Thermodynamics and transport properties of *n*-butane computed by molecular dynamics using a rigid interaction model

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With a simple rigid four-center interaction model we computed the thermodynamics and transport properties of liquid *n*-butane by equilibrium molecular dynamics. Unlike previous works, which investigated only one state near the boiling point with semiflexible models, this work considers six states ranging from the boiling point to the triple point. In contrast to the studies based on semiflexible potential models, our calculations give good agreement with experiment for states near the boiling-point state. Reasonable agreement with experiment was achieved for the pressure and the shear viscosity at denser states near the triple point. The equilibrium time-correlation functions were computed for different shapes of the model molecules. Their time dependence leads to interesting conclusions concerning the anisotropic behavior of the molecules in the liquid state. Unlike the correlation functions, the transport coefficients were found to be nearly independent of the molecule shape. This explains partially why our rigid potential model is successful.

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I. INTRODUCTION

Ryckaert and Bellemans introduced the semiflexible four-center model potential for computation of several properties of liquid *n*-butane in 1975 [1]. Since then this potential or related ones were used throughout to compute static or dynamic properties of *n*-alkanes by equilibrium as well as nonequilibrium molecular-dynamics (MD) methods [2–4]. Whereas the semiflexible model could reproduce satisfactory equilibrium properties and the self-diffusion coefficient [1–4], it did not prove to generate the experimental collective transport coefficients in reasonable approximation (see, for example, Ref. [3]). For the boiling point of *n*-butane, the model gives too large shear viscosity values [2–4].

Very recently, Chynoweth, Klomp, and Michopoulos [5] obtained a reasonable shear viscosity of *n*-butane at the boiling point using a flexible model involving stretch potentials between the C—C bonds. However, the collective time-correlation functions, which are of essential importance for understanding the transport processes, were not studied in that work. Furthermore, the flexible model is rather complex both for MD performance and for distinguishing physical mechanisms.

Marechal, Ryckaert, and Bellemans [3] first observed the long-time behavior of the time-correlation function for the shear viscosity of *n*-butane. It is now clear that this kind of long-time tails is typical for liquids composed of anisotropic molecules. The long-time behavior makes it difficult to determine the viscosity accurately by MD [6–8], particularly near triple-point conditions where the *n*-alkane liquids were not yet investigated by MD.

We show here that a simple *rigid* four-center interaction model leads to acceptable thermodynamics and reasonable transport coefficients when the Green-Kubo integrands are determined with enough precision to account for the long-time behavior. The computations were done for several liquid states of *n*-butane in order to show unambiguously the usefulness of the present potential model.

In particular, we investigate the effect of the molecular shape on the collective time-correlation functions and the resulting transport coefficients. The long-time behavior of time-correlation functions for the shear viscosity is discussed in detail.

II. MODEL POTENTIALS AND MD CALCULATIONS

For the MD calculations, we assumed rigid four-center molecules interacting via center-center Lennard-Jones (LJ) pair potentials, which may be written in the following form:

$$U_{\mathrm{LJ}}(\alpha,\beta)=4\epsilon\sum_{i=1}^{4}\sum_{j=1}^{4}\left[\left[\frac{\sigma}{r_{ij}^{\alpha\beta}}\right]^{12}-\left[\frac{\sigma}{r_{ij}^{\alpha\beta}}\right]^{6}\right],$$

where α,β denote molecules and i,j denote "atomic" centers, namely, a methyl or a methylene group. The σ and ϵ denote the LJ potential parameters of the center-center interactions.

Two different shapes of the *n*-butane molecule were investigated: a flat (*trans*) one [Fig. 1(a)], with all the four

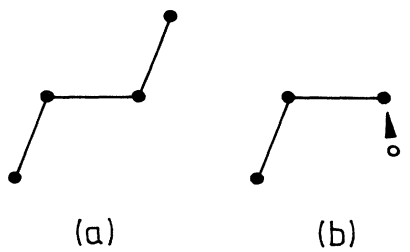

FIG. 1. Two rigid models of the *n*-butane molecule.

TABLE I. Parameters of the four-center rigid Lennard-Jones potential models for the molecular interaction in liquid n-butane.

