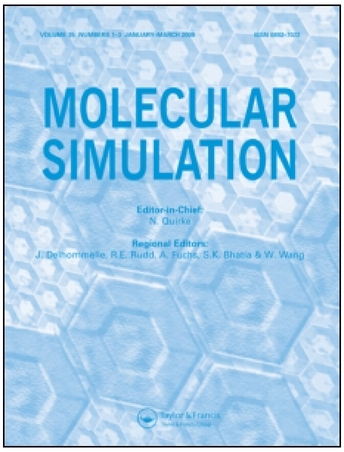

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NON-IDEAL DPD FLUIDS

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We propose a new method for implementing conservative forces in a dissipative particle dynamics (DPD) system. We allow multibody interactions, and use information on the macroscopic equilibrium behaviour of the system. We show that it is then possible to induce a fluid/fluid phase transition, and also that the local structure is then less pronounced than in previous models. This last feature is desirable in the description of fluids at a mesoscopic scale.

Keywords: Dissipative particle dynamics, fluid/fluid phase transition, EOS

PACS numbers: Molecular dynamics and particle methods 02.7ϕ. Ns; Liquid–Liquid transitions 64.7ϕ. Ja; Theorm and models of liquid structure 61.2ϕ. Gy

INTRODUCTION

Dissipative Particle Dynamics (DPD) was introduced in the early nineties as a novel way of simulating fluids at a mesoscopic scale (Hoogerbruge *et al.*). It is composed by N point particles that interact pairwise with each other with 3 different kind of forces. On top of the usual conservative forces that can be derived from a Hamiltonian, dissipative and random forces are also introduced. They mimic the effect of viscous damping between fluid elements and the thermal noise of the fluid elements, respectively. In order to ensure a proper thermal equilibrium, their amplitudes have to be related (Español *et al.*). The hydrodynamic behaviour of this system has been explored in certain detail (Marsh *et al.*), although still work has to be done. All the forces have a finite interaction range r_c, and their amplitudes decay according to a weight function $w(r_{ij})$ to avoid spurious jumps at r_c.

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In this presentation we will focus on the conservative interaction. Up to now this force has been taken to depend on the distance between a pair of particles. Moreover, it has been taken a smooth, monotonous function of the distance. This leads to a equation of state (EOS) that is quadratic in the density, and exhibits no fluid/fluid phase transition. This kind of forces will induce structure in the fluid (reminiscent of atomic behaviour) on the length scales in which the force is acting, which is taken conventionally to be of the same range as the other interactions for computational ease.

MODEL

We consider that the system has a total energy

$$U = \sum_{i=1}^{N} \psi_i(\{\vec{r}_k\}) \tag{1}$$

where ψ_i is the energy of particle i, which depends on the positions of all the other particles. In DPD, the temperature and total number of particles of the system are fixed, and accordingly, we interpret U as a free energy. Moreover, since the DPD particles have translational degrees of freedom, the ideal contribution to the free energy is already contained in their motion. Therefore, the energy U is in reality the excess free energy of the system.

The force acting on particle i due to this energy will be given by

$$\vec{F}_i = -\sum_{j=1}^{N} \frac{\partial \psi_j(\{\vec{r}_k\})}{\partial \vec{r}_i} \tag{2}$$

DPD particles can be regarded as fluid elements; it is then not unreasonable to assume that the excess free energy associated to every particle is a function of its local density. If we introduce such a density as

$$n_i = \frac{1}{[w]} \sum_j w(r_{ij}) \tag{3}$$

and assume that the dependence on the other particles' positions is implicit in n_i (*i.e.*, $\psi_i(\{\vec{r}_k\}) = \psi(n_i)$), then the force acting on particle i can be written as

$$\vec{F}_i = -\sum_j (\psi_i' + \psi_j') \frac{w_{ij}'}{[w]} \hat{e}_{ij} \equiv \sum_j \vec{F}_{ij} \tag{4}$$

As usual, $[w]$ is the average value of the weight function. Note that the sum is for particles within the interaction range r_c. The dashes $'$ mean derivatives with respect to the corresponding variables. Note also that the total force acting on particle i can still be written as an additive pair-wise force.

Since the functional U can be interpreted as an excess free energy, one is then able to prescribe the free energy of the system and from there deduce the forces acting on the particles. This procedure is similar to the approach followed in Lattice-Boltzmann to introduce non-ideal fluid behaviour in a phenomenological way (Swift *et al.*, 1996).

