874(1)	0.102(1)	77.2(1)	25.0(2)	10
<i>n</i> -hexadecane	A	298	26.02(3)	0.902(1)	0.085(1)	226.5(4)	-6.4(2)	30
		323	25.34(2)	0.895(1)	0.091(1)	217.5(2)	-6.6(2)	40
		373	24.49(2)	0.886(1)	0.098(1)	206.8(3)	-6.8(2)	15
<i>n</i> -hexadecane	B	298	23.10(4)	0.872(1)	0.109(1)	189.3(6)	3.2(2)	31
		323	22.70(4)	0.867(1)	0.112(1)	184.6(5)	4.5(2)	28 ^c
		323 ^d	22.66(2)	0.867(1)	0.113(1)	183.7(3)	5.1(1)	50
		373	21.94(2)	0.858(1)	0.119(1)	175.1(3)	7.0(1)	45
		373 ^d	22.00(2)	0.860(1)	0.118(1)	175.9(3)	7.3(1)	20

^aIn practice, because of round-off error, the minimum uncertainty on the last reported digit is 1.

^bSystem of 32 molecules.

^cFor the calculation of viscosity we used a somewhat longer 31.5 ns run.

^dSystem of 128 molecules.

IV. VISCOSITY CALCULATION METHODOLOGY

In analogy with the self-diffusion coefficient, which can be calculated using the single-particle velocity correlation function, we can compute the shear viscosity η using the equilibrium fluctuations of the off-diagonal components of the stress tensor.²⁶ Averaging over the three off-diagonal components will improve the statistical convergence of the calculation. Davis and Evans¹⁰ have shown that, for a statistically isotropic system, we can further improve the convergence of the calculation using the equilibrium fluctuations of the symmetrized traceless portion ($P_{\alpha\beta}$) of the stress tensor ($\sigma_{\alpha\beta}$). $P_{\alpha\beta}$ includes two independent diagonal components and the (generalized) G-K formula, with the appropriate weight factors, can be written as

$$\eta = \frac{V}{10k_B T} \int_0^\infty \left\langle \left(\sum_{\alpha\beta} P_{\alpha\beta}(t) P_{\alpha\beta}(0) \right) \right\rangle dt. \quad (1)$$

Here V and T are the temperature and volume of the system, respectively, k_B is the Boltzmann constant and

$$P_{\alpha\beta} = (\sigma_{\alpha\beta} + \sigma_{\beta\alpha})/2 - \delta_{\alpha\beta} \left(\sum_{\gamma} \sigma_{\gamma\gamma} \right). \quad (2)$$

For a system of N atoms (molecules),

$$\sigma_{\alpha\beta}(t) = \frac{1}{N} \left[\sum_i v_\alpha^i(t) v_\beta^i(t) + \sum_{i>j} f_\alpha^{i,j}(t) (r_\beta^i(t) - r_\beta^j(t)) \right], \quad (3)$$

where v_α^i and r_α^i represent, respectively, the α component of the velocity and position of the i th atom (molecule center-

of-mass) and $f_\alpha^{i,j}$ is the α component of the force exercised on atom (the center-of-mass of molecule) i due to atom (molecule) j . In Fig. 1, we show the equivalence of the atomic and molecular versions of the (generalized) G-K relation for model B of *n*-hexadecane at 298 K. This equivalence was first discussed for *n*-butane by Marechal and Ryckaert.⁶ Cui *et al.*¹⁵ presented a more detailed analysis for

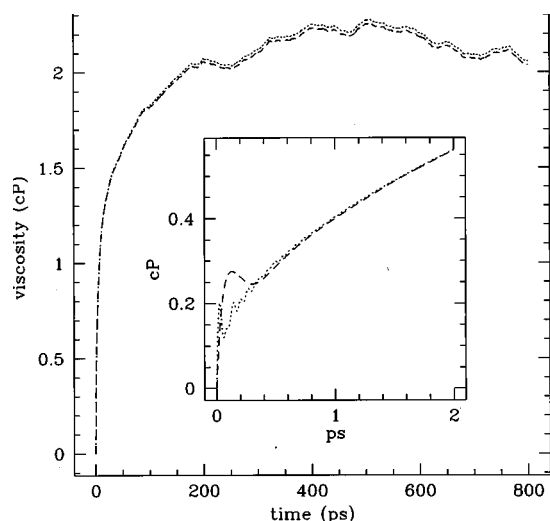


FIG. 1. Comparison of Green-Kubo calculation [Eq. (1)] for molecular (dashed line) and atomic (dotted line) shear-stress of *n*-hexadecane at 298 K (model B). Here we integrate the correlation up to a time roughly twice the rotational diffusion time ($\tau_R = 330$ ps). The correlation itself was averaged over the entire run ($\approx 95 \tau_R$). We find that the two calculations agree at all times larger than ≈ 1 ps (inset). Following the criterion suggested in Sec. V, we estimate the statistical uncertainty of this calculation to be in the range 10 to 15%.

