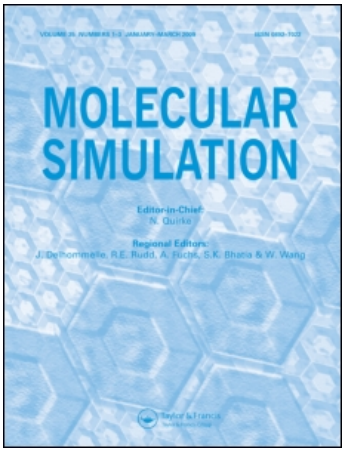

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Non-Equilibrium Molecular Dynamics Calculation of the Shear Viscosity of Carbon Dioxide/Ethane Mixtures

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NON-EQUILIBRIUM MOLECULAR DYNAMICS CALCULATION OF THE SHEAR VISCOSITY OF CARBON DIOXIDE/ETHANE MIXTURES

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Non-equilibrium molecular dynamics simulations of the shear viscosity of mixtures of carbon dioxide and ethane at a fixed total density (20 mole-dm^3) and at five compositions ranging from pure carbon dioxide to pure ethane are reported. In this study, two-site Lennard-Jones potential models are used for all the inter-molecular interactions. The cross parameters of ethane/carbon dioxide potential have been fitted to the azeotrope of the mixture. Results from the simulations are in good agreement with experimental data. In particular, a plateau region in the experimental data as a function of composition is reproduced by the simulations but is not predicted by extended corresponding states correlations.

KEY WORDS: Mixture; shear viscosity; intermolecular potentials; molecular dynamics; carbon dioxide; ethane

1 INTRODUCTION

Carbon dioxide/hydrocarbon mixtures are of significant interest in many areas of technology including natural gas processing and enhanced oil recovery research. The behavior of the viscosity of carbon dioxide and hydrocarbons mixtures plays an important role in many of these processes. In this paper, we report non-equilibrium molecular dynamics (NEMD) [1, 2] simulations of the shear viscosity of mixtures of carbon dioxide and ethane at a fixed total density and at five compositions. This study is part of an ongoing research program utilizing NEMD as a tool to study the fundamental basis for the transport properties of molecular fluids (in particular, carbobn dioxide) and their mixtures [3, 4, 5].

NEMD has recently emerged as a very efficient tool for calculating the transport properties of molecular fluids. (For reviews of NEMD algorithms, see Evans and Morriss [1, 2]; for a review of applications, see Cummings and Evans [6].) In general, NEMD involves simulating a system at steady state away from equilibrium, where the steady state is attained through the aplication of an external field. The ratio of the field-induced current to the field itself gives the transport coefficient of interest. The sllod algorithm, attributed to Hoover and Ladd [7] and briefly described in the following section, is used in conjunction with shearing boundary conditions to apply an external strain field to a fluid. This sets up a steady state planar Couette flow which permits the calculation of the shear viscosity from the ratio of the off-diagonal element of the pressure tensor to the strain rate. The

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Newtonian viscosity is obtained as the zero strain rate extrapolation of the strain rate dependent shear viscosity.

The intermolecular potential models chosen for the carbon dioxide/ethane mixture have two Lennard-Jones force centers for each molecule. In the case of the ethane molecule, each center represents a CH_3 group. In the case of the carbon dioxide molecule, each center approximately represents an oxygen atom. However, since there is no explicit inclusion of the carbon atom, the diameter of the oxygen site and the distance between the two oxygens are adjusted accordingly. The pair interactions between an α-type molecule and a β-type molecule can be written as $u_{\alpha\beta}(\mathbf{r}_{12}, \mathbf{\Omega}_1, \mathbf{\Omega}_2)$:

$$u_{\alpha\beta}(\mathbf{r}_{12}, \mathbf{\Omega}_1, \mathbf{\Omega}_2) = \sum_{a=1}^{2} \sum_{b=1}^{2} U_{\alpha\beta}^{ab}(r_{\alpha\beta}^{ab}) \tag{1}$$

and

$$U_{\alpha\beta}^{ab}(r) = 4\epsilon_{\alpha\beta}^{ab}\left[\left(\frac{\delta_{\alpha\beta}^{ab}}{r}\right)^{12} - \left(\frac{\delta_{\alpha\beta}^{ab}}{r}\right)^{6}\right] \tag{2}$$

