Simulation of Heat Transfer with Gas-liquid Coexistence Using Dissipative Particle Dynamics

THESIS

Presented in Partial Fulfillment of the Requirements for the Degree Master of Science in the Graduate School of The Ohio State University

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2016

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Abstract

Dissipative particle dynamics (DPD) is a useful method in simulating transport phenomena on a mesoscale. However, the original model of this method is not suitable for simulating heat transfer and coexistence of gas and condensed states. In this study, internal energy and an attractive force term are introduced into the DPD model. Simulation work shows that this modified DPD method is able to study heat transport in such multi-phase systems.
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Introduction

Heat transfer on nano scale is a topic of interest in many fields of engineering. To study transport phenomena on such scale, macroscopic analysis in which fluids are treated as continuum is not appropriate. On the other hand, molecular dynamics (MD) that simulates the fluids based on the behavior of molecules is also inapplicable since it requires large amount of computations that's impossible for computers even today.

To study the transport phenomena on nano scale, a simulation method called dissipative particle dynamics (DPD) is used. It is first proposed by Hoogerbrugge and Koelman in 1992[1] and basically developed to its current form by Español and Warren in 1995[2]. DPD is a coarse-grained simulation method in which the 'particles' represent clusters of many molecules, or small 'bulks' of fluids and solids. The size of dissipative particles, or the degree of coarse-graining, can be adjusted according to the purpose of simulation.

DPD is successful in studying binary systems[3][4], colloidal suspensions[5], polymer solutions[6], and flow patterns in different kinds of geometry[7][8][10]. However, simulation of heat transfer with liquid and gas coexistence is a new area for DPD since the original method has two weaknesses which makes simulating such systems impossible. In this study, a new modified form of DPD will be used and its ability to simulate such systems will be tested.
Methodology

I. Equations of motion in DPD

In DPD, the mass of each particle and particle numbers are fixed, thus conserving total mass. Newton's equation of motion is applied to particles and each particle $i$ is subjected to pair-wise particle interactions:

$$\frac{dr_i}{dt} = v_i$$

$$\frac{dv_i}{dt} = f_i$$

Here we set the mass of each particle as unity for simplicity.

II. Interaction forces in DPD

Inter-particle interactions can be divided into three kinds: the conservative force, the dissipative force, and random force:\(^{[1]}\):

$$f_i = \sum_{j \neq i} f_{ij}^C + f_{ij}^D + f_{ij}^R$$

The subscript $ij$ indicates the force exerted by particle $j$ on particle $i$.

The conservative force results from the potential between particles. It is usually constructed as:
in which the weight function

\[ w_c(r) = \begin{cases} 
1 - r, & r < 1 \\
0, & r \geq 1 
\end{cases} \]

Here \( a_{ij} \) is the parameter that determines the intensity of conservative force, \( r = \| r_{ij} \| = \| r_i - r_j \| \) and \( e_{ij} = r_{ij}/r \). The unit of length is called cutoff radius \( r_{cut} \), beyond which there are no interactions among particles.

The function form of conservative force in DPD indicates a soft interaction potential between particles, unlike that between atoms or single molecules (e.g. Lenard-Jones potential). In the physical sense, the DPD particles are clusters of molecules which can indeed penetrate each other, so a soft repulsive force is appropriate. And a soft potential that doesn't change drastically with \( r \) as particles are very close to each other makes larger time step in simulation possible, which increases speed and reduces computational cost.

The dissipative and random forces are constructed as follows:

\[ f_{ij}^D = -\gamma w_D(r)(e_{ij} \cdot v_{ij})e_{ij} \]

\[ f_{ij}^R = \sigma w_R(r)\xi_{ij} e_{ij} \]

where \( \gamma \) and \( \sigma \) are intensity parameters for each forces, \( w_D \) and \( w_R \) are weight functions that depends on the distance between two particles, \( v_{ij} = v_i - v_j \) is the relative velocity
between two particles, and $\xi$ is a random variable that has a zero mean and a variance of unity.