the case of model A of *n*-decane at the 480 K state point. Their implementation of model A includes bond stretching and the (running) integral in the atomic G-K formula shows stronger oscillations at short times than observed in our fixed bond-length model²⁷ (see inset of Fig. 1). In both cases, however, the running values of atomic and molecular integrals converge on time scales much shorter than the characteristic time required for the two integrals to reach the (same) plateau value.

Alternatively, in analogy with the Einstein relation for self-diffusion, we can compute the shear viscosity using the mean-square “displacement” of the time integral of the shear components of the stress-tensor²⁸

$$\eta = \lim_{t \rightarrow \infty} \frac{V}{20k_B T t} \left\langle \left(\sum_{\alpha\beta} (L_{\alpha\beta}(t) - L_{\alpha\beta}(0))^2 \right) \right\rangle, \quad (4)$$

where

$$L_{\alpha\beta}(t) = \int_0^t P_{\alpha\beta}(t') dt'. \quad (5)$$

This integral has the dimensions of an angular momentum, but, in a system with periodic boundary conditions, cannot be directly expressed in terms of particle positions and velocities.²⁸ Here we are applying to the Einstein relation the same generalized formulation adopted for the G-K formula in Eq. (1).

A direct numerical comparison of the two methods of calculating the shear can be made by rewriting Eq. (1) for the viscosity as a double integral of the time correlation of the $P_{\alpha\beta}$ tensor

$$\eta = \lim_{t \rightarrow \infty} \frac{V}{10k_B T t} \int_0^t dt' \int_0^{t'} dt'' \left\langle \left(\sum_{\alpha\beta} P_{\alpha\beta}(t'') P_{\alpha\beta}(0) \right) \right\rangle dt''. \quad (6)$$

Applying these two methods [Eqs. (4) and (6)] and using $\sigma_{\alpha\beta}$ expressed in terms of atomic or molecular variables, we can now calculate the shear viscosity as the limiting slope of four distinct curves that can be compared on a single plot. The equivalence of the results so obtained is demonstrated in Fig. 2. Again we observe early convergence of the running values of the four integrals.

In order to perform the calculation, we first record the value of the stress tensor components, in the atomic and molecular representation, at each time-step. Using fast Fourier transform, we can then easily calculate the stress correlation using all available information (typically $10^6 - 10^7$ data points). Even so, some care must be taken in the integration of the stress correlation which, in the atomic representation, exhibits strong oscillatory behavior: The fastest oscillations have a period of 50 fs which is only 10 times our integration time-step (5 fs); see Fig. 3. Because of these fast oscillations in the atomic stress autocorrelation, it is clear that a reduction in sampling could lead to serious errors in the evaluation of the G-K formula, Eq. (1) [or Eq. (6)]. In contrast, a practical advantage of the Einstein relation is that the time integration of the stress tensor components can be performed on-line and the integrated values saved every few steps with

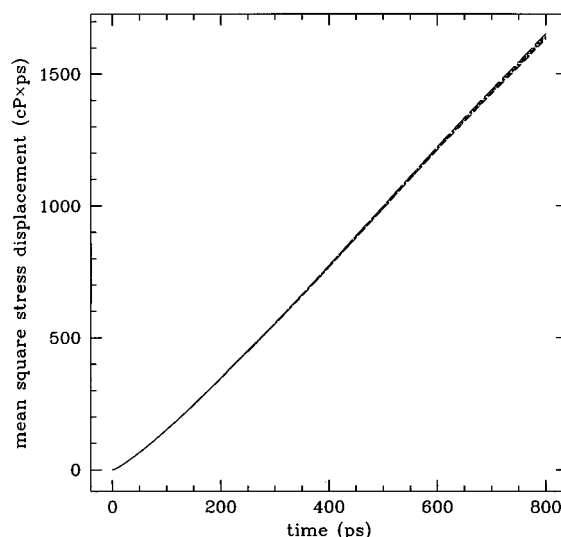


FIG. 2. Comparison of Green-Kubo and Einstein calculations [Eqs. (4) and (6)] for molecular and atomic shear-stress. Units are chosen so that the viscosity can be directly read from the slopes of the four curves. In the time range 400 to 800 ps (roughly 1 to 2 τ_R), the four values are all within 1% of their average: 2.18 cP. Note that this variation is one order of magnitude smaller than the statistical uncertainty.

no loss of information. Here, as in the case of the self-diffusion calculation, we are essentially constructing a random walk and all integration steps contribute equally to the final result. When using the G-K relation, on the other hand, we have to rely on the accurate integration of a rapidly varying function over a time interval much shorter than the entire simulation run.