where a and b represents sites in distinct species α and species β molecules respectively, $r_{\alpha\beta}^{ab}$ is the distance between site a in molecule α and site b in molecule β, and $\epsilon_{\alpha\beta}^{ab}$ and $\sigma_{\alpha\beta}^{ab}$ are the well depth and the zero point for the interaction between sites a and b of molecules α and β. The site-site distances l_α, the distance between two sites within a species α molecule, are also required in order to completely specify the potential models. The parameters for pure carbon dioxide and pure ethane are taken from the literature [8]. Fincham and co-workers [9] performed molecular dynamics simulation of this carbon dioxide and ethane potential model in order to study the azeotrope in the binary phase equilibria at the temperature $T = 269.25$ K and various compositions. They found that in order to obtain an azeotrope they needed to fit the cross interaction parameters σ_{ab} and ϵ_{ab} of the mixture model to the experimental data over a range of temperatures and densities along the orthobaric curve. We adopt their cross interaction parameters for our simulations. The cross interaction parameters of the potential model are also given in Table 1. It is interesting to compare the cross interaction parameters with those one would obtain by use of the usual Berthelot rules,

$$\epsilon_{\alpha\beta}^{ab} = \sqrt{\epsilon_{\alpha\alpha}^{aa}\epsilon_{\beta\beta}^{bb}}, \quad \sigma_{\alpha\beta}^{ab} = \frac{\sigma_{\alpha\alpha}^{aa} + \sigma_{\beta\beta}^{bb}}{2} \tag{3}$$

so that, using the superscript B to indicate Berthelot,

$$\epsilon_{CO_2/C_2H_6}^{B}/k_B = 149.8\,\text{K}, \quad \sigma_{CO_2/C_2H_6}^{B}/k_B = 3.278\,\text{Å} \tag{4}$$

Table 1 The site-site Lennard–Jones intermolecular potentials for carbon dioxide and ethane mixture.

Interactions	ϵ/k_B(K)	σ(Å)	l(Å)
CO_2–CO_2	163.3	3.035	2.37
C_2H_6–C_2H_6	137.5	3.520	2.45
CO_2–C_2H_6	120.0	3.277	—

Thus the Lennard–Jones distance parameter given in Table 1 is essentially given by the Berthelot value while the Lennard–Jones energy parameter is lower than that predicted by the Berthelot rules resulting in less attraction between unlike species and positive deviations from ideality.

The aim of this paper is to examine the compositional dependence of the mixture shear viscosity. The experimental measurements of shear viscosity of carbon dioxide and ethane mixture, reported in Table 4, indicate that at the fixed density 20 mole/dm^3, there is a plateau between $x_{CO_2} = 0.5$ and $x_{CO_2} = 0.75$ [10, 11, 12]. (Note that the experimental results are isochoric but not isothermal and correspond to a temperature range of 150–280 K. The experimental data of Diller *et al.* do not contain a full set of isochoric–isothermal data for a range of composition. However, Diller *et al.* singled out the isochoric set of data reported in Table 4 for comparison with extended corresponding states correlations.) This composition dependence of the shear viscosity is somewhat more complicated than the composition dependences obtained for other mixtures [13, 14]. It has been suggested that this unusual composition dependence of the shear viscosity may be related to the occurrence of an azeotrope in carbon dioxide/ethane mixture phase equilibria [10]. The extended corresponding state (ECS) model developed by Ely and Hanley fails to predict the plateau behavior of shear viscosity of carbon dioxide/ethane mixture [10]. By employing a mixture potential model developed to predict the azeotrope in the carbon dioxide/ethane mixture phase equilibria, we wish to predict the unique composition dependence of the shear viscosity of carbon dioxide/ethane mixture from molecular simulation.

In the next section, we will give a brief description of the NEMD sllod algorithm used for our simulations. A more detailed description is provided in the Appendix. Then, in Section 3, the results of the shear viscosity from the NEMD simulations will be reported and compared with the experimental data. In order to assess the importance of the non-Berthelot cross interaction parameters, we report NEMD simulations of carbon dioxide/ethane mixtures using the Berthelot cross interaction parameters given in Equation 4. We present our conclusions in Section 4.