When subjected to statistical mechanic analysis (fluctuation-dissipation theorem), it is found that the dissipative and random forces should have the following relationship so that the system can reach an equilibrium under a prescribed temperature $T$:

$$w_D(r) = w_R(r)^2$$

$$\gamma = \frac{\sigma^2}{2k_B T}$$

where $k_B$ is the Boltzmann constant. It is common to choose $w_D(r)$ and $w_R(r)$ as

$$w_D(r) = w_R(r)^2 = \begin{cases} (1 - r)^2, & r < 1 \\ 0, & r \geq 1 \end{cases}$$

The choice of parameters $a$, $\gamma$, and $\sigma$ generally has no physical basis, but they influence the properties of simulated fluids, e.g. compressibility, viscosity, Schmidt number, etc.

They are chosen to fit the fluids simulated and to maintain the simulation accuracy.

All inter-particle forces are antisymmetric ($f_{ij} = -f_{ji}$) and act along the line on the centers of two particles. Thus, the momentum and angular momentum of the system are also conserved.

### III. Modification of conservative force

However, as mentioned, the traditional DPD method needs two main modifications in order to study heat transfer in gas-liquid systems.
The first is on the form of conservative force. According to the weight function $w_C$ described above, the inter-particle potential is purely repulsive and has no attractive effect. This results in a gas like behavior of the simulated fluids, and cannot simulate the coexistence of gas and condensed states. In order to fix this problem, we adopt a new form of conservative force that includes an attraction term:

$$f_{ij}^c = -\frac{dU}{dr} e_{ij}$$

$$U(r) = a_{ij}[AW_1(r,r_{cut,1}) - BW_2(r,r_{cut,2})]$$

in which $U$ denotes the potential energy between two particles, $W_1$ is the repulsive weight function and $W_2$ is the attractive weight function. Their cutoff radius for $W_1$ and $W_2$ can be chosen to be different. Figure 1 from [12] shows the new form of $U$ with different choice of $A,B$ and $r_{cut}$ and are compared with purely repulsive potential (dashed line).
The work of Liu et. al.\cite{12} shows that this form of conservative force is able to simulate coexistence of gas and condensed state.

**IV. Introduction of internal energy**

The other place that requires modification is that, in DPD, due to dissipative force and random force, the mechanic energy of particles it not conserved. The dissipative force is always opposite to the relative velocity, thus slowing down particles without increasing their potential energy, while the random force can kick the particles around. The result is that traditional DPD cannot maintain a temperature gradient and be used to study heat.
transfer. To fix this problem, Espanol\textsuperscript{[13]}, and Avolos and Mackie\textsuperscript{[14]} independently developed two kinds of new DPD method with energy conservation (DPDE). In this study, the construction of Espanol is adopted.

For each particle i, we assign an internal energy $\epsilon_i$, and an entropy $s_i$, so that there exists a temperature $T_i$ such that $\frac{1}{T_i} = \frac{\partial s_i}{\partial \epsilon_i}$. The internal energy is subjected to two parts of change:

$$\frac{d\epsilon_i}{dt} = \epsilon_i^V + \epsilon_i^C$$

The viscous heating term

$$\epsilon_i^V = \frac{1}{2} \sum_{j \neq i} w_D \gamma (v_{ij} \cdot \epsilon_{ij})^2 - \sigma_{ij}^2 \omega_R (v_{ij} \cdot \epsilon_{ij}) \xi_{ij}$$

is the change rate of internal energy due to the effect of dissipative force and random force. In other words, it is the internal energy transformed from mechanic energy of DPD particles.

The conduction term

$$\epsilon_i^C = \sum_{j \neq i} \left[ \kappa_{ij} \omega_C (r) \left( \frac{1}{T_i} - \frac{1}{T_j} \right) + \alpha_{ij} \omega_R (r) \zeta_{ij} \right]$$

results from the temperature difference between particles. $\kappa_{ij}$ is the thermal conductivity, $\omega$ is weight function that depends on r. This conduction also has a random part whose amplitude is $\alpha_{ij}$ and has the random variable $\zeta_{ij}$. 