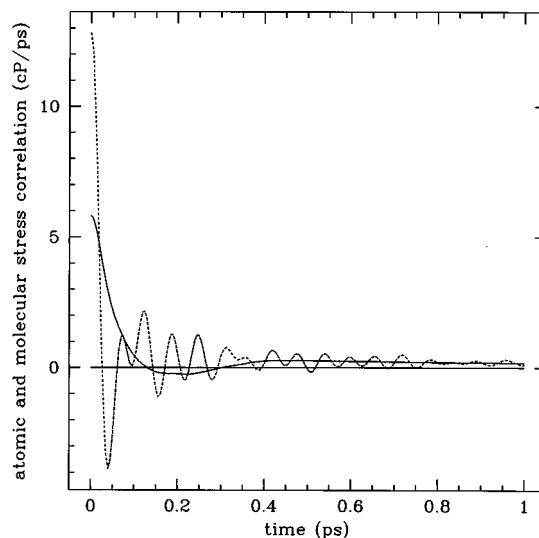


FIG. 3. Comparison of the short-time behavior of the time correlation functions of molecular (solid line) and atomic (dotted line) shear-stress. The integral of the two functions over the interval shown, 1 ps, is essentially identical (see inset of Fig. 1). We have also plotted here the time-correlation functions obtained averaging only the off-diagonal contributions from the molecular and from the atomic stress tensor. On the scale of the plot, at short times, these curves are indistinguishable from the total averages.

TABLE V. Self-diffusion (D), rotational diffusion (τ_R) and viscosity (η) results. Uncertainties in the last reported digit(s) are given in parenthesis. Data for systems of 64 molecules, unless otherwise specified.

Substance	Model	T	D_{EMD} (10^{-6} cm ² /s)	D_{exp}	τ_R (ps)	η_{EMD} (cP)	η_{exp}
<i>n</i> -decane	A	298	16.5(3)	14.0 ^a	57(2)	0.670(40)	0.8498(3) ^b
		298 ^c	15.8(2)	14.0 ^a	56.5(4)	0.664(15)	0.8498(3) ^b
		480	75(1)		10.4(2)	0.184(6)	0.196(6) ^d
<i>n</i> -decane	B	298	15.0(2)	14.0 ^a	49(1)	0.596(28)	0.8498(3) ^b
		298 ^c	14.20(15)	14.0 ^a	51.5(5)	0.612(15)	0.8498(3) ^b
		480	72(1)		9.5(2)	0.180(6)	0.196(6) ^d
<i>n</i> -hexadecane	A	298	5.76(8)	3.79 ^e	300(15)	1.68(25)	3.078(62) ^f
		323	9.2(1)	6.32 ^e	179(6)	1.11(10) ^g	1.845(37) ^f
		373	17.8(2)		84(3)	0.67(7)	0.895(18) ^f
<i>n</i> -hexadecane	B	298	3.75(5)	3.79 ^e	332(15)	2.18(30)	3.078(62) ^f
		323	6.3(1)	6.32 ^e	193(8)	1.37(14)	1.845(37) ^f
		323 ^h	6.61(5)	6.32 ^e	196(8)	1.49(10)	1.845(37) ^f
		373	13.6(2)		86(2)	0.68(4)	0.895(18) ^f
		373 ^h	14.5(2)		86(2)	0.72(7)	0.895(18) ^f

^aPulsed-field-gradient NMR result from our laboratories. The estimated uncertainty of the reported value is $\pm 10\%$. See Ref. 1.

^bFrom Table IX of Dymond and Øye (Ref. 29).

^cSystem of 32 molecules.

^dExperimental viscosity for pressures in the range 10–14 MPa, from Ref. 30.

^ePulsed-field-gradient NMR result from Ref. 31. The declared overall accuracy of the reported values is $\pm 2.5\%$.

^fFrom Table VI of Dymond *et al.* (Ref. 24). In parenthesis, we give the uncertainty corresponding to the declared accuracy of the measurements ($\pm 2\%$).

^gFor the same calculation, we previously reported a value of 1.14 cP (Ref. 32). The new (slightly different) value, 1.11 cP, and the associated statistical error were determined using the uniform procedure described at the end of Sec.V.

