Detailed balance and ***H***-theorems for dissipative particle dynamics

1998 J. Phys. A: Math. Gen. 31 6561

(http://iopscience.iop.org/0305-4470/31/31/003)

J. Phys. A: Math. Gen. **31** (1998) 6561–6568. Printed in the UK PII: S0305-4470(98)93610-1

Detailed balance and H-theorems for dissipative particle dynamics

C A Marsh†§ and P V Coveney†‡‖

† Department of Theoretical Physics, University of Oxford, Keble Road, Oxford OX1 3NP, UK
‡ Schlumberger Cambridge Research, High Cross, Madingley Road, Cambridge CB3 OE2, UK

Received 23 April 1998

Abstract. An extension of the H-theorem for dissipative particle dynamics (DPD) to the case of a multicomponent fluid is made. Detailed balance and an additional H-theorem are proved for an energy-conserving version of the DPD algorithm. The implications of these results for the statistical mechanics of the method are discussed.

1. Introduction

Interest in the rheological and dynamical properties of complex fluids [1] over the past decade has seen the introduction of several new techniques for their simulation on *mesoscopic* length scales. These methods include lattice-gas automata (LGA), lattice-Boltzmann equation (LBE) and dissipative particle dynamics (DPD) [2]. The aim of this paper is to explore some of the statistical mechanical properties of the rapidly evolving DPD model, and to extend these results in order to keep pace with new developments being made in the algorithms.

The DPD method was originally introduced by Hoogerbrugge and Koelman [3] as a discrete time algorithm; this was subsequently modified and reinterpreted as a discrete time approximation to an underlying system obeying Langevin dynamics (with momentum conservation) by Español and Warren [4], in order to guarantee the existence of a Gibbsian (specifically a canonical) equilibrium state. Applications of the model include colloidal suspensions [5], polymer suspensions [6] and binary mixtures [7, 8]. A dynamical theory has been presented [9, 10] for the continuous time limit and the equilibrium for finite timestep has been investigated [11].

We briefly describe the implementation of the DPD method. The system consists of a set of N discrete particles which move in continuous space and in discrete timesteps, the interval between which may be reduced to being infinitesimal. At each timestep δt, the particles' momenta are updated by a momentum-conserving interaction with each particle inside a neighbourhood of radius R_0. This interaction includes three distinct forces, which can be described as *conservative* $\boldsymbol{F}^{\mathrm{C}}$, *dissipative* $\boldsymbol{F}^{\mathrm{D}}$ and *random* $\boldsymbol{F}^{\mathrm{R}}$. Between each tick of the clock, the particles all propagate freely according to their velocities. In the limit of continuous time, the DPD equations of motion are most effectively described in terms of

§ E-mail address: c.marsh1@physics.ox.ac.uk
‖ E-mail address: coveney@cambridge.scr.slb.com

0305-4470/98/316561+08$19.50

the following stochastic differential equations:

$$\dot{\boldsymbol{v}}_i = \sum_{j \neq i} \{\boldsymbol{F}_{ij}^{\mathrm{C}} + \boldsymbol{F}_{ij}^{\mathrm{D}} + \boldsymbol{F}_{ij}^{\mathrm{R}}\} \tag{1}$$

$$\dot{\boldsymbol{r}}_i = \boldsymbol{v}_i \tag{2}$$

for each particle labelled by the subscript i. The forces take the following forms:

$$\boldsymbol{F}_{ij}^{\mathrm{C}} = -\frac{1}{m}\frac{\partial \phi}{\partial r_{ij}} \tag{3}$$

$$\boldsymbol{F}_{ij}^{\mathrm{D}} = -\gamma w_{\mathrm{D}}(r_{ij})[\boldsymbol{e}_{ij} \cdot \boldsymbol{v}_{ij}]\boldsymbol{e}_{ij} \tag{4}$$

$$\boldsymbol{F}_{ij}^{\mathrm{R}} = \sigma w_{\mathrm{R}}(r_{ij})\boldsymbol{e}_{ij}\zeta_{ij} \tag{5}$$

where ϕ is a potential energy, $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$ is the relative separation vector and $\boldsymbol{e}_{ij}$ is the unit vector in the direction of $\boldsymbol{r}_{ij}$; for simplicity, all particles are assumed here to have the same mass m. The functions $w_{\mathrm{D}}(r_{ij})$ and $w_{\mathrm{R}}(r_{ij})$ are weighting functions which limit the action of the dissipative and random forces to a finite range R_0. The random elements ζ_{ij} are Gaussian white noise with zero mean: $\overline{\zeta_{ij}} = 0$. They are uncorrelated for different pairs of particles and for different times: $\overline{\zeta_{ij}(t)\zeta_{kl}(t')} = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\delta(t - t')$. It should be noted that these forces conserve both momentum and angular momentum but not energy.

