Computer Simulation Studies of the Critical Enhancement of Thermal Conductivity of Carbon Dioxide

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ABSTRACT

The method of nonequilibrium molecular dynamics (NEMD) has been used to examine the thermal conductivity of model carbon dioxide along the critical isotherm. An intermolecular potential model for which the coexistence curve and the critical point of carbon dioxide have been previously estimated has been used. The NEMD method is based on applying a fictitious heat field on the molecular system and measuring the heat flux generated. Thermal conductivity is then calculated using linear response theory and Green-Kubo relations. Simulations were carried out on systems with 108 to 864 carbon dioxide molecules (324 to 2592 active interaction sites, respectively). At the critical point, this leads to a system size of between 26Å and 51Å. The translational and rotational contributions to thermal conductivity have also been calculated.

The results show clear evidence of critical enhancement of thermal conductivity and confirm our belief that these enhancements can be calculated using molecular simulations. The present study is, we believe, the first to investigate critical effects on thermal conductivity of a nonspherical fluid using molecular simulations.

KEY WORDS: carbon dioxide; critical enhancements; nonequilibrium molecular dynamics; thermal conductivity; transport properties.

1. INTRODUCTION

The enhancement of thermal conductivity in the vicinity of the gas-liquid critical point is a well-known phenomenon. Experimental evidence of this anomalous behavior has been established by heat transfer and light scattering techniques for many compounds including, carbon dioxide, steam, ethane, ammonia [1], nitrogen, oxygen, argon [2,3] and more recently the refrigerant R134a [4]. Several theories have been developed to understand this behavior and semi-empirical methods have attempted to account for the enhancement using correlations [1,2,5,6,7,8]. In this work, the critical enhancement of the thermal conductivity of carbon dioxide is investigated using the method of nonequilibrium molecular dynamics (NEMD). Such computer simulation methods provide a level of detail that is normally difficult to obtain with experiments. This information can then be used to understand this behavior at the molecular level.

Carbon dioxide is of significant importance to the chemical process industry. Supercritical carbon dioxide has gained importance in recent years as a solvent for chemical reactions [9,10]. An intermolecular potential model for carbon dioxide has been developed recently [11] for which the liquid-vapor coexistence curve and the critical point have been estimated. We have used this potential in this study for calculating the thermal conductivity values in the critical region using the nonequilibrium molecular dynamics method. The purpose of this study is to calculate the thermal conductivity enhancements in the critical region and examine the contributions to the total thermal conductivity from the translational and rotational parts, which can be readily obtained using the NEMD method. A previous study on argon has shown that these critical enhancements can indeed be obtained using computer simulations [12].

2. THEORY

In this work the non-canonical linear response theory method for polyatomics is used [13]. In this method, an external field is used to increase the energy of all particles in the system with more than the average energy and decrease it for those with less than the average energy. This leads to a heat flux in the system, whose magnitude is used to estimate the thermal conductivity. The equations of motion given below show how such an external field can be incorporated in an NEMD study.

$$\dot{\boldsymbol{r}}_i = \boldsymbol{p}_i/m \tag{1}$$

$$\dot{\boldsymbol{p}}_i = \sum_j \boldsymbol{f}_{ij} + (\boldsymbol{E}_i - \boldsymbol{E})\boldsymbol{F}(\boldsymbol{t}) + \frac{1}{2}\sum_j \boldsymbol{f}_{ij}.[\boldsymbol{r}_{ij}\boldsymbol{F}(\boldsymbol{t})] - \frac{1}{2\boldsymbol{N}}\sum_{jk} \boldsymbol{f}_{jk}[\boldsymbol{r}_{jk}.\boldsymbol{F}(\boldsymbol{t})] - \alpha\boldsymbol{p}_i \tag{2}$$

$$\boldsymbol{I}_{xx}^{p}\frac{d\omega_{ix}^{p}}{dt} = \Gamma_{ix}^{p} + \omega_{iy}^{p}\omega_{iz}^{p}(\boldsymbol{I}_{yy}^{p} - \boldsymbol{I}_{zz}^{p}) + \frac{1}{2}\sum_j \Gamma_{ijx}^{p}[\boldsymbol{r}_{ij}\boldsymbol{F}(\boldsymbol{t})] \tag{3}$$