^hSystem of 128 molecules.

The calculation of the stress tensor in the atomic representation involves adding up non-bonded (LJ) and bonded contributions. For the UA model, the LJ contribution to the virial can be calculated by a straightforward application of Eq. (3). For the AUA model, care must be taken to properly account for the fact that LJ centers of force and atom positions do not coincide. To our knowledge this point has not been discussed before and technical details are presented in the Appendix. The bonded contributions to the virial are essentially the same for the two models and, following Eq. (3), can be expressed in terms of pairs interactions,²⁵ although the unsymmetrized version of the virial can also be used.⁵ Because we keep bond lengths constant, we need to include in the virial calculation the (large) contribution of the bond constraint forces.

V. DIFFUSION AND VISCOSITY RESULTS

Results for the self-diffusion coefficient D and the shear-viscosity η are collected in Table V, where we also list the values of the rotational relaxation time τ_R . The calculation of η was discussed in detail in the previous section. D is obtained from the slope of the mean-square displacement of the molecular center of mass, averaged over all the molecules (N_{mol}) in the system and all available initial times. Note that, in taking the average, the sum of the mean-square displacements for the N_{mol} molecules should be divided by

$N_{mol} - 1$, to account for the fact that the center of mass of the system does not move. An analogous procedure is necessary when calculating the velocity autocorrelation function.¹³ To calculate τ_R , we consider the first-order angular correlation of the longest principal axis of a molecule's ellipsoid of inertia. At intermediate times, this correlation (obtained again as an average over molecules and initial times) is well described by a simple exponential relaxation, uniquely characterized by the time constant τ_R (see paper I for details).

The diffusion results presented here are in agreement with those reported in papers I and II, but are statistically more accurate, due again to the more stringent requirements of the viscosity calculation. The differences between models A and B are confirmed. The diffusion constant for model A is systematically higher than model B, with the relative difference increasing for slower diffusion (longer molecule/lower temperature). It is also clear that model B describes the experimental results for hexadecane considerably better than model A. The new (and somewhat unexpected) result is that the viscosity values calculated in the two models are considerably closer than the diffusion values, that is, the product of viscosity and diffusion is different in the two models. Also, both models clearly underestimate the experimental viscosities at temperatures close to the (experimental) melting points of the materials investigated. Note, by contrast, that model A (using a harmonic potential to enforce bond connectivity) was found to reproduce the experimental viscosity

of *n*-decane at the high-temperature state point (480 K) listed in Table III (see Refs. 14 and 33). Using the fixed-bond-length version of the model, we calculate a value of η which is a few percent smaller than the previous calculations, but well within their reported accuracy (Table V). We also find that model B gives similar results to model A at this high temperatures.

Besides comparing with experimental results, valuable insights can be gained by a direct comparison of all the calculated constants in Table V. For *n*-hexadecane, we observe larger percentage differences between the self-diffusion constants of models A and B than observed for the corresponding τ_R or η values. For *n*-decane, we note that model A exhibits slightly higher self-diffusion and, at the same time, somewhat higher viscosity than model B. The τ_R values for the two models of *n*-decane match the trend in the viscosity (higher τ_R 's for model A) rather than the self-diffusion. These are the first indications of how the three quantities relate to each other, the central topic of the next section. They may also offer clues to the differences in the molecular factors controlling diffusion and viscosity. In papers I and II, we attributed the differences in calculated self-diffusion for models A and B to differences in dynamical flexibility (frequency of torsional rearrangements) of the two molecular models. Model A, more dynamically flexible, gives consistently higher diffusion constants. It should be stressed, however, that the main effect of increased dynamical flexibility is to reduce the temperature dependence of diffusion. This will typically lead to higher diffusion constants (for longer molecules) at low temperatures for the more flexible model, but the effect will become less marked (for shorter molecules) at higher temperatures. Furthermore, at any given temperature, the transport properties of a molecular system will also be affected by the "average" shape of the molecules. The results reported here and in papers I and II indicate that the differences in molecular geometry between models A and B (model B describes a more compact molecule) do not play a major role in determining the observed differences in their (translational) diffusion constants. On the other hand, as can be seen from the results in Table V, the product of the calculated viscosity and diffusion constants is consistently lower for model B and this seems to correlate with the more compact molecular structures (smaller R_g^2 's) obtained from this model.³⁴ Preliminary tests, however, indicate that a simple optimization of the torsional potential of model B is insufficient to provide an *n*-alkane model with the correct diffusion and viscosity as a function of *n* and *T*. A more global force field optimization is required.