The algorithm presented above is the traditional, isothermal DPD method. Following a brief description of the statistical mechanical concepts involved in this method, we present an H-theorem for the multicomponent extension to this isothermal DPD fluid. We then briefly describe the alternative energy-conserving DPD model and examine detailed balance and an H-theorem in this context.

2. On detailed balance and H-theorems

It is important at the outset to explain the significance and importance of the statistical mechanical properties of detailed balance and the so-called H-theorem. Detailed balance is known to be a sufficient, but not necessary, condition which ensures that a Gibbsian equilibrium state exists in the ensemble representation of a dynamical system. It is possible for systems not satisfying detailed balance to exhibit equilibrium states; however, characterizing these is then a much harder task. The virtue of the modifications made by Español and Warren to the original DPD algorithm is that, in the limit of continuous time, the N-body DPD system then satisfies the detailed balance condition, thereby guaranteeing the existence of a well-defined equilibrium state.

In the literature, at least two separate kinds of 'H-theorem' can be distinguished. First, any Markov chain or process which has an equilibrium distribution will have an H-theorem associated with it, in the sense of possessing a Lyapounov function that changes monotonically with time. Indeed, a whole class of Lyapounov functions achieve this; the class is defined as the expectation of any convex function of the relative-to-equilibrium probability density. The proof of such H-theorems follows directly from the linear equation (also referred to as the 'master equation') for the N-body distribution function. Detailed balance plays a role here, in that it specifies what the equilibrium distribution is; this information is needed to write down the Lyapounov function.

However, the arguably more famous Boltzmann H-theorem is quite a different notion, and is of much more restricted validity. Boltzmann's H-function is defined in terms of the *one*-body distribution function, and its time-monotonicity can only be derived if we know the kinetic equation obeyed by this reduced distribution. Moreover, this equation is

nonlinear so that the choice of H is now much more restricted; for the Boltzmann equation itself, only the expectation of the logarithm of this reduced probability distribution suffices. In proving Boltzmann's H-theorem, use is made of the property of detailed balance.

Note in passing that time-symmetry is a stronger property than detailed balance; the former implies the latter, but is not implied by it. Thus, detailed balance is obeyed by both Newton's equations of motion and by dissipative particle dynamics, although the former is time-symmetric while the latter is not.

The existence of an H-theorem for a given system can be used to check on the numerical stability of any algorithm implemented to simulate it; numerical instabilities which lead to non-monotonicity of the H-functional concerned can then be precluded. The issue of the existence of detailed balance and related H-theorems is thus clearly of importance for the various mesoscale modelling and simulation techniques.

By contrast with (continuous time) DPD, virtually all interacting lattice-gas and lattice-Boltzmann models have no known detailed balance condition; therefore, their equilibrium states are generally unknown, while the lack of any associated H-theorems makes the real-valued lattice-Boltzmann methods, in particular, susceptible to poorly understood numerical instabilities. Indeed, because detailed balance is not satisfied in such models, it makes their theoretical analysis by standard methods of nonequilibrium statistical mechanics well nigh impossible.

3. H-theorem for multicomponent, isothermal DPD

Detailed balance and an H-theorem (of the first kind mentioned in section 2, i.e. for the full N-body distribution) for the single component DPD fluid have already been demonstrated [9]. The proof of detailed balance for general DPD models of interacting multicomponent fluids has also been derived [13]. Here, we aim to extend this form of H-theorem to the case of a multicomponent fluid, which includes the case of binary immiscible fluids [7, 8].

It has been demonstrated [13] that the evolution equation for the N-particle distribution function is the Fokker–Planck equation for the multicomponent fluid: $\partial_t P = \mathcal{L}^{\mathrm{MC}} P$, where the multicomponent Fokker–Planck operator $\mathcal{L}^{\mathrm{MC}}$ is defined as