In the above equations, $\boldsymbol{r}_i$ is the center of mass position of molecule i, m, the mass, $\boldsymbol{p}_i$, the linear momentum, $\boldsymbol{f}_{ij} = -\partial\phi_{ij}/\partial\boldsymbol{r}_i$, where ϕ_{ij} is the intermolecular potential, and $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$. N is the number of particles in the system. $\bar{E}$ is the average energy per particle, while E_i is for particle i. $\boldsymbol{F(t)}$ is the external field, which for simplicity is usually kept fixed at a constant value, and with only one non-zero component (e.g. in the z direction). α, the thermostatting multiplier ensures constant translational kinetic energy. $\boldsymbol{\omega}^{\boldsymbol{p}}$ is the principal angular velocity and Γ_{ij}^{p} is the principal torque on i due to j only, while Γ_{i}^{p} is that on i due to all other molecules. $\boldsymbol{I}^{\boldsymbol{p}}$ is the principal moment of inertia. Eq. (3) applies to the x component of $\boldsymbol{\omega}^{\boldsymbol{p}}$. Similar equations can be written for the y and z components.

The thermal conductivity, λ, can then be estimated from the equation (limiting value for $\mathbf{F}(t) \to 0$),

$$\lambda^{\text{total}} = \frac{1}{T}\frac{\langle J_Q(t \to \infty)\rangle}{F(t)} \tag{4}$$

where T is the temperature and the heat flux vector is given by,

$$\boldsymbol{J}_Q = \frac{1}{\boldsymbol{V}}\left[\sum_i \boldsymbol{E}_i \frac{\boldsymbol{p}_i}{\boldsymbol{m}} + \frac{1}{2}\sum_{ij} \boldsymbol{r}_{ij}\left(\frac{\boldsymbol{p}_i}{\boldsymbol{m}}.\boldsymbol{f}_{ij} + \omega_i^p.\Gamma_{ij}^p\right)\right] \tag{5}$$

In Eq. (5), V is the volume of the simulation cube.

For studying the contributions to thermal conductivity from various modes, $\boldsymbol{J}_Q$ can be broken up into a rotational part given by,

$$\boldsymbol{J}_Q^{rot} = \frac{1}{2\boldsymbol{V}}\left[\sum_i \left(\omega_i^p.\boldsymbol{I}^p.\omega_i^p\right)\frac{\boldsymbol{p}_i}{\boldsymbol{m}} + \frac{1}{2}\sum_{ij} \boldsymbol{r}_{ij}\left(\omega_i^p.\Gamma_{ij}^p\right)\right] \tag{6}$$

where the remaining part is referred to as the translational contribution. The rotational contribution to thermal conductivity can then be estimated from,

$$\lambda^{\text{rot}} = \frac{1}{T}\frac{\left\langle J_Q^{rot}\ (t \to \infty)\right\rangle}{F(t)} \tag{7}$$

so that the total thermal conductivity is now given by,

$$\lambda^{\text{total}} = \lambda^{\text{rot}} + \lambda^{\text{tr}} \tag{8}$$

The rotational contributions can broken up further into contributions from the inertial term and the torque term, identified by the first and second terms in Eq. (6), respectively, and can be written as,

$$\lambda^{\text{rot}} = \lambda^{\text{rot-inertial}} + \lambda^{\text{rot-torque}} \tag{9}$$

3. MODEL CARBON DIOXIDE

The intermolecular potential function for carbon dioxide is a simple site-site model and uses point charges and Lennard-Jones interactions centered at each atom [11]. The model (named EPM2 in [11]) was shown to predict the liquid-vapor coexistence curve and the critical point reasonably well, but under predicts the liquid coexistence densities by 1% to 2% at temperatures between 221 K and 289 K. However, given a critical temperature of 304 K for carbon dioxide, this is not a serious drawback for the purposes of calculating thermal conductivity values near the critical point. Table I lists the intermolecular potential parameters for carbon dioxide. The critical temperature and density of carbon dioxide are 10.81 and 0.1342, respectively, in reduced units (all values are reduced with carbon-carbon parameters). The Lennard-Jones interactions were treated with a spherical cutoff distance of 10 Å in the simulation.

The simulations were carried out on systems ranging in size from 108 (324 sites) to 864 (2592 sites) carbon dioxide molecules. The initial configuration for the molecular positions was that of an FCC structure. The translational and rotational equations of motion were solved using Gear's fifth and fourth order predictor-corrector methods respectively. We allowed 250,000 time steps for equilibration. An additional 800,000 to 1,000,000 time steps were required for the thermal conductivity to converge. A reduced time step of 0.0005 was used. The gaussian thermostat (α in Eq. (2)) was used to ensure constant translational temperature. With the thermostat on and

translational velocity rescaling every time step, the correct temperature was maintained to at least four significant digits. Linear and angular momenta were conserved. As a further check, the program was tested with the thermostat off and a field strength of zero (conventional equilibrium molecular dynamics) to ensure that the total energy was conserved. The density of the system was varied from $0.70\rho_C$ to $1.30\rho_C$ along the critical isotherm, where ρ_C is the critical density.