A comparison of the results for different system sizes presented in Table V seems to indicate a slight tendency of *D* to increase with system size. This is consistent with results for butane obtained by Daivis and Evans.¹³ A corresponding size-dependence for η , if present, remains within the relatively large statistical uncertainties of our viscosity results. To establish a basis for estimating these uncertainties, we performed, for both models A and B, a 100 ns simulation using a system of 32 *n*-decane molecules at 298 K. This allowed us to perform block averages using 10 ns (≈ 200

τ_R) segments. The results of this analysis indicates that in order to obtain 10% statistical uncertainties in the calculated viscosity, runs of between 100 and 200 τ_R are necessary. If, as we believe, τ_R is the only relevant relaxation time in the problem and we make the conservative assumption that, for viscosity, statistical uncertainty is not reduced by increasing the system size, we can use this result to obtain a useful estimate of the statistical error for all the systems and state points investigated. One should also keep in mind that there is a trade-off between trying to minimize statistical and systematic errors of viscosity (and diffusion) calculations. For example, if one obtains the viscosity using the Einstein approach (Fig. 2), it is important to take the slope of the corresponding curve(s) at the earliest possible time, to minimize statistical error, and at late times to reduce systematic effects. We find that taking the slope between τ_R and $2\tau_R$ is a reasonable compromise at the level of accuracy of our calculations. Furthermore, when comparing different models and/or state points, it is important to adopt a consistent procedure. For the systems of 32 (*n*-decane) molecules, we find that the statistical errors for *D* and τ_R are only 2 to 3 times smaller than for η . These errors are however expected to scale as the inverse square root of the system size.

VI. CONNECTION WITH ROUSE DYNAMICS OF POLYMERS

The characteristic relaxation time τ from the Rouse model of polymer dynamics³⁵ is

$$\tau = \frac{12M\eta}{\pi^2\rho RT}, \quad (7)$$

where ρ is the density of the system, *M* is the molecular mass and *R* the gas constant. Within the context of NEMD viscosity calculations of alkanes,^{8,12} τ was shown to provide a good estimate of the critical shear rate ($\gamma_c = 1/\tau$) that characterizes the transition between the Newtonian and the non-Newtonian (shear-thinning) regime of the viscosity curve as a function of shear-rate.³⁶ It is physically reasonable to expect, and has been verified numerically,⁵ that the inverse of the rotational-diffusion time (τ_R) is also a measure of the same characteristic shear-rate. For short (unentangled) linear chains, it is natural therefore to invert Eq. (7),

$$\eta_\tau = \frac{\pi^2\rho RT}{12M} \tau_R, \quad (8)$$

and use it to estimate the system viscosity from the calculated rotational diffusion.³⁷ From a practical standpoint, the main advantage is that the calculation of the rotational diffusion, a single-particle property, can be expected to have a faster statistical converge than the direct viscosity calculation. The results listed in Table VI confirm this expectation and clearly indicate that this method provides a semi-quantitative way of estimating viscosity of linear (or quasi-linear) molecules. To become fully quantitative, we would have to account for the relatively small (<20% for *n*-hexadecane) discrepancies observed, which are state-point and model dependent. This approach could be particularly

TABLE VI. Comparison of estimated (η_D and η_τ) and calculated viscosity (η_{EMD} and η_{NEMD}). η_τ is obtained from Eq. (8) and η_D from Eq. (9). η_{EMD} and η_{NEMD} are calculated using equilibrium (this paper) and non-equilibrium MD methods respectively. N_{mol} is the number of molecules used in each of our simulations.

Substance	Model	N_{mol}	T (K)	η_D (cP)	η_τ	η_{EMD}	η_{NEMD}^a
<i>n</i> -decane	A	64	298	0.15(1)	0.591(12)	0.670(40) ^b	0.61(8) ^c
		32	298	0.15(1)	0.587(4)	0.664(15) ^b	0.61(8) ^c
		64	480	0.04(1)	0.147(2)	0.184(6) ^d	0.197(10) ^e
<i>n</i> -decane	B	64	298	0.15(2)	0.510(10)	0.596(28)	
		32	298	0.16(1)	0.535(5)	0.612(15)	
		64	480	0.04(1)	0.134(3)	0.180(6)	
<i>n</i> -hexadecane	A	64	298	0.64(3)	2.09(10)	1.68(25)	1.63(28) ^c
		64	323	0.41(2)	1.32(4)	1.11(10)	1.24(12) ^c
		64	373	0.23(1)	0.68(2)	0.67(7)	
<i>n</i> -hexadecane	B	64	298	0.87(4)	2.31(10)	2.18(30)	
		64	323	0.54(2)	1.42(5)	1.37(14)	
		128	323	0.52(2)	1.43(4)	1.49(10)	
		64	373	0.27(1)	0.699(14)	0.68(4)	
		128	373	0.25(1)	0.70(2)	0.72(7)	
<i>n</i> -tetracosane	A	100	333	1.2(2) ^g	2.8(5) ^g		2.56(35) ^c
squalane	A	100	333	2.7(3) ^c	5.2(6) ^h		5.4(5) ^f