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Similarly to dissipative force and random force, according to statistical mechanic analysis\(^{[15]}\), we have:

\[
\kappa_{ij} = \frac{\alpha_{ij}^2}{2}
\]

\[
\omega_c = \omega_R^2
\]

With the change rate of internal energy constructed as above, it is ensured that the total sum of internal energy and mechanic energy of DPD particles is also a constant of motion.

Now, with all the governing equations specified for DPD system, we can choose the parameters, initialize the system and set boundary conditions so that the fluids, nano clusters and system boundaries are well simulated, and then we can run the simulation using integration method from reference [16] and [17].
Simulation and Analysis

In the present study, we set $A=2.0$, and $B=1.0$~$1.02$ in conservative force for different cases in. $\sigma$ in dissipative force is determined through a series of trial, to be described later. Let $s_i = C_V \ln \epsilon_i$ in which heat capacity $C_V$ is set to be $100$. Set $\alpha=100$ in heat conduction. $T$ ranges from $1.8$ to $2.7$, box sizes range from $5 \times 5 \times 10$ to $5 \times 5 \times 45$, and the number of particles, ranging from $1500$~$4500$, is adjusted in each case to fit proper density. In each case, periodic boundary condition is used, and the temperature gradient is prescribed by creating a cold bin on the top of the simulation box and a hot bin at the bottom of the box. This is accomplished by swapping the slowest particles in the hot bin to the cold bin and vice versa with fixed frequency.

I. Simulating heat transport in pure gas

First, heat transport in pure gas phase is simulated. Simulation is conducted under different temperatures with different intensity of attraction in conservative force ($B$ value). The number of particles and box size are adjusted so that the gas density fits that of saturated vapor, which is obtained from Liesen (2016)\(^{[18]}\).

Temperature gradient is added after relaxation of particle positions and equilibration of velocities. During the simulation, different $\sigma$ value in dissipative force is tested. Since
particle density is low in the gas phase, when \( \sigma \) value is low, there is not enough exchange between mechanic energy and internal energy, resulting in a discrepancy between the temperature profile based on particle velocities and that based on particle internal energy. On the other hand, when \( \sigma \) value is too high, the integration will generate larger error and smaller time step will be needed, which increases computational cost. Figure 2 shows how the relative difference between the thermal conductivity calculated from two kinds of temperature profiles changes with different \( \sigma \) value.

![Relative Difference of Two Thermal Conductivity vs \( \sigma \) Value](image)

**Figure 2. Relative Error under Different \( \sigma \) Value**

Based on these tests, \( \sigma \) value is chosen to be 400.

When steady state is reached, as expected, a linear temperature profile is got except for in and near the hot bin and cold bin, as is illustrated in Figure 3:
Figure 3. Temperature Profile Based on Particle Velocities (tk) and Internal Energy (ti) in Pure Gas System (Average T=2.2)

Thermal conductivities under different conditions are listed in Table 1 and Table 2.

<table>
<thead>
<tr>
<th>Average System Temperature</th>
<th>k Based on Kinetic Energy</th>
<th>k Based on Internal Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.20</td>
<td>35.8</td>
<td>38.0</td>
</tr>
<tr>
<td>2.40</td>
<td>53.6</td>
<td>54.9</td>
</tr>
<tr>
<td>2.50</td>
<td>83.2</td>
<td>84.2</td>
</tr>
<tr>
<td>2.60</td>
<td>147</td>
<td>149</td>
</tr>
<tr>
<td>2.70</td>
<td>277</td>
<td>276</td>
</tr>
</tbody>
</table>

Table 1. Thermal Conductivity (k) under Different Temperatures for B=1.02
As seen from the table, thermal conductivity increases with the increase of gas temperature. This is reasonable since the collision and heat conduction of particles are responsible for heat transfer, while higher temperature leads to higher density of saturated vapor and faster particle movements.

In general, thermal conductivity based on kinetic energy is slightly smaller than that based on internal energy. This is reasonable since the temperature gradient created by manipulating the temperature based on kinetic energy ($tk$), so $tk$ has a slightly larger slope than $ti$, thus resulting in a smaller conductivity.