Given the pair forces acting between the particles, for a homogeneous system (assume that the pair distribution function is flat) using the virial theorem we obtain the EOS

$$p = \rho k_B T - \frac{[w'r]}{2}\rho^2\psi' \tag{5}$$

It is worth noting that currently efforts are being carried out to formulate a general thermodynamic formalism from which to derive the dynamics of DPD particles (Español *et al.*, 1999).

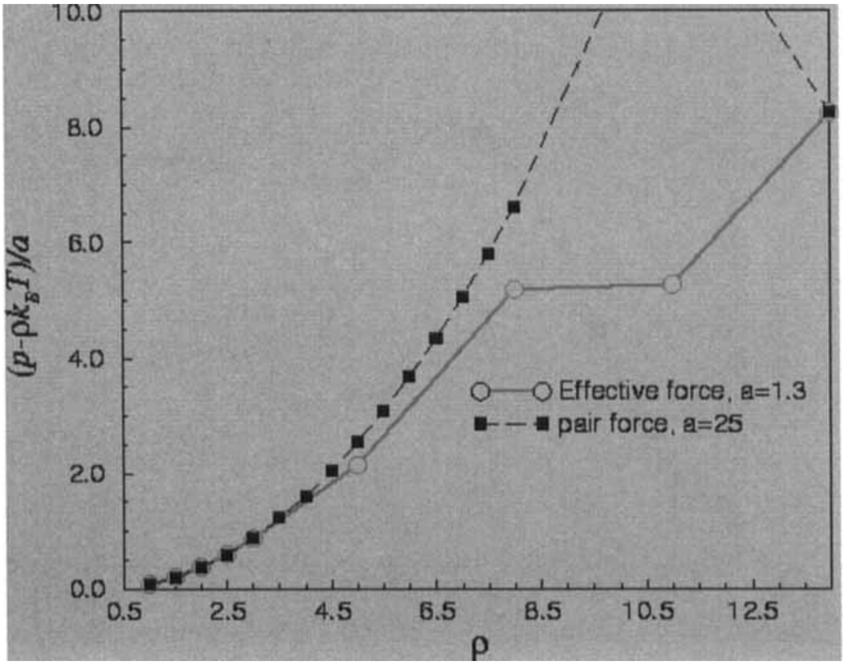

FIGURE 1 Pressure as a function of the density for the model described in the section, using the usual pair-wise force, and with the force proposed here.

COMPARISON WITH PREVIOUS MODELS

Before considering more general free energies, we use the introduced formalism to compare with the behaviour of the non-ideal fluid introduced by Groot and Warren (Groot *et al.*, 1998), which has an equation of state quadratic in the density. In this model the conservative force is taken to be:

$$\vec{F}_{ij} = a(1 - r_{ij}/r_c)\hat{r}_{ij} \tag{6}$$

We choose a function $\psi = 3 * a'/(4 * \pi * r_c^4)$. In Figures 1 and 2 we compare the EOS and the pair distribution function in both models for a 3D-DPD fluid with $a = 25$ and $a' = 1.3$, respectively. It can be seen that for low densities both EOS have the same behaviour. At larger densities, there is a phase transition to an ordered state, that takes place at different densities in the two models due to the different character of the interactions. It also seems that the pre-transitional behaviour in both models is different. This fact indicates that, due to the collective character of the interactions in the proposed models, the fluctuations will also have a different character.