^aFor direct comparison, we performed (Ref. 38) fixed-bond NEMD simulations of model A of *n*-decane ($N_{mol}=32$, $\eta=0.680(42)$) at 298 K and *n*-hexadecane ($N_{mol}=100$, $\eta=1.71(14)$) at 300 K, using the 298 K density). This state point for *n*-hexadecane was also used in Ref. 5.

^bFor model A with harmonic bond potential (A_{hb}), Cui *et al.* (Ref. 5) reported a G-K calculation using a system of 100 molecules: 0.64(5) cP.

^cFrom Ref. 5, model A_{hb} .

^dThe results of two G-K calculations for model A_{hb} were reported: 0.190(15) cP (Ref. 14) and 0.191(12) cP (Ref. 33).

^eFrom Ref. 33, model A_{hb} .

^fFrom Gupta *et al.* (Ref. 39), model A_{hb} .

^gFor these viscosity estimates we have used the results already presented in paper I (1.5 ns run).

^hHere we have used the results of a new 10 ns run: $\tau_R = 1.24$ ns and $D = 1.53 \cdot 10^{-6}$ cm²/s. From the results presented in paper I (3 ns run) we obtain $\eta_\tau = 4.8(9)$ cP.

useful in situations (state-points/molecules) for which an accurate ($\leq 10\%$) full calculation is impractical. It should be made clear that this is a non-trivial result, since the alkanes considered in this study are too short to be treated as Rouse chains. The equilibrium configurations are not Gaussian, as can be seen (Table IV) by the *n*-dependence of the shape parameters (l_i^2) and of the R_{ce}^2/R_g^2 ratio (> 6). If we attempt to estimate the viscosity using the molecular self-diffusion constant D and square radius of gyration R_g^2 ,³⁵

$$\eta_D = \frac{\rho R T R_g^2}{6 M D}, \quad (9)$$

we grossly underestimate the viscosity obtained by direct calculation (see Table VI), even though Eqs. (8) and (9) are equivalent for a Rouse chain. From the data it is also apparent, however, that these discrepancies decrease with increasing chain length. This is confirmed when applying Eqs. (8) and (9) to the diffusion data for longer chains.⁴⁰ For the longest chain we have studied, *n*-C₆₆, the two formulas lead to consistent estimates for the viscosity.⁴⁰ In the language of polymer dynamics, these results indicate that, for short alkanes, the monomeric friction coefficients associated with

rotational and translational diffusion⁴¹ are different and that they will converge as the molecule becomes longer and the chain's conformations more Gaussian. A similar point was made by Paul *et al.*⁴² in their analysis of the diffusion dynamics of *n*-C₄₄. Here we can add that the monomeric friction coefficient associated with the rotational diffusion appears to exhibit a much weaker *n*-dependence than the coefficient for the translational diffusion. As a test of the range of applicability of our methodology, in Table VI we also compare η_D and η_τ for tetracosane and squalane with the corresponding NEMD results.

VII. COMPARISON OF EMD AND NEMD METHODS

One important question that we would like to address is what is the best option for practical viscosity calculations for linear and branched alkanes; in particular, if it is more efficient to use NEMD or EMD techniques. Neglecting any methodological difficulties with NEMD methods,¹⁶ one can ask which is more efficient in terms of CPU time for a given level of statistical accuracy. From a conceptual standpoint, EMD viscosity calculations are no more difficult than diffu-

sion calculations. Equilibrium calculations for the two quantities can in fact be performed, as indicated in Sec. IV, along very similar lines. From a practical standpoint, the only crucial difference between diffusion and viscosity is the amount of computational effort required to achieve a given level of (statistical) accuracy in the calculation.⁴³