**II. Simulating heat transport in liquid-gas system**

To simulate the liquid-gas system, a greater number density of particles is set for each temperature and $B$ value. After reaching equilibrium, a phase coexistence system is got.

Temperature gradient is introduced using the same method as in pure vapor simulation. After reaching steady state, density and temperature profiles are got, which are illustrated in Figure 4 and Figure 5, respectively.
Figure 4. Density Profile in Gas-liquid System (B=1.02, T=2.5)

Figure 5. Temperature Profile in Gas-liquid System (B=1.02, T=2.5)
As seen from the Figure 4, there is high density area and low density area in the system, representing liquid and gas phase, and a transient area representing the interface. Unlike on the macroscopic level, there is not a sharp interface.

As seen from Figure 5, the temperature profile within gas or liquid area is nearly linear, while there is a curved transient temperature profile in the interfacial area. To characterize heat transfer property of such a system, overall heat transfer coefficient is calculated. In this study, this coefficient $U$ is defined as

$$U = \frac{q}{T_H - T_C}$$

where $q$ is the heat flux, $T_H$ is the temperature at the boundary of the hot bin and the bulk, and $T_C$ is the temperature at the boundary of the cold bin and the bulk.

The overall heat transfer coefficient under different conditions are listed in Table 3. Still, $U$ is calculated using temperature profile based on kinetic energy ($U_k$) and on internal energy ($U_i$)

<table>
<thead>
<tr>
<th>B</th>
<th>T</th>
<th>$U_k$</th>
<th>$U_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.02</td>
<td>2.0</td>
<td>3.36</td>
<td>3.31</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>12.5</td>
<td>12.6</td>
</tr>
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<td></td>
<td>2.4</td>
<td>25.7</td>
<td>25.7</td>
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<td></td>
<td>2.5</td>
<td>36.1</td>
<td>36.0</td>
</tr>
<tr>
<td>1.01</td>
<td>2.0</td>
<td>8.4</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>23.4</td>
<td>23.6</td>
</tr>
<tr>
<td>1.00</td>
<td>1.8</td>
<td>3.41</td>
<td>3.38</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>20.6</td>
<td>19.9</td>
</tr>
</tbody>
</table>

Table 3. Overall Heat Transfer Coefficient under Different Temperatures and B Values
III. Systematic difference between two temperature profile.

It is noticed, as in Figure 3 and Figure 5, there is always a slight difference between tk and ti, and tk is always slightly higher. A hypothesis is that, this is caused by the way tk is calculated. tk is calculated using canonical ensemble\(^2\), but the systems studied are actually isolated systems. To examine this hypothesis, one can use large box size in further study so that a small part of the large system can be seen as an isothermal system while the rest of the large system can serve as a heat bath. If the hypothesis is true, this systematic error should be eliminated.

IV. Critical point temperature and B

When the 'two-phase' simulation reaches certain temperature, we will get density and profiles in which gas, liquid and interfacial area cannot be well distinguished, as illustrated in Figure 6 and Figure 7:

![Figure 6. Density Profile around Critical Point](image)

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Figure 7. Temperature Profile around Critical Point

Compare with data from Liesen (2016)[18], we can find this is because the system is close to critical point. The observation is that, the higher the B value, the higher the critical point temperature.

In van der Waals equation of state

\[ P = \frac{RT}{V-b} - \frac{a}{V^2} \]

\( a \) is the parameter that represents the intensity of interactions among particles. The relationship between critical temperature \( T_C \) and \( a \) is:

\[ T_C = \frac{8a}{27Rb} \]

Higher B leads to higher a in vdW equation of state, thus making \( T_C \) higher.
Conclusion

This study shows that DPDE, with the introduction of a attraction term in the conservative force and internal energy of particles, can be used to simulate heat transfer phenomena in the gas-liquid coexistence system, and heat transfer properties in such systems can be calculated. In general, this indicates DPDE's potential in study heat transfer in more complex systems with phase coexistence.
References