2 NON-EQUILIBRIUM MOLECULAR DYNAMICS ALGORITHM

In this Section, we briefly describe the sllod algorithm and the equations of motions used in our simulations.

The sllod algorithm for simple fluids is described elsewhere [1]; for molecular fluids, Simmons and Cummings [15] describe the major features of the algorithm. We have used a straightforward modification of the Simmons and Cummings algorithm which is described in detail in the Appendix.

The translational equations of motion for a simulated binary system of N molecules with molecule i having streaming velocity $\boldsymbol{u}_i = (\gamma y_i, 0, 0)$, where γ is the strain rate, are

$$\left.\begin{aligned} d\boldsymbol{r}_i/dt &= \boldsymbol{p}_i/m_i + \boldsymbol{r}_i \cdot \nabla \boldsymbol{u}_i \\ d\boldsymbol{p}_i/dt &= \boldsymbol{F}_i - \boldsymbol{p}_i \cdot \nabla \boldsymbol{u}_i - \lambda \boldsymbol{p}_i \end{aligned}\right\} \tag{5}$$

where, for molecule i, m_i, $\boldsymbol{r}_i$, $\boldsymbol{p}_i$ and $\boldsymbol{F}_i$ represent mass, the position of the center of

mass, peculiar translational momentum and force on the center of mass. The term "peculiar" is used to indicate that part of the translational motion that is essentially thermal: i.e., it consists of the translational momentum with the convective contribution subtracted out. These translational equations are supplemented with rotational equations of motion as described in the Appendix. The parameter λ is used to constrain the translational motion so that the translational kinetic energy is fixed at the required temperature, thus yielding an isokinetic simulation. For the algorithm to be homogeneous, the boundary conditions must be consistent with the equations of motion. Thus, we employ the Lees–Edwards [16] "sliding brick" boundary conditions. The fourth order Gear's predictor-corrector method described in detail by Evans and Morriss (1984a) is used to solve the equations of motion.

The pressure tensor **P** and the viscosity η are calculated from the expressions, Equation 15 and 16, given in the Appendix. The strain rate dependent shear viscosity, hydrostatic pressure $p = (1/3)Tr(\mathbf{P})$ and configurational internal energy are predicted by mode-mode coupling theory to follow the asymptotic expressions [17, 18, 19, 20]

$$\eta = \eta_0 - \eta_1 \gamma^{1/2} \tag{6}$$

$$p = p_0 + p_1 \gamma^{3/2} \tag{7}$$

$$u_{\text{conf}} = u_0 + u_1 \gamma^{3/2} \tag{8}$$

The quantities with zero subscript are the zero strain rate quantities, so that η_0 is the Newtonian viscosity.

3 RESULTS AND DISCUSSION

The simulations of the carbon dioxide/ethane mixtures were performed on systems of 108 molecules with time step $\Delta t = 10^{-15}$ sec for five reduced strain rates $\gamma^* = \gamma\sigma_{CO_2}(m_{CO_2}/\epsilon_{CO_2})^{1/2} = 0.16$, 0.36, 0.64, 1.0 and 1.44. The spherical cutoff for the intermolecular potentials is 9.105 Å. For each state point, an equilibration run takes 20 ps and the simulation results are averaged over 100 ps. The simulations were performed on an IBM Powerstation 320. Details of the simulations are given in the Appendix.

In Table 2 we report configurational internal energy and viscosity obtained from the simulations for the carbon dioxide/ethane mixture model with intermolecular

Table 2 Viscosities obtained from NEMD simulations at the fixed density $\rho = 20$ mole/dim$_3$ and at various mole fractions of carbon dioxide and reduced strain rates.