In the following we assume that the characteristic relaxation time that defines the minimum integration interval required for the G-K (or Einstein) calculations of viscosity and diffusion is essentially the same. To within a factor of order one, we could use in both cases the rotational diffusion time (τ_R). This indicates that, independently of system size, the length of the MD run should not be less than $\approx 2\tau_R$. The value of diffusion that we calculate in an EMD simulation of this length is then obtained as an average over the diffusion (mean-square displacement to $\approx 2\tau_R$) of all the molecules in the system (typically ≈ 100 in our simulations) along the three Cartesian directions (for a total of ≈ 300 independent contributions): diffusion is a single-particle property. Shear viscosity, however, is a collective property of the system. For a statistically isotropic system this means that, regardless of size, there are only five contributions to average: the independent components of the symmetrized, traceless portion of the stress-tensor (the trace itself gives the pressure of the system). This would indicate that to obtain the same level of precision in a viscosity calculation it may be necessary to run the system up to ≈ 60 times longer than for a diffusion calculation (≈ 60 ns instead of ≈ 1 ns). The relative difference between the two calculations may in practice be less than suggested by this rough estimate: Spatial correlations between molecules tend to reduce the effective number of independent contributions to the diffusion calculation. By performing very long equilibrium calculations 50–100 ns) for *n*-decane and *n*-hexadecane at room temperature, we have determined more precisely the time required to obtain a given statistical precision for a viscosity calculation (see end of Sec. V). This also allows us to compare the relative efficiency of equilibrium and non-equilibrium MD calculations of viscosity for a higher range of values (1–5 cP) than previously considered.

A comparison of efficiency between the two methods also involves a determination of how finite-size effects depend on molecular chain-length. Since larger systems are required to simulate longer alkanes, it is important to ascertain if the statistical variance of the viscosity in the EMD calculation is in fact independent of the system size, as our previous argument assumes. Numerical evidence for atomic Lennard-Jones systems suggests that, for typical system sizes, this is in fact the case.⁴⁴ While we have not attempted a systematic study of this point, which would require substantially longer simulations for larger systems than reported here, it does appear that this holds true for our systems. The variance of the viscosity calculated by NEMD, on the other hand, appears to exhibit a $N^{-1/2}$ dependence,⁴⁴ where N is the number of particles in the system, making possible a trade-off between system-size and length of the simulation and significantly reducing the limitations of finite-size effects

(longer transients may still be expected for simulations of larger systems).

Currently, the more widely applied NEMD method for shear-viscosity calculation involves the imposition of a velocity gradient across the simulation cell so as to describe a system under Couette flow.^{5–12} This corresponds to the application of a constant strain-rate on the system and the calculated quantity (response) is the associated shear-stress. Viscosity is obtained as the ratio of stress over strain-rate. A second strategy involves the shearing of a system confined between plates, where we must distinguish between the (nominal) shear-rate of the plates and the actual strain-rate induced in the confined liquid.³² Commercial MD codes, such as MSI CERIUS2 and DISCOVER3⁴⁵ programs, offer a different approach: A constant (external) shear-stress is applied and the induced strain as function of time (and therewith the strain-rate) is measured. A main limitation of this methodology, as presently implemented, is the difficulty of performing steady state measurements and, therefore, of effectively separating systematic and statistical uncertainties in the calculation.

All non-equilibrium methods require in principle to extrapolate to zero-shear (i.e. equilibrium) viscosity using several data point obtained at varying shear-rates. Shear thinning behavior is observed at shear-rates larger than the inverse rotational-diffusion time. While various schemes have been proposed to extrapolate the Newtonian (shear-independent) viscosity from the high-shear data, this procedure appears to be the greatest source of uncertainty for high precision calculations.⁴⁶ Cui *et al.*⁵ have recently used NEMD to determine the shear viscosity of C_{10} , C_{16} and C_{24} , close to their respective (normal pressure) melting temperatures. Their results seem to indicate that the high-shear data are not very sensitive to the significant mass and limited temperature variations considered: Important information is lost in the shear thinning regime. This makes it difficult to accurately determine viscosity without actually entering the Newtonian regime, where extrapolation becomes unnecessary. As indicated above, the rotational-diffusion time controls the transition between Newtonian and shear-thinning regime and an accurate NEMD simulation in the Newtonian regime (of which 2–3 would be necessary) may therefore require averaging times $\geq 10\tau_R$ for each shear-rate. EMD simulations are controlled essentially by the same time scale and typically require averaging times $\geq 100\tau_R$, depending on accuracy required. This analysis seems to indicate that, for comparable system size, NEMD simulations may have a slight advantage versus EMD simulations with regard to the determination of shear viscosity for the systems of interest (assuming no overhead, such as a reduction in time-step in the NEMD simulations), but the extra effort required by the EMD approach seems more than justified if other equilibrium (transport) properties are of interest. Also, methodological issues regarding the thermostating of systems of flexible molecules under shear¹⁶ will need to be resolved, in order to confidently apply the NEMD approach to large molecules. On the other hand, if we are specifically interested in studying how flow modifies static molecular properties and,

more generally, in order to gain physical insight into the molecular processes influencing viscosity, NEMD simulations may be required. The application of shearing plates also requires that one carefully check the dependence of the results from the inter-plate separation, since confinement effects are known to be important.³⁵