$$\mathcal{L}^{\mathrm{MC}} = -\left[\sum_{\alpha}\sum_{i_\alpha} \boldsymbol{v}_{i_\alpha}\cdot\frac{\partial}{\partial \boldsymbol{r}_{i_\alpha}} + \sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\frac{\boldsymbol{F}^{\mathrm{C}}_{i_\alpha j_\beta}}{m}\cdot\frac{\partial}{\partial \boldsymbol{v}_{i_\alpha}}\right] + \sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\frac{\gamma}{m}w_{\mathrm{D}}(r_{i_\alpha j_\beta})\left[\boldsymbol{e}_{i_\alpha j_\beta}\cdot\frac{\partial}{\partial \boldsymbol{v}_{i_\alpha}}\right]\boldsymbol{e}_{i_\alpha j_\beta}\cdot\left[\boldsymbol{v}_{i_\alpha j_\beta} + \frac{\theta}{m}\left(\frac{\partial}{\partial \boldsymbol{v}_{i_\alpha}} - \frac{\partial}{\partial \boldsymbol{v}_{j_\beta}}\right)\right] \quad (6)$$

where α and β are sums over different types of particles and i_α and j_β sum over all particles of each type. The parameter θ is the equilibrium temperature defined through the fluctuation-dissipation theorem as: $\theta = m\sigma^2/2\gamma$. The relevant H-functional for the multicomponent case is a simple extension of that in the single component case. As expected for an isothermal system, it is just the expectation of the associated free energy $\langle U - \theta S\rangle$, where U is the internal energy, θ is the equilibrium temperature as defined above, S is the global entropy, and the expectation is taken using the full N-particle distribution function, P:

$$\mathcal{F}[P(\boldsymbol{\Gamma}, t)] = \int \mathrm{d}\boldsymbol{\Gamma}\, P\left\{\sum_{\alpha}\sum_{i_\alpha}\left[\frac{m v_{i_\alpha}^2}{2} + \frac{1}{2}\sum_{\beta}\sum_{j_\beta} V(r_{i_\alpha j_\beta})\right] + \theta \ln P\right\}. \quad (7)$$

Using the time-evolution operator for the multicomponent system (6), it is possible to show that

$$\frac{\mathrm{d}\mathcal{F}}{\mathrm{d}t} = -\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\int \mathrm{d}\mathbf{\Gamma}\,\frac{\gamma w_{\mathrm{D}}(r_{i_\alpha j_\beta})}{P}\left[\boldsymbol{e}_{i_\alpha j_\beta}\cdot\left[\boldsymbol{v}_{i_\alpha j_\beta}+\frac{\theta}{m}\left(\frac{\partial}{\partial \boldsymbol{v}_{i_\alpha}}-\frac{\partial}{\partial \boldsymbol{v}_{j_\beta}}\right)\right]P\right]^2. \tag{8}$$

It is then apparent that the time derivative of the functional $\mathcal{F}$ is the sum of negative definite terms, and therefore that the functional itself is monotonically decreasing in time. The appropriate equilibrium distribution for the multicomponent system occurs when this functional stops decreasing. It is easy to show that this occurs when it reaches the Gibbsian distribution for the associated conservative system, i.e. as if the dissipative and random forces were not present:

$$P_{\mathrm{eqm}} = \frac{1}{Z_{\mathrm{MC}}}\exp\left\{-\frac{1}{\theta}\sum_{\alpha}\sum_{i_\alpha}\left[\frac{m v_{i_\alpha}^2}{2}+\frac{1}{2}\sum_{\beta}\sum_{j_\beta}V(r_{i_\alpha j_\beta})\right]\right\} \tag{9}$$

Z_{MC} being the multicomponent canonical partition function, defined in the normal way.

4. Energy-conserving DPD

An energy conserving version of DPD has recently been presented by Español [12]. This involves the introduction of an internal energy variable ϵ_i for each DPD particle (now interpreted as a cluster of atoms or molecules, into which the dissipated energy is assumed to flow). There is an entropy $s(\epsilon_i)$ which needs to be specified in order to describe a given system, and the temperature is defined in the usual thermodynamic way as $\theta_i = (\partial s(\epsilon_i)/\partial\epsilon_i)^{-1}$. It is then possible to formulate a new DPD algorithm which conserves the total energy of the system, as well as momentum and angular momentum [12]. An appropriate set of stochastic differential equations is

$$\dot{\boldsymbol{r}}_i = \boldsymbol{v}_i \tag{10}$$

$$\dot{\boldsymbol{v}}_i = \sum_{j\neq i}\left[\frac{1}{m}F_{ij}^{\mathrm{C}} - \gamma_{ij}w_{\mathrm{D}}(r_{ij})(\boldsymbol{e}_{ij}\cdot\boldsymbol{v}_{ij})\boldsymbol{e}_{ij} + \sigma_{ij}w_{\mathrm{R}}(r_{ij})\boldsymbol{e}_{ij}\zeta_{ij}\right] \tag{11}$$