To ensure that the thermal conductivity values were independent of the strength of the external field, we carried out our preliminary studies with F_Z^* ranging from 0.025 to 0.05. Fig. 1 shows that the effect of field strength (at $T = T_C$ and $\rho = 1.30\rho_C$) on the thermal conductivity is negligible (T_C is the critical temperature). For all results reported in this study, a value of 0.025 was used for the field, to avoid any possible field strength dependence. The accuracy of the thermal conductivity values reported is estimated to be ± 0.03.

4. RESULTS AND DISCUSSION

Fig. 2 shows the results obtained for the thermal conductivity of carbon dioxide at a temperature of $1.32T_C$ for densities ranging from $0.80\rho_C$ to $1.20\rho_C$. The thermal conductivity increases smoothly with density and does not show any critical enhancements, as is to be expected at state conditions away from the critical point. We will use such non-critical density dependence of thermal conductivity to interpret our results along the critical isotherm.

Fig. 3 shows the thermal conductivity of model carbon dioxide along the critical isotherm at densities between $0.70\rho_C$ and $1.30\rho_C$ for systems with 108, 256, and 500 molecules. The results show thermal conductivity increasing with density as expected, as well as clear evidence of enhancement in the vicinity of the critical point in all systems. Although the enhancements are smaller than those obtained experimentally, they clearly cannot be attributed to the statistical error of the results, which is estimated to be ± 0.03. We also did an 864-molecule simulation at the critical point and obtained results identical to the 500-molecule system, within the statistical uncertainty (see Table II). The critical behavior is all the more evident if Fig. 2 is compared with Fig.1. The rather large enhancements of thermal conductivity seen in experimental studies [1] can perhaps be obtained with

a larger potential cutoff distance than that used here and prescribed by [11] for the intermolecular potential function used in this study. Unfortunately, increasing the cutoff distance changes the critical point and finding the new critical point requires a rather extensive set of new simulations. In fact [11] is almost entirely devoted to determining the critical point for the carbon dioxide potential. In addition, since the critical point in [11] was determined by extrapolation, it also possible that there is some error in the critical point estimated for the carbon dioxide potential. Other possibilities include contributions from polarizability or molecular vibrations that were not included in our model, which might also contribute to the enhancement of the thermal conductivity of carbon dioxide in the critical region. In spite of these reservations, it is clear that even our rather simple model shows clear evidence of anomalous behavior in the critical region.

The thermal conductivity of fluids obtained using NEMD is known to show system size dependence (especially in smaller systems) and this was observed by us as well. However, our results showed a stronger size dependence in the critical region. This is evident in Table II, where for a non-critical state condition, the increase in thermal conductivity when going from a 108 particle system to an 864 particle system is about 2.6%, while at the critical point, it is about 11%. Both of them do not appear to be size dependent beyond the 864 particle system.

Table III shows the translational and rotational contributions to thermal conductivity along the critical isotherm for a 256-molecule system. There appear to be no indications from the results that any of these contributions play a relatively more significant role (for example, translational versus rotational contributions) in the critical enhancement of thermal conductivity.

5. CONCLUSIONS

The enhancement of thermal conductivity in the critical region was investigated using the NEMD method. The study shows that critical effects are observable using molecular simulations. Further studies with much larger cutoff distances are perhaps needed to see larger enhancements as well as other potential contributions. There is also a need to obtain a more accurate estimate of the critical point for the potential model used. For carbon dioxide, which is a nonspherical molecule, polarizability and molecular vibrations may also play a role.

6. ACKNOWLEDGMENTS

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Table I. Lennard-Jones Site-Site Parameters[1] for Carbon Dioxide [11]

Parameter	Value
ε_{CC}	28.129 K
ε_{CO}	47.588 K
ε_{OO}	80.507 K
σ_{CC}	2.757 Å
σ_{CO}	2.892 Å
σ_{OO}	3.033 Å
l_{CO}	1.149 Å
q_C	+0.6512 e
Molecular Weight	44.01 g/gmol

[1] ε and σ are the Lennard-Jones well depth and core diameter in the interatomic potential, $\phi(r)=4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^{6}]$. The subscripts refer to the particular atomic pair interaction. l_{CO} is the carbon-oxygen bond length. q_C is the charge on the carbon center (positive). There are two equal negative charges on the oxygen centers so that the net charge on the molecule is zero.