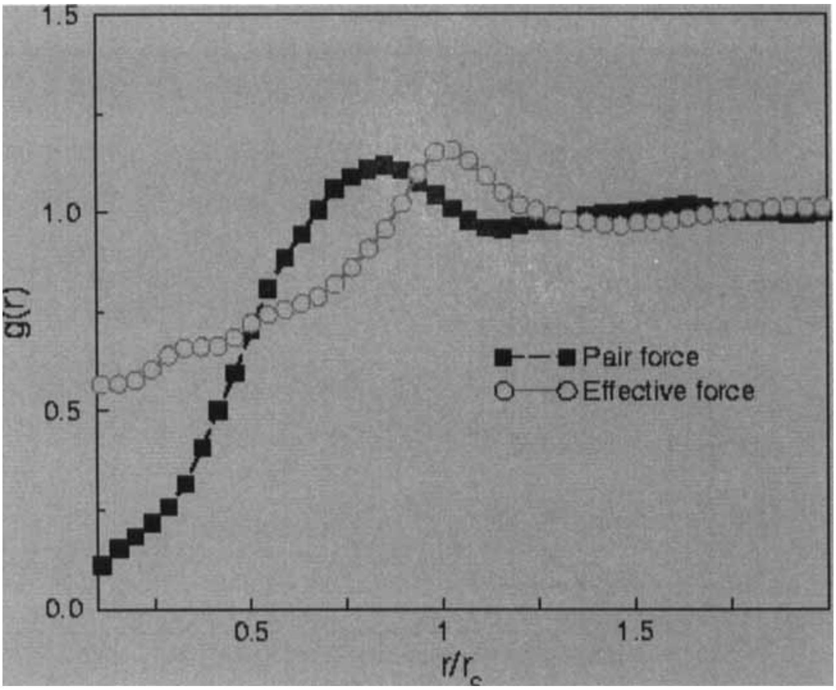

FIGURE 2 Radial distribution function.

The pair distribution function (Fig. 2) for $\rho = 3$, is also different in both models. Although any force will produce certain structure, it can be seen that in the model proposed the structure is less pronounced than in the previous one, again due to the multi-body interaction.

LIQUID/GAS EQUILIBRIUM

If we consider the excess free energy of the van der Waals fluid,

$$\mathcal{F}^{ex} = -a\rho^2 - k_B T \rho \ln(1 - b\rho) \tag{7}$$

we can again derive the appropriate expression for the effective force between the DPD particles, $\psi = (-an_i - k_B T \ln(1 - bn_i))$. In Figure 3 we show, for a 2-D DPD fluid, the EOS obtained and its comparison with the theoretical prediction.

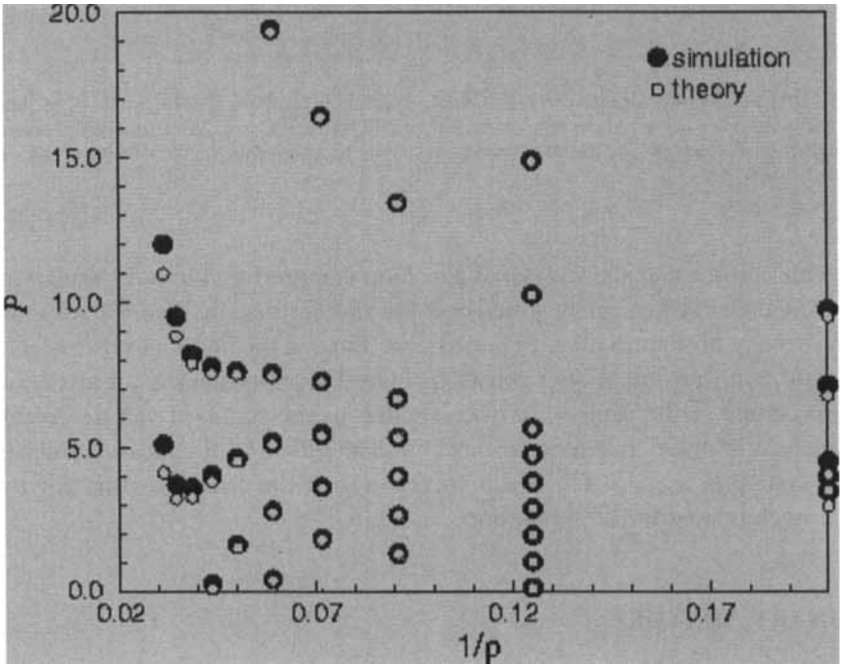

FIGURE 3 Equation of state for a 2-D van der Waals fluid. The different sets of data points correspond to different temperatures.