Model	Bond length (10^{-10} m)	ϵ/k_B (K)	σ (10^{-10} m)	Bond angle (deg)	Dihedral angle (deg)
S	1.53	72	3.923	109.5	60
F	1.53	72	3.923	109.5	180
F1	1.53	72	3.870	109.5	180

atoms in the same plane, and a spatial (*gauche*) one [Fig. 1(b)] with a 60° dihedral angle. In real liquids, these two configurations correspond to the stable and metastable structures of the n-butane molecules, respectively. In order to facilitate comparison with other works, we adopted potential parameters as well as the bond length and angle from Ref. [4]. As usual [1,4,5], the four interaction sites were furthermore assumed to bear equal masses of 2.41×10^{-26} kg. The two resulting rigid models shall be abbreviated here by F model and S model. As will be seen later, the F model did not lead to fully satisfactory pressure; the σ was therefore optimized in test MD runs to reflect the experimental thermodynamic properties. The new flat model is denoted by F1 model. All the potential and structure parameters of the various models are listed in Table I.

The method of constraints was used for our MD performance exploiting vector and bond constraints for the flat molecule models and solely bond constraints for the S model [9]. Our fully vectorized form of the MD program has been described elsewhere [10]. We list the technical details of the present runs in Table II.

MD systems with 108 molecules are used throughout in this work, while 32 molecule systems [11] proved to be too small to achieve thermal equilibrium at high density. Because we wanted to pay much attention to the collective long-time behavior of the relevant time-correlation functions which requires heavy computations, we did not try to use larger systems.

We studied six dense thermodynamic states of the saturated liquid n-butane including a near triple-point state. These states represent nearly zero-pressure states for which the experimental transport coefficients are reported [12,13]. We note that the boiling-point states investigated in Refs. [1–5] differ a bit, but can be regarded as identical for our present purpose of comparison. Experimental shear viscosity values seem not to be available for the triple-point state of n-butane.

As we use equilibrium MD to study the transport properties, the Green-Kubo integrals over the relevant equilibrium time-correlation functions determine the transport coefficients. The Green-Kubo expressions used in this work have been discussed at length in Refs. [2] and [15] and shall not be repeated. For common liquid states, the Green-Kubo integrals converge rapidly to the asymptotic values which give the transport coefficients. However, for states in the broader neighborhood of the triple point of molecular liquids, the time-correlation functions for the shear and bulk viscosities take on an awkward chair form and display a long-time behavior, which makes it very difficult to obtain the plateau value of the time integral [6,8]. So each MD study of the viscosity of molecular liquid must pay attention to the reliable determination of the corresponding time-correlation function.

III. RESULTS

A. Thermodynamics

For the states mentioned above, we have computed the pressure using our rigid models. Furthermore, we calculated the internal energy for the boiling-point state to compare with other MD works based on semiflexible models. Our results, which are given in Tables III and IV, include long-range corrections as described in Refs. [6] and [14]. Roughly speaking, all of the models can reproduce reasonable thermodynamics in respect to the large uncertainties incorporated in the MD results. In particular, the thermodynamic properties of the boiling-point state are well represented by the rigid as well as the semiflexible models, as expected, due to the relatively low density. However, a tendency of the F model to produce higher pressure, especially at higher density, is noticeable, while the F1 model and S model give "exact" results compared with experiment.

TABLE II. Technical details of the MD computations.

Number of molecules (N)	108
Number of interaction centers	4
Time step	0.5×10^{-14} s
Number of time steps	2×10^5–10^6 for transport coefficients
after equilibration	5×10^3–10^4 for pressure and $C_2(t)$
Starting configuration	liquidlike
Cutoff radius for the	2.5σ–4.8σ
LJ potential	(standard 3.0σ)
Computation time	119s ($N=108$, S model)
per 1000 steps (Cyber 205)	107s ($N=108$, F and F1 models)

TABLE III. States and pressure of liquid n-butane computed by MD with the rigid four-center LJ models. The chosen states are practically zero-pressure states.

State	Temperature (K)	Density ($g\,cm^{-3}$)	Pressure (bar) S model	F model	F1 model
1	283	0.6010	50±150	150±150	100±150
2	223	0.6519	50±200	250±200	50±200
3	213	0.6616	70±200	250±200	0±200
4	203	0.6712	80±250	300±250	50±250
5	193	0.6807	150±250	350±250	50±250
6	183	0.6900	180±250	380±250	−50±250

B. Time-correlation functions

1. Near the boiling point

For state 1, we plot the normalized time-correlation functions (TCF's) of the shear viscosity η_s and the Green-Kubo integrals $\eta_s(t)$ of the three n-butane models in Figs. 2 and 3. The integrals are so normalized that $\eta_s(\infty)=\eta_s$. Since the amplitude of the TCF's at long times will be too small to be demonstrated, we omitted them in the TCF plots. Instead, we show their effect more clearly via the time dependence of the Green-Kubo integrals in Fig. 3.