	$x = 1.0$		$x = 0.74$		$x = 0.49$		$x = 0.25$		$x = 0.0$	
γ^*	u^*_{conf}	η (cp)	u^*_{conf}	η (cp)	u^*_{conf}	η (cp)	u^*_{conf}	η (cp)	u^*_{conf}	η (cp)
1.44	−4.39	0.097	−7.26	0.117	−7.51	0.128	−8.10	0.148	−9.42	0.191
1.0	−4.42	0.100	−7.33	0.121	−7.62	0.128	−8.22	0.155	−9.61	0.212
0.64	−4.43	0.100	−7.35	0.121	−7.65	0.131	−8.35	0.169	−9.87	0.228
0.36	−4.43	0.096	−7.40	0.129	−7.76	0.142	−8.58	0.171	−10.19	0.281
0.16	−4.44	0.101	−7.39	0.138	−7.88	0.131	−8.59	0.170	−10.28	0.311

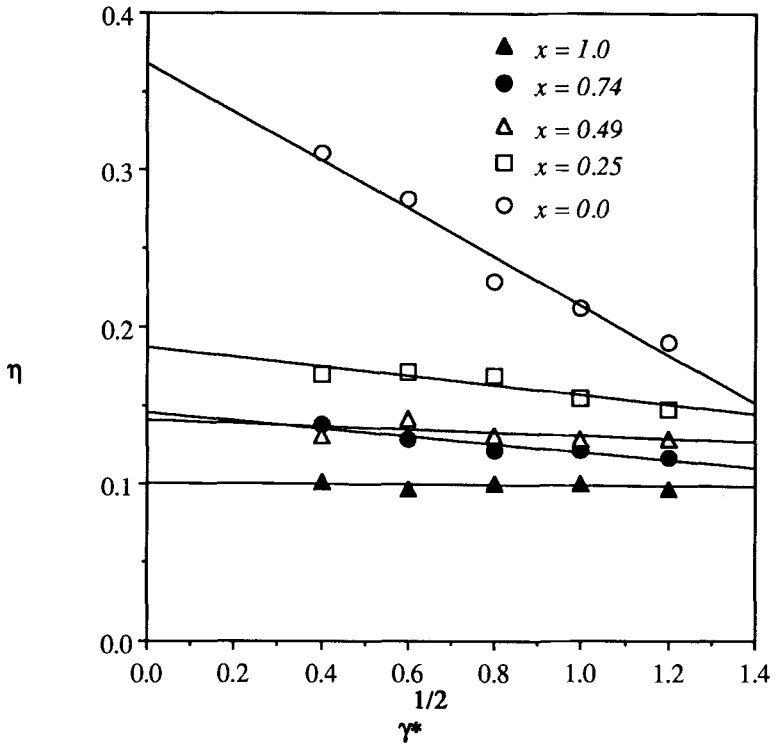

Figure 1 The viscosity η obtained from NEMD simulation for CO_2/C_2H_6 mixture model at the density 20 mole/dm$_3$ and various mole fractions of carbon dioxide as a function of $\gamma^{*1/2}$. The symbols are simulation results and the straight lines are least squared fits.

potential parameters given in Table 1. The strain rate dependent shear viscosity was least squares fitted to the asymptotic formula given in Equation 6. Figure 1 shows the strain rate dependent viscosity for each of the compositions at the fixed density. The viscosity follows the asymptotic relation Equation 6 quite well. We also performed NEMD simulations at the mixture states using the Berthelot parameters in the cross interaction, Equation 4. The results for internal energy and shear viscosity are given in Table 3. We note that the internal energies are, as expected, more negative for the Berthelot rule parameters.

Table 3 Viscosities obtained from NEMD simulations at the fixed density ρ = 20 mole/dm$_3$ and at various mole fractions of carbon dioxide. Berthelot mixing rules are used for the carbon dioxide/ethane potential.

	$x = 0.74$		$x = 0.49$		$x = 0.25$	
γ^*	u^*_{conf}	η (cp)	u^*_{conf}	η (cp)	u^*_{conf}	η (cp)
1.44	−8.10	0.129	−8.49	0.133	−8.84	0.151
1.00	−8.15	0.126	−8.58	0.135	−8.92	0.160
0.64	−8.19	0.128	−8.59	0.150	−8.99	0.162
0.36	−8.22	0.129	−8.62	0.149	−9.02	0.170
0.16	−8.23	0.133	−8.59	0.155	−9.03	0.169

Table 4 Comparison between shear viscosity calculated via NEMD and experimental data [10, 11, 12].

x_{CO_2}	ρ (mole/dem^3)	T (K)	η_{exp} (cp)	η_{NEMD} (cp)	η_{NEMD-B} (cp)
1.0	20.091	280.0	0.0917	0.10	0.10
0.73978	20.068	280.0	0.1234	0.14	0.13
0.49245	19.929	240.0	0.1336	0.14	0.17
0.25166	19.724	210.0	0.1726	0.18	0.18
0.0	19.957	150.0	0.3212	0.36	0.36