Table II. Thermal Conductivity of Carbon Dioxide Away From the Critical Point ($T = 1.32T_C$ and $\rho = 1.20\rho_C$), λ_{NC}, and at the Critical Point, λ_C, as a function of system size

N	λ_{NC}	λ_C
108	3.80	3.15
256	3.82	3.33
500	3.95	3.45
864	3.90	3.49

Table III. Translational and Rotational Contributions to the Thermal Conductivity of Carbon Dioxide along the Critical Isotherm for a 256 Particle System

ρ/ρ_c	λ^{tr}	λ^{rot}	$\lambda^{rot\text{-}torque}$	λ^{total}
0.80	1.82	0.74	0.41	2.56
0.90	2.02	0.84	0.50	2.86
0.95	2.02	0.98	0.61	3.00
1.00	2.31	1.02	0.69	3.33
1.05	2.27	1.00	0.69	3.27
1.10	2.50	1.10	0.72	3.60
1.20	2.46	1.32	0.94	3.78

FIGURE CAPTIONS

Fig. 1. Effect of field strength (F_Z^*) on the thermal conductivity (λ) of carbon dioxide at $T = T_C$ and $\rho = 1.30\rho_C$.

Fig. 2. Thermal conductivity of carbon dioxide along the isotherm $T = 1.32T_C$. The line represents the least squares fit of the data.

Fig. 3. Thermal conductivity of carbon dioxide along the critical isotherm for systems with 108, 256, and 500 particles. The thermal conductivity of the 864 particle system at the critical point is 3.49 ± 0.03. The lines are interpolations.

FIGURE 1.

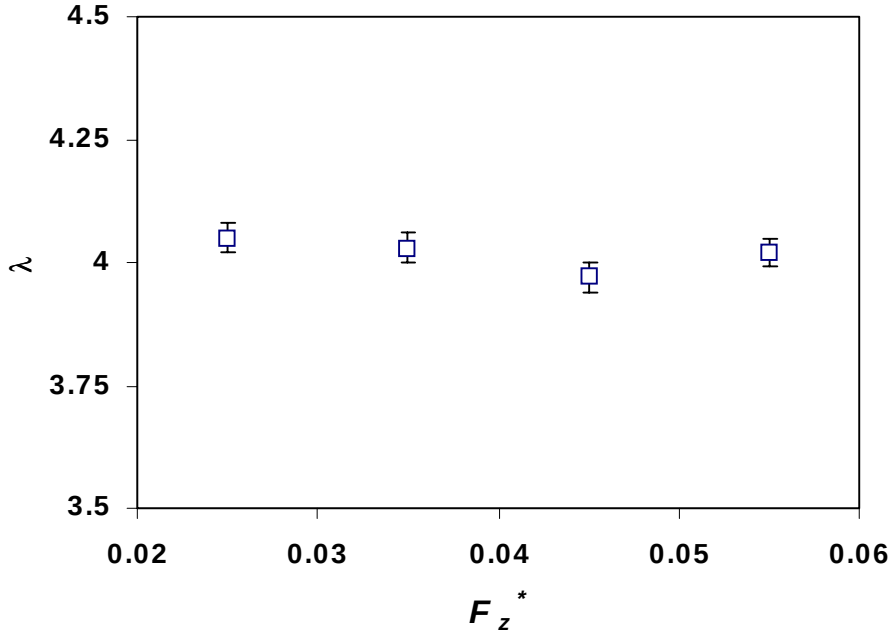


FIGURE 2.