As seen in Fig. 2, the TCF's of the two flat models are practically equal. The difference in the σ of these two models is in fact negligible at lower density. Furthermore, the TCF's of a flat and a spatial model differ essentially in the short-time range of 0.3 ps as shown in Fig. 2. The TCF of the S model decays monotonically at short times, while the TCF's of the flat models decay in an oscillatory manner. This difference of the short-time behavior of the TCF's is clearly a result of the different anisotropy of the models. This is in accordance with all our previous findings: globular, not very anisotropic molecule models lead to straightforwardly decaying TCF's, whereas linear, flat, or complex structured models show an oscillating short-time decrease (see, for example, Refs. [6,15,16]).

2. Near the triple point

At high density, a more complex situation arises for the TCF's of the shear viscosity and their integrals. An example is shown for state 6 in Figs. 4 and 5.

At short times ($t<0.5$ ps) the TCF's of the three models behave in the same way as in the case of lower density, namely, a monotonic decay for a spatial model and an oscillatory decay for a flat model. However, the long-time behavior of the TCF's is completely different from that near the boiling point. For states 2–6, the TCF's keep a weak positive amplitude up to more than 10 ps. The computation of such remarkable long-time behavior requires extremely long MD runs, obviously longer than for benzene and cyclohexane [6,8]. It is of interest to note that the TCF's of the F and F1 models have more pronounced long-time tails than that of the S model. This confirms what we have previously observed for liquid nitrogen [16], that more anisotropic molecules lead to an enhanced long-time behavior. In contrast to the low-density case, the TCF's of the two flat models differ considerably, excepting the short-time range. So the effect of σ becomes much more important at high density.

C. Shear viscosity coefficients

States near the boiling point cause no problems for the evaluation of transport coefficients. As shown in Fig. 3, the Green-Kubo integrands of all the three rigid models converge to their plateau values within 3–4 ps. In fact, the integrals reach about 90% of the total already during the first 2 ps.

By contrast, the evaluation of the shear viscosity at high density is very difficult both with respect to the MD runs and their statistical analysis. In view of the long-time behavior discussed in Sec. III B, it was necessary to integrate the TCF's for η_s up to more than 10 ps.

The η_s integrals of the three models approach their asymptotic limits in very different ways, as shown in Fig.

TABLE IV. Thermodynamics properties of liquid n-butane near the boiling point.

	Present work	Ref. [2]	Ref. [4]	Experiment
Temperature (K)	283	273	291	273
Density ($g\,cm^{-3}$)	0.601	0.601	0.583	0.601
Pressure (bar)	50±150 (S) 150±150 (F) 100±150 (F1)	127	480	1
Internal energy (units of Nk_BT)	−8.6 (S) −8.5 (F) −8.4 (F1)		−10.3	−8.8

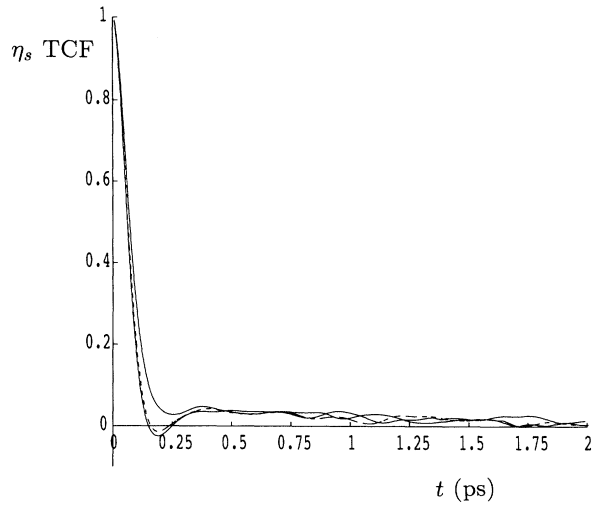

FIG. 2. Shear viscosity TCF of model liquid *n*-butane for state 1. Upper line, S model; dashed line, F model; lower line, F1 model.