The viscosities from the experimental measurements and the simulations (extrapolated to zero strain rate and denoted by NEMD) are reported in Table 4 and are plotted against composition at fixed density in Figure 2. The agreement between the simulation and the experiment is good. We should note that the estimated error in the final, extrapolated simulation results presented in Table 4 is 5–10%. The simulation results slightly overestimate the experimental data, especially for pure ethane. This is probably due to the deficiencies in the potential model. We expect that better potential models (i.e., models which take into account the quadrupole moments in carbon dioxide and ethane molecules) would yield better agreement. The viscosity obtained from the simulations shows a plateau behavior between $x = 0.5$ and $x = 0.75$. Figure 2 shows that the extended corresponding states (ECS) model [10] does not describe adequately the composition dependence of the shear viscosity of the mixture.

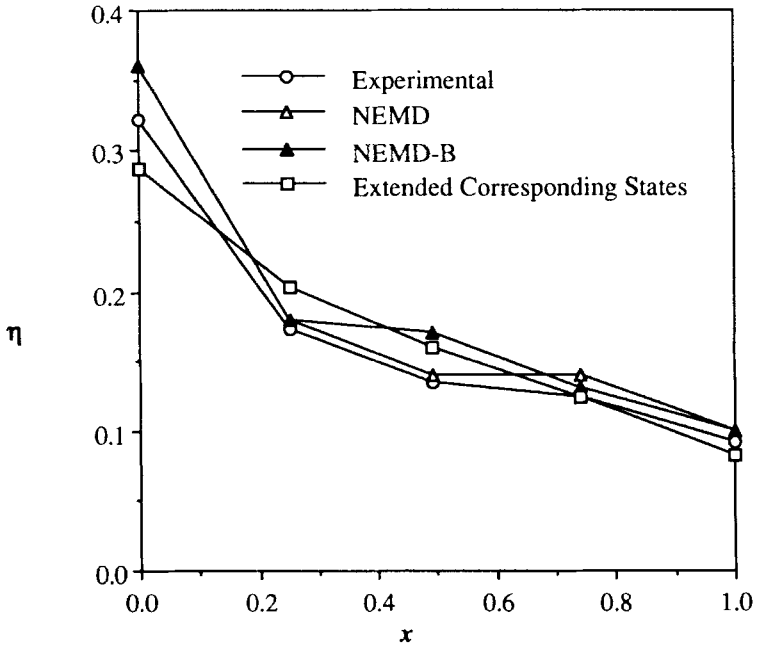

Figure 2 The dependence of the viscosity in carbon dioxide/ethane mixtures on carbon dioxide mole fraction at fixed density 20 mole/dm$_3$. The NEMD results are obtained with the non-Berthelot cross interaction parameters given in Table 1 while the NEMD-B results use the Berthelot parameters, Equation 4. Note that straight lines are drawn betwewen points as aids to the eye.

In order to evaluate the role that the non-Berthelot cross interaction plays in the NEMD results, we have also shown in Figure 2 the viscosity predicted in the NEMD simulations using the Berthelot-derived cross interaction parameters given by Equation 4. These results are denoted as NEMD-B in Figure 2. It is evident that the Berthelot rules lead to shear viscosities that do not exhibit a strong plateau over the composition range $0.5 < x < 0.75$, but there is evidence of a plateau in the region $0.25 < x < 0.5$. Note that only for the equimolar mixture is there any statistically significant deviation from the results with the non-Berthelot mixing rules.

The small effect of the non-Berthelot mixing rules might have been predicted since for the cross interaction parameters given in Table 1 only the Lennard-Jones energy parameter ϵ_{CO_2/C_2H_6} deviates from its Berthelot value. Variations in this parameter are equivalent to temperature variations at fixed ϵ which have smaller effects on viscosity than density variation (which in an isochoric system can be effectively brought about by changes in the Lennard–Jones σ). Thus it is reasonable to find that the viscosity is affected only in small ways by the use of a non-Berthelot value for ϵ_{CO_2/C_2H_6}. We would expect greater differences with a non-Berthelot value for the cross interation σ parameter.