VIII. CONCLUSIONS

We have performed extensive simulations of linear alkanes to assess the practical feasibility of EMD viscosity calculations in the cP viscosity range (about ten times higher than previously considered with EMD). Our results show that equilibrium methods, while somewhat more computer intensive than equivalent NEMD calculations, remain competitive in this viscosity range.⁴⁷ As part of this work, we have demonstrated the numerical equivalence of the Green-Kubo and Einstein approach to the calculation of viscosity (in both the molecular and atomic representations) and established a practical criterion for estimating the statistical uncertainty of the viscosity calculation, based on the length of the simulation run in units of τ_R . An analysis of the relation between self-diffusion, rotational diffusion and shear viscosity was conducted in the framework of the Rouse model of polymer dynamics, leading to the establishment of a practical, semi-quantitative way of estimating viscosity from the results of comparatively short diffusion calculations. Finally, the quantitative comparison between the two models of *n*-alkanes investigated offers insights into the different molecular factors controlling diffusion and viscosity, while clearly pointing to the need of further (global) optimization of the force field parameters.

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APPENDIX: ATOMIC STRESS TENSOR FOR AUA MODEL

In the AUA model, each LJ-interaction force center (*c*) is shifted a distance *d* from the reference atom (*c0*):

$$\mathbf{r}^c = \mathbf{r}^{c0} + d\mathbf{n}(\mathbf{r}^{cj}), \quad (\text{A1})$$

where the orientation of the shift vector (**n**) is a function of the position of *c0* and its nearest-neighbors, comprising together the base atoms (*cj*). The calculation of the LJ contribution to the atomic stress tensor can now be performed in two stages. First, following Eq. (3), we can add up the contributions to the tensor of individual pairs of interaction centers, using the minimum-image pair distance. Then, the accumulated forces on each center (**r^c**) can be transferred to the base atoms (**r^{cj}**) and, concurrently, the corresponding correction to the stress tensor can be made. The force transfer involves assigning the accumulated values for the force center (**f^c**) to the “bonded” atom (**r^{c0}**) and adding shift-

dependent corrections (**f^{cj,c}**) to the same atom and its bonded neighbors (base atoms). Because the transfer of forces from the LJ centers to the base atoms is equivalent to a bonded intramolecular interaction, the minimum-image convention is here trivially satisfied (as for all bonded forces). The corresponding (virial) correction to the (α, β) component of the stress tensor can then be expressed as

$$\sum_c \sum_{cj} f_{\alpha}^{cj,c} (r_{\beta}^{cj} - r_{\beta}^{c}), \quad (\text{A2})$$

where the $f_{\alpha}^{cj,c}$ depend linearly on *d* and $\sum_{cj} \mathbf{f}^{cj,c} = \mathbf{0}$. As usual, the complete stress tensor in the atomic representation is strictly symmetric.

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hand, suggests an inverse relation between the product of D and η and the characteristic molecular dimension R , $D\eta \approx K_B T/R$. Note also that, if we consider the limit of Gaussian chains and identify R with R_g , the Stokes-Einstein equation would predict a different chain-size dependence for η and D (Ref. 48). This is in contradiction with the well established Rouse scaling of unentangled polymer dynamics (Ref. 35).

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⁴⁷Upon completion of this paper, we received a manuscript by S. T. Cui which presents G-K calculations of viscosity for model A of *n*-hexadecane, at the 323 K state point, and *n*-decane at 298 K. A comparison of EMD and NEMD techniques for the calculation of viscosity is presented. The general conclusions of the paper, in this regard, agree with ours. The author indicates the possibility of long transients in the establishment of the asymptotic viscosity values for *n*-alkanes using the G-K formula. As discussed in Sec. V, choosing the appropriate region of the G-K or Einstein plot to use for the estimation of viscosity involves a trade-off between statistical accuracy and systematic errors. We feel that our choice of using the τ_R to $2\tau_R$ region of the plot is a reasonable compromise at the typical level of accuracy ($\approx 10\%$) of our calculations. As more statistically accurate calculations become (routinely) available, the entire issue of systematic errors in viscosity estimation will need to be reassessed.

⁴⁸S. Milner (personal communication).