5. While the $\eta_s(t)$ of the S model reaches nearly 90% of the coefficient in the first 4 ps, only about 75% of the total integrals of the flat models is reached within 4 ps and the contribution after 8 ps is still about 20%. This suggests clearly that the long-time contribution to the shear viscosity becomes more important when the fluid contains molecules of stronger anisotropy, as we discussed earlier [7,8].

Differences between η_s values of the three models lie generally within the mutual error limits. Hence, in comparison with the normalized TCF's, the molecular shape dependence of the transport coefficients appears to be small. The insensitivity of the shear viscosity to the molecular conformations was also observed by Edberg,

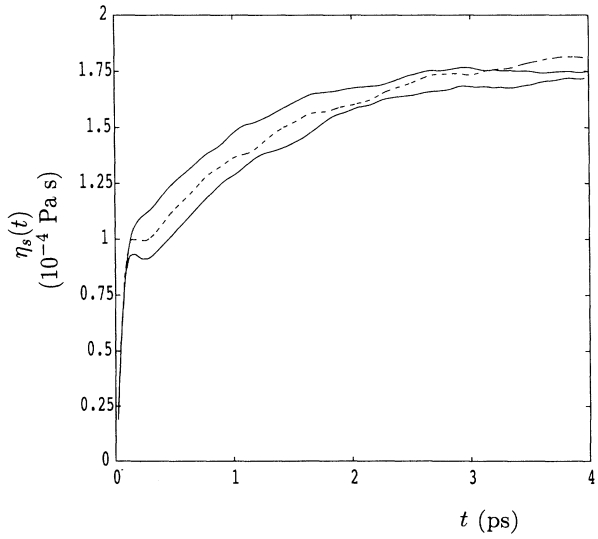

FIG. 3. Integral of the η_s TCF of model liquid *n*-butane for state 1. Upper line, S model; dashed line, F model; lower line, F1 model.

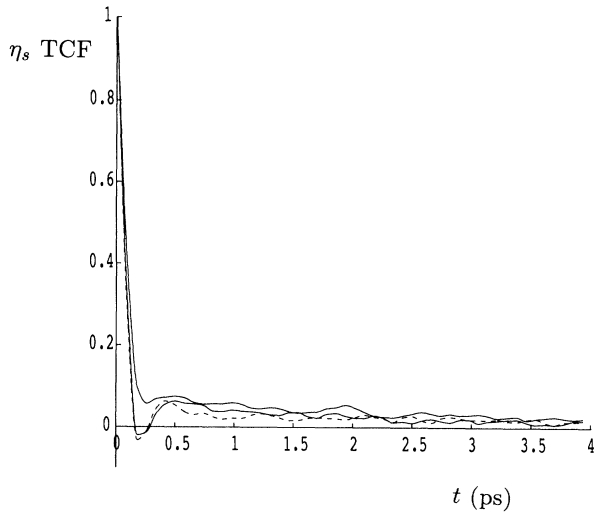

FIG. 4. Figure 1, but for state 6.

Morriss, and Evans [4] for the semiflexible *n*-butane models at the boiling point conditions, where fully *trans* as well as *gauche* models (corresponding to our F and S models, respectively) were investigated by nonequilibrium MD. That the F model with longer molecules predicts slightly higher shear viscosity than the S model is also in agreement with the results for their semiflexible counterparts [4]. Furthermore, the "thinner" F1 model generates smaller shear viscosity than the "thicker" F model, as expected.

For all the six states of *n*-butane considered in Table III, we compare the computed shear viscosity coefficients with the experimental values in Table V. The MD results of the shear viscosity are on the whole reasonable for both flat and spatial models. Especially, the agreement with experiment near the boiling point is excellent. However, at higher density a systematically lower shear viscosity is predicted by the rigid models.