4 CONCLUSIONS

We reported non-equilibrium molecular dynamics simulations of the shear viscosity of carbon dioxide/ethane mixtures at a fixed total density (20 mole/dm^3). The simulation results for the Newtonian viscosity are in good agreement with the experimental data. In particular, a plateau region in the experimental data as a function of composition is reproduced by the simulations. We also found that, although the use of the non-Berthelot ϵ_{CO_2/C_2H_6} is necessary for predicting the azeotrope in carbon dioxide/ethane mixture vapor-liquid equilibrium (since pressure exhibits a strong dependence on the strength of attractive interactions) and to predict the correct location of the plateau region in the mixture viscosity, the differences between the mixture shear viscosity computed with and without non-Berthelot values for ϵ_{CO_2/C_2H_6} were quite small and most pronounced for the equimolar mixture.

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APPENDIX A: SIMULATION METHODOLOGY

In this Appendix we document in a consistent fashion all the important elements of the simulations performed.

A.1 *Intermolecular Potentials*

As discussed in the Introduction, the Fincham *et al.* (1986) models for carbon dioxide and ethane treat both molecules as homonuclear diatomics within the site-site formalism, so that Equations 1 and 2 can be simplified to

$$u_{\alpha\beta}(\boldsymbol{r}_{12}, \boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2) = \sum_{a=1}^{2} \sum_{b-1}^{2} U_{\alpha\beta}(r_{\alpha\beta}^{ab}) \tag{9}$$

and

$$U_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right] \tag{10}$$

The values for $\epsilon_{CO_2/CO_2} \equiv \epsilon_{CO_2}$, $\epsilon_{C_2H_6}$, ϵ_{CO_2/C_2H_6}, σ_{CO_2}, $\sigma_{C_2H_6}$, σ_{CO_2/C_2H_6}, l_{CO_2} and $l_{C_2H_6}$ are given in Table 1. The Berthelot values for ϵ_{CO_2/C_2H_6} and σ_{CO_2/C_2H_6} are given in Equation 4.

A.2 *Algorithm*

The equations of motion for a simulated binary system of N molecules with the streaming velocity for molecule i given by $\boldsymbol{u}_i = (\gamma y_i, 0, 0)$, where γ is the strain rate, are [15]

$$\left.\begin{aligned} d\boldsymbol{r}_i/dt &= \boldsymbol{p}_i/m_i + \boldsymbol{r}_i \cdot \nabla \boldsymbol{u}_i \\ d\boldsymbol{p}_i/dt &= \boldsymbol{F}_i - \boldsymbol{p}_i \cdot \nabla \boldsymbol{u}_i - \lambda \boldsymbol{p}_i \end{aligned}\right\} \tag{11}$$

$$\left.\begin{aligned} d\boldsymbol{L}_i/dt &= \boldsymbol{T}_i \\ \boldsymbol{L}_i^p &= \mathbf{A}_i \boldsymbol{L}_i \\ \omega_{i\beta}^p &= L_{i\beta}^p / I_{i\beta}, \quad \beta = x, y, z \\ \frac{d}{dt}\begin{pmatrix} q_{i1} \\ q_{i2} \\ q_{i3} \\ q_{i4} \end{pmatrix} &= \frac{1}{2}\begin{pmatrix} -q_{i3} & -q_{i4} & q_{i2} & q_{i1} \\ q_{i4} & -q_{i3} & -q_{i1} & q_{i2} \\ q_{i1} & q_{i2} & q_{i4} & q_{i3} \\ -q_{i2} & q_{i1} & -q_{i3} & q_{i4} \end{pmatrix}\begin{pmatrix} \omega_{ix}^p \\ \omega_{iy}^p \\ \omega_{iz}^p \\ 0 \end{pmatrix} \end{aligned}\right\} \tag{12}$$