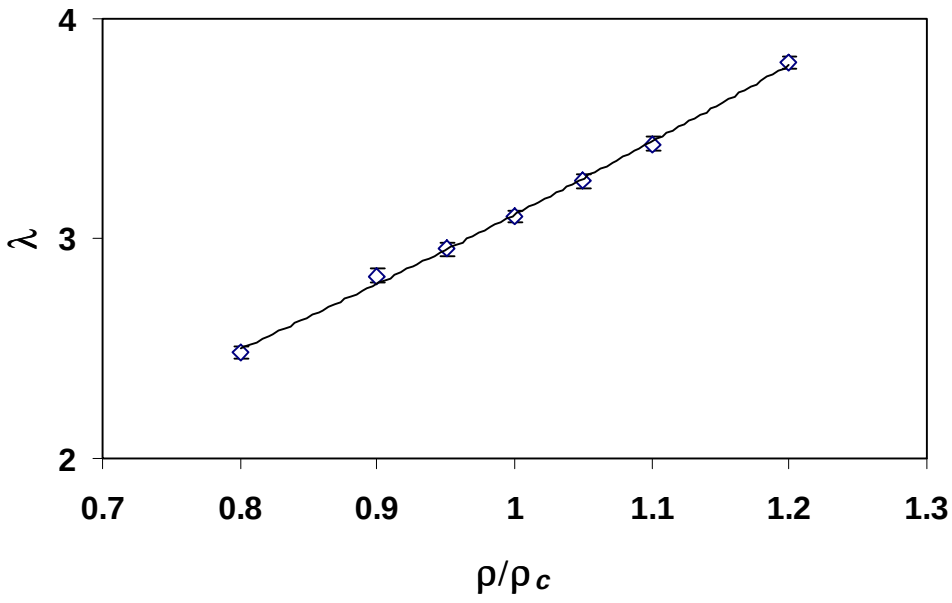
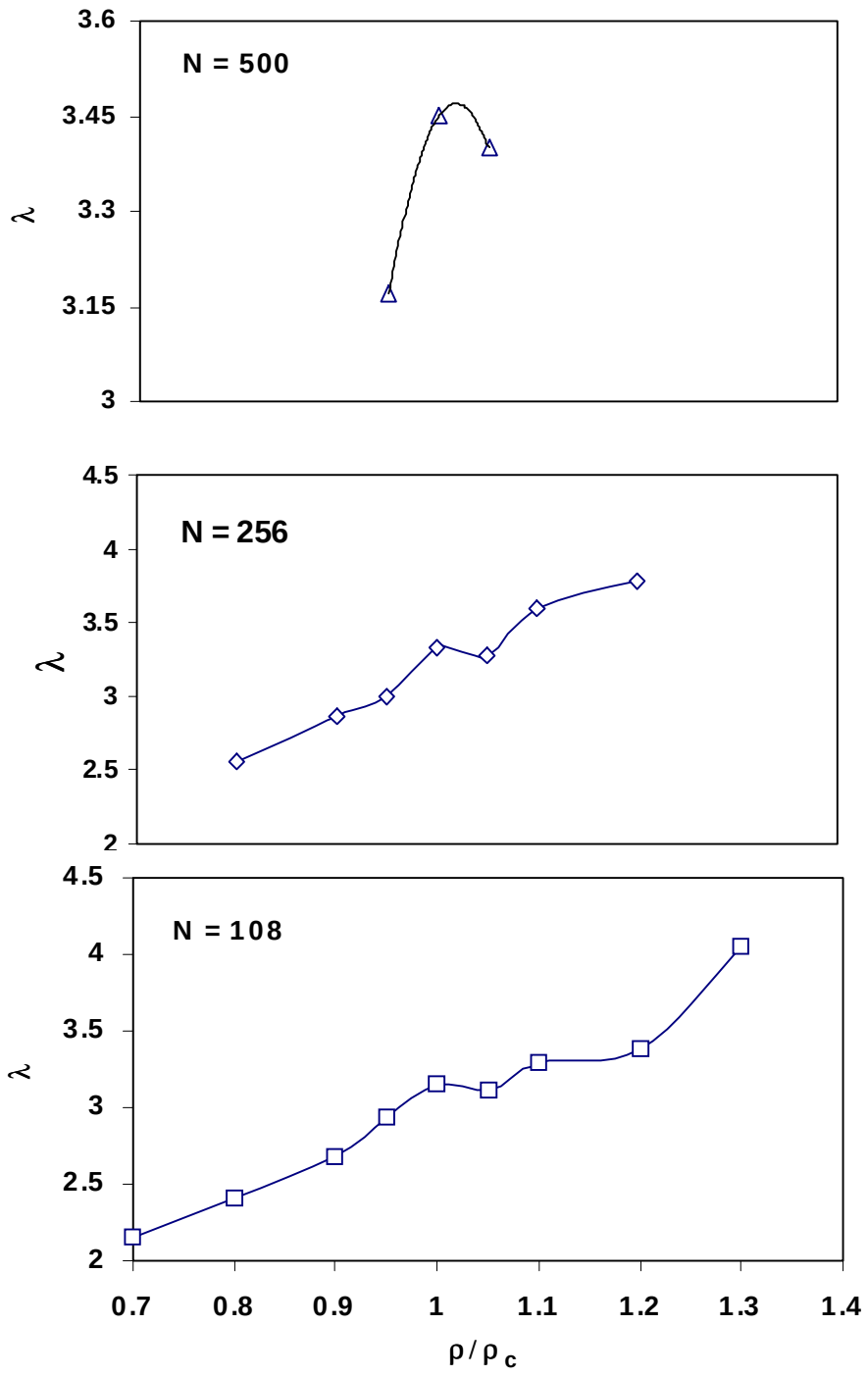


FIGURE 3.


N = 500
N = 256
N = 108
λ
3.6
3.45
3.3
3.15
3
4.5
4
3.5
3
2.5
2
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
ρ / ρ c