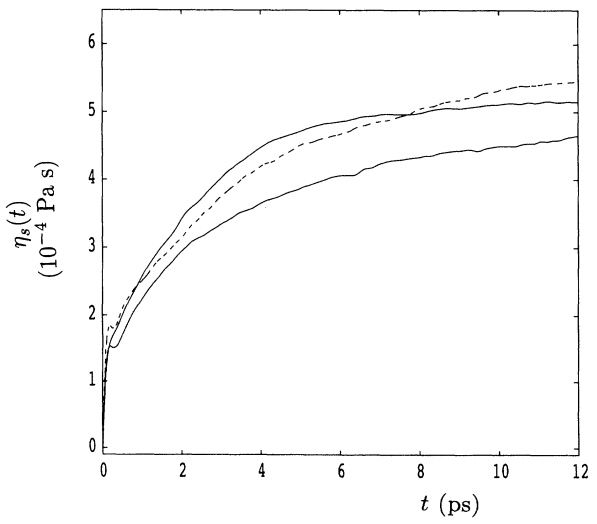

FIG. 5. Figure 2, but for state 6.

TABLE V. Shear viscosity coefficients computed for the three rigid model *n*-butane liquids compared with experimental results.

	$10^4\eta_s$ (Pa s)			
State	S model	F model	F1 model	Experiment
1	1.7±0.2	1.8±0.2	1.7±0.2	2.0
2	3.0±0.2	3.1±0.2	2.9±0.2	3.5
3	3.3±0.5	3.5±0.5	3.2±0.5	4.0
4	4.2±0.7	4.3±0.7		4.6
5	4.7±0.7	4.8±0.7		5.3
6	5.2±1.0	5.6±1.0	4.8±1.0	6.3

IV. CONCLUSIONS AND DISCUSSIONS

In contrast to the semiflexible model, which failed to give satisfactory collective transport coefficients, the rigid model proposed here leads to reasonable thermodynamic and transport properties of *n*-butane in a wide range of liquid states. In particular, acceptable shear viscosity coefficients were obtained even for states near the triple point. However, for the latter states, care must be taken of the awkward long-time behavior of the η_s TCF's.

Our calculations of the three rigid models demonstrate how the collective time-correlation functions are affected by the molecular structure. In particular, the long-time behavior of the η_s TCF's was found to be conformation dependent. The long-time behavior appeared to be more significant in liquids composed of flat molecules than in those of spatial molecules. This is in accordance with all our previous findings for nitrogen and benzene, as well as cyclohexane liquids [6–8,16]. The long-time behavior becomes more pronounced for increasing anisotropy of the molecule.

It is of interest to compare the η_s TCF's functions of the rigid models with those of the semiflexible model. For the latter, the only existing result is that of Marechal, Ryckaert, and Bellemans [3] for the liquid *n*-butane at the boiling point. A comparison of the η_s TCF's and their normalized integrals can be made in terms of Figs. 1a and 2a of Ref. [3]. The plots in Figs. 1a and 2a are, in fact, in good agreement with those of our Figs. 2 and 3. However, the "long-time tail" stressed by Marechal, Ryckaert, and Bellemans is not comparable with the long-time behavior near the triple point discussed in our works. The tail behavior found by Marechal and coworkers is in fact a "usual" decay of the η_s TCF's in molecular systems far away from the triple point in view of our recent findings that the η_s TCF's show long-time behavior of around 10 ps at states near the triple point.

In our recent work [7], we were indeed able to relate the strong orientational correlations in dense molecular fluids to the long-time behavior of the collective TCF's. Furthermore, the reorientational TCF's were found to have similar long-range behavior as the η_s TCF's in dense nitrogen, benzene, and cyclohexane liquids [6–8]. In this work, the second-order reorientational TCF $C_2(t)$ was also calculated for unit vectors parallel to the methyl-methyl axes of the *n*-butane molecule. The $C_2(t)$ TCF's of all the three models were found to have a tail behavior comparable to that of the η_s TCF's. This confirms our idea discussed in detail in Ref. [7]. In particular, the decay times of the two kinds of TCF's agree well. So $C_2(t)$, which is a one-particle TCF that can be easily evaluated by short MD runs, can be exploited to estimate the time range necessary for the η_s Green-Kubo integration. This recipe was used successfully in our works [6,8].

Compared with the normalized η_s TCF's, only slight differences were found between the shear viscosity coefficients of the various rigid models. The insensitivity of the shear viscosity to the molecular conformation explains partially why our rigid model is successful.

The molecule number dependence, which was found to be significant for nonequilibrium MD calculations [5], is likely to be small in equilibrium MD. Our equilibrium MD studies [6,8] indicated little influence of the molecule number on the results, if systems larger than 108 molecules are used. So the present results, which are based on systems with 108 molecules, cannot be improved with use of larger MD systems.

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