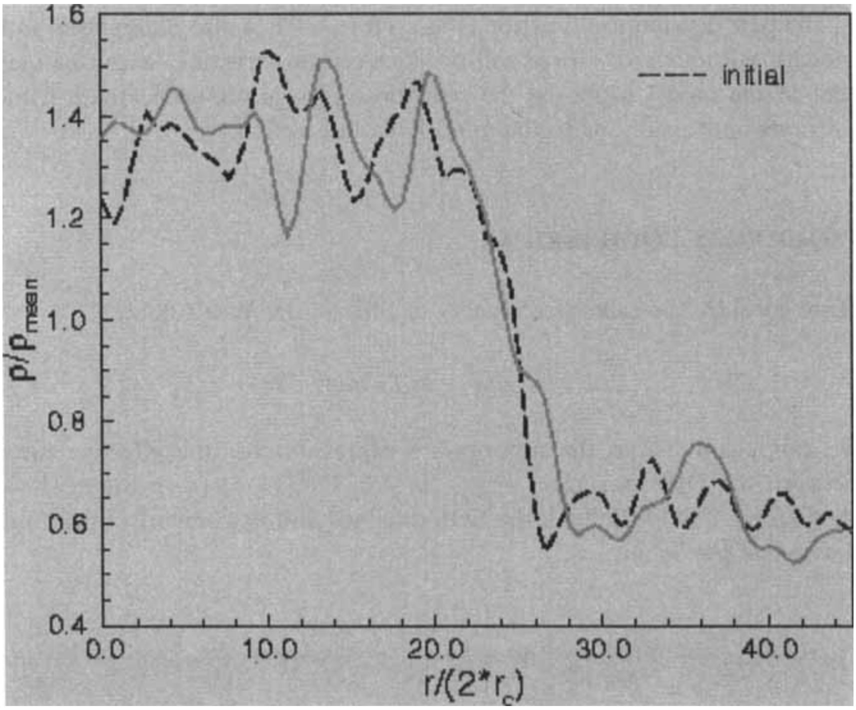

FIGURE 4 Density profile for a 2-D fluid. The initial profile is a step profile. The thick continuous line corresponds to times in which the DPD particles have diffuse on average several interaction diameters. The dashed curve corresponds to an average of the density profiles at short times.

One can see that the van der Waals loop is reproduced in our simulation, and that the agreement is quite good for all densities. In Figure 4 we show the density profiles that are obtained if we start, in the liquid/gas coexistence region, with an initial step density profile. For convenience, an attractive term, cubic in the denisty, has been added to the standard van der Waals equation of state. The temperature $T = 0.85 * T_c$, and the mean density in the system is $\rho_{\mathrm{mean}} = 8.5$, which correponds to the critical density for the parameters used in the simulation.

BINARY MIXTURE

Finally, we have also analysed the behavior of a binary mixture, composed of two types of particles: A and B. In this case, we assume that the excess

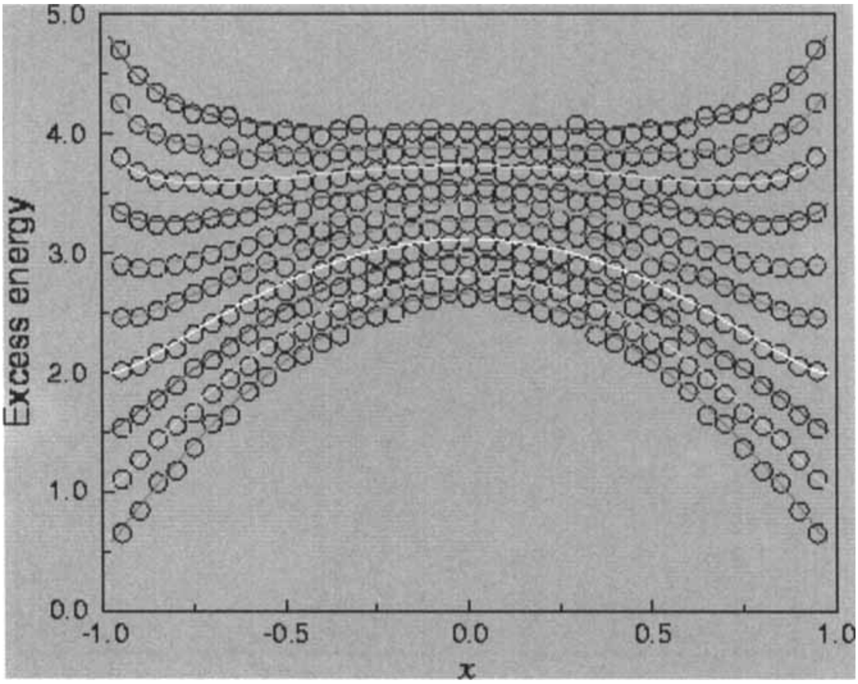

FIGURE 5 Comparison of the excess energy computed for a 2-D DPD fluid with the theoretical prediction. Different curves correspond to different temperatures.

energy of the system is described by the usual quadratic term

$$\mathcal{F}^{ex} = \lambda \sum_i n_{Aj} n_{Bj} \tag{8}$$

n_{Aj} means the concentration of A-type particles surrounding particle j. The force acting on a pair of particles can be accordingly expressed as

$$\vec{F}_{ij} = -\lambda(n\hat{t}_j i + n\hat{t}_i j) w'_{ij} \hat{e}_{ij} \tag{9}$$

where $\hat{t}_i j$ refers to the opposite kind of particles of particle j (*i.e.*, A if j is a B particle, B otherwise). In the Figure 5 we compare the measured energy with the prediction based on Eq. (8).