In these equations, for molecule i, m_i, $\boldsymbol{r}_i$, $\boldsymbol{p}_i$, $\boldsymbol{\omega}_i$, $\boldsymbol{L}_i$, $\boldsymbol{F}_i$ represent mass, the position of the center of mass, peculiar translational momentum, angular velocity, angular momentum, force on the center of mass and torque in the laboratory frame. The principal (or molecular) frame quantities have superscript p. The matrix $\mathbf{A}_i$ is the rotation matrix that converts the laboratory frame coordinates of molecule i to molecular frame coordinates and is a function of the orientation of the molecule. The q_{ij}, $j = 1, \ldots, 4$ are the quaternions for representing the orientation of molecule i in such a way that the equations of motion are singularity-free [21]. These equations are the same as those for a pure molecular fluid except for the dependence of the mass m_i and the moments of inertia $I_{i\beta}$ on molecule index i. The

parameter λ is used to constrain the translational motion so that the translational kinetic energy is fixed at the required temperature. The functional form of the term involving λ follows from the application of Gauss's principle of least constraint [22] where the isokinetic constraint is

$$\frac{1}{2}\sum_{i=1}^{N}\frac{\boldsymbol{p}_i^2}{m_i}-\frac{3}{2}Nk_BT=0 \tag{13}$$

and k_B is Boltzmann's constant and T is the absolute temperature. This leads to the following equation for λ:

$$\lambda=\sum_{i=1}^{N}\frac{1}{m_i}(\boldsymbol{p}_i\cdot\boldsymbol{F}_i-\boldsymbol{p}_i\boldsymbol{p}_i\bullet\nabla\boldsymbol{u})/\sum_{i=1}^{N}\frac{\boldsymbol{p}_i^2}{m_i} \tag{14}$$

where $\bullet$ indicates the full contraction of two second order tensors and N is the number of molecules in the simulation cell. For the algorithm to be homogeneous, the boundary conditions must be consistent with the equations of motion. Thus, we employ the Lees–Edwards [16] 'sliding brick' boundary conditions. The fourth order Gear's predictor-corrector method described in detail by Evans and Morriss [1] is used to solve the equations of motion.

A.3 *Evaluation of Properties*

The pressure tensor $\mathbf{P}$ is calculated from the expression

$$PV=\sum_{i=1}^{N}m_i\boldsymbol{v}_i\boldsymbol{v}_i+\sum_{i=1}^{N}\boldsymbol{r}_i\boldsymbol{F}_i \tag{15}$$

where V is the volume of the system and $\boldsymbol{v}_i=\boldsymbol{p}_i/m_i$ is the peculiar velocity of molecule i (i.e., its velocity with its convective component subtracted out). The strain rate dependent shear viscosity η is obtained from the constitutive relation [23],

$$\mathbf{P}_{xy}^{0s}=-2\eta(\nabla\boldsymbol{u})_{xy}^{0s} \tag{16}$$

where $\mathbf{A}^{0s}$ denotes the symmetric, traceless part of the tensor $\mathbf{A}$. The configurational internal energy, u_{conf}, is calculated from the usual expression

$$u_{\text{conf}}=\sum_{1\leqslant i<j\leqslant N}u_{ij}(\boldsymbol{r}_{ij},\boldsymbol{\Omega}_i,\boldsymbol{\Omega}_j) \tag{17}$$

A.4 *Valuation of Simulation Codes*

The simulation codes were validated by performing calculations in the absence of strain and without a thermostat. Under such conditions, the total energy (configurational plus kinetic) should be conserved. We verified that the time step used in the simulations (10^{-15} sec) was sufficiently low that energy was conserved to better than 1%. For isokinetic simulations (i.e., with the Gaussian thermostat),

both in the presence and absence of strain the translational temperature was found to vary by less than one part in 10000.

A.5 *Calculation Details*

The simulations were run at the highest strain rate initially for a long period (at least 20 ps) to ensure that the initial face centered cubic (fcc) lattice structure was erased. For the mixture systems, the fcc lattice was initialized with, for example, every fourth molecule being a carbon dioxide molecule for $x_{CO_2} = 0.25$.

For a given mixture or pure fluid system, after equilibration at the highest strain rate the simulations were run for 100 ps (100000 time steps) at the highest strain rate in blocks of 20000 time steps. The average values of the properties in each block were then used as five data points to analyze statistically in order to calculate a mean value and standard deviation. The standard deviations were the basis for assessing the error in the simulations. The strain rate was then set to the next lowest strain rate, equilibriated for 20 ps, run for 100 ps and analyzed statistically. This was repeated down to the lowest strain rate.

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