If the temperature is chosen smaller than the critical temperature $T_c = \lambda/(z\rho^2)$ the system will phase separate. In Figure 6 we show the time dependent concentration profile, if the initial state corresponds to a step profile. One can see the development of an interface of a finite width. Also shown is the total density across the interface, which is essentially constant across the system.

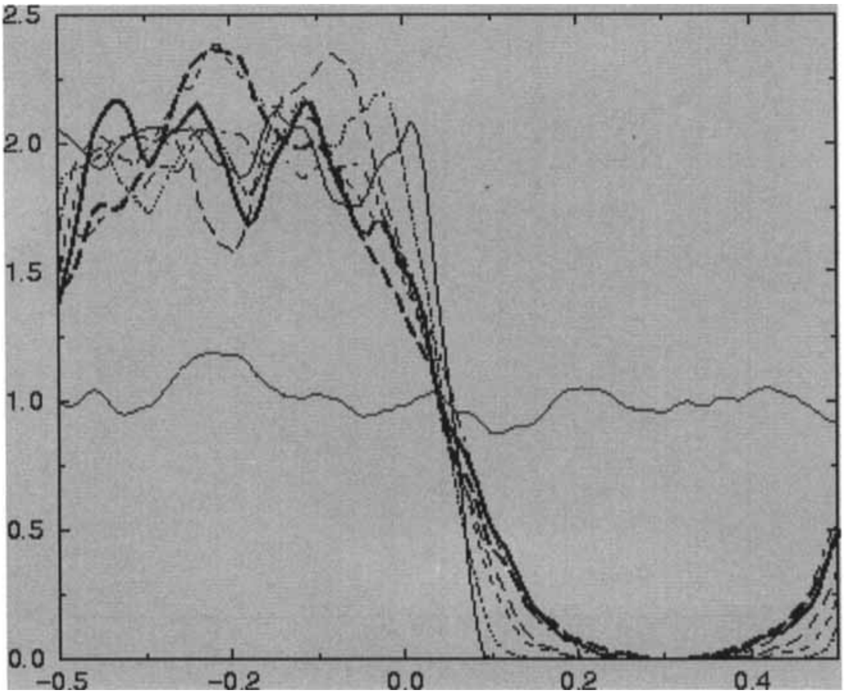

FIGURE 6 Time dependent concentration profile for a 2-D binary mixture. The initial profile is a step profile. The thick continuous line corresponds to the final state. Also shown in a different colour the total density across the interface.

CONCLUSIONS

We have presented a new way of implementing the conservative forces between DPD particles.

Rather than assuming a force that depends on the inter-particle separation, we have introduced a force that depends on the local density. The force can be thought as derived from the excess free energy of the system, which gives freedom to choose the thermodynamics of the system (with the restriction to isothermal processes).

On top of the freedom in the free energy, this new type of forces induces less structure in the fluid at short distances, which is a desirable property of a mesoscopic simulation, in order to enforce a proper separation of length scales.

At the mean field level, this new formalism can be understood as a density functional theory for the DPD fluid. Using then standard techniques, it is easy to derive expressions for the interfacial properties (Pagonabarraga *et al.*, 1999).

References

Hoogerbruge, P. J. and Koelman, J. M. V. (1992) Simulating microscopic hydrodynamic phenomena with dissipative particle dynamics. *Europh. Lett.*, **19**, 155.

Español, P. and Warren, P. B. (1995) Statistical mechanics of dissipative particle dynamics. *Europh. Lett.*, **30**, 191.

Marsh, C., Bacxk, G. and Ernst, M. H. (1997) Static and dynamic properties of dissipative particle dynamics. *Phys. Rev. E*, **56**, 1676; Pagonabarraga, I., Hagen, M. H. J. and Frenkel, D. (1998) Self-consistent Dissipative Particle Dynamics Algorithm. *Europh. Lett.*, **42**, 377.

Swift, M. R., Orlandini, E., Osborn, W. R. and Yeomans, J. (1996) Lattice Boltzmann simulations of liquid-gas and binary fluid systems. *Phys. Rev. E*, **54**, 5041.

Groot, R. D. and Warren, P. B. (1998) DPD: Bridging the gap between atomistic and mesoscopic simulation. *J. Chem. Phys.*, **107**, 4423.

Pagonabarraga, I. and Frenkel, D., Preprint.

Español, P., Serrano, M. and Öttinger, H. C. (1999) *Phys. Rev. Lett.*, **83**, 4542.