$$\dot{\epsilon}_i = \frac{m}{2}\sum_{j\neq i}\Bigg[\gamma_{ij}w_{\mathrm{D}}(r_{ij})(\boldsymbol{v}_{ij}\cdot\boldsymbol{e}_{ij})^2 - \sigma_{ij}^2 w_{\mathrm{R}}^2(r_{ij}) - \sigma_{ij}w_{\mathrm{R}}(r_{ij})(\boldsymbol{e}_{ij}\cdot\boldsymbol{v}_{ij})\zeta_{ij} + \kappa_{ij}\left\{\frac{1}{\theta_i}-\frac{1}{\theta_j}\right\}A_{\mathrm{D}}(r_{ij}) + \alpha_{ij}A_{\mathrm{R}}(r_{ij})\zeta_{ij}^{\epsilon}\Bigg]. \tag{12}$$

Here the functions $A_{\mathrm{D}}(r_{ij})$ and $A_{\mathrm{R}}(r_{ij})$ are additional weighting functions for what can be interpreted as the *conduction* and *random heat flux* terms respectively, while κ_{ij} and α_{ij} are their strengths; ζ_{ij}^{ϵ} are random elements which are uncorrelated to the elements ζ_{ij} and have zero mean $\overline{\zeta_{ij}^{\epsilon}} = 0$. They are uncorrelated for different times and different pairs of particles and are antisymmetric: $\overline{\zeta_{ij}^{\epsilon}(t)\zeta_{kl}^{\epsilon}(t')} = (\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk})\delta(t-t')$. We also note that the strengths of the random and dissipative forces (σ and γ) can now, in general, vary for different particle pairs.

Following the original derivation [12], we make the additional assumptions

$$A_{\mathrm{D}}^2(r) = A_{\mathrm{R}}(r) \qquad \alpha_{ij}^2 = 2\kappa_{ij} \qquad w_{\mathrm{R}}^2(r) = w_{\mathrm{D}}(r) \tag{13}$$

which mean that the Fokker–Planck equation for the evolution of the N-particle distribution function P, can be written as

$$\partial_t P = [\mathcal{L}_{\mathrm{C}} + \mathcal{L}_{\mathrm{VH}} + \mathcal{L}_{\mathrm{HC}}]P \tag{14}$$

where the operators on the right-hand side are defined as follows:

$$\mathcal{L}_{\mathrm{C}} = -\sum_i \boldsymbol{v}_i \cdot \frac{\partial}{\partial \boldsymbol{r}_i} - \sum_{j\neq i} \frac{\boldsymbol{F}_{ij}^{\mathrm{C}}}{m} \cdot \frac{\partial}{\partial \boldsymbol{v}_i} \tag{15}$$

$$\mathcal{L}_{\mathrm{VH}} = \frac{1}{2}\sum_{j\neq i} w_{\mathrm{D}}(r_{ij}) L_{ij} \left[\gamma_{ij}(\boldsymbol{v}_{ij}\cdot\boldsymbol{e}_{ij}) + L_{ij}\frac{\sigma_{ij}^2}{2} \right] \tag{16}$$

$$\mathcal{L}_{\mathrm{HC}} = \sum_{j\neq i} A_{\mathrm{D}}(r_{ij}) \frac{\partial}{\partial \epsilon_i}\left[\frac{1}{\theta_j} - \frac{1}{\theta_i} + \frac{\partial}{\partial \epsilon_i} - \frac{\partial}{\partial \epsilon_j}\right]\kappa_{ij} \tag{17}$$

$$L_{ij} = \boldsymbol{e}_{ij}\cdot\left[\frac{\partial}{\partial \boldsymbol{v}_i} - \frac{\partial}{\partial \boldsymbol{v}_j} - \frac{m}{2}\boldsymbol{v}_{ij}\left[\frac{\partial}{\partial \epsilon_i} + \frac{\partial}{\partial \epsilon_j}\right]\right] \tag{18}$$

where the subscripts C, VH and HC refer to the *conservative*, *viscous heating* and *heat conduction* terms respectively.

5. Detailed balance for energy-conserving DPD

If the evolution operator for a system is $\mathcal{L}$ and we designate its adjoint by the operator $\mathcal{L}^\dagger$, then the detailed balance constraint [14] can be written in the following way:

$$\mathcal{L}P_{\mathrm{eqm}}\varphi = P_{\mathrm{eqm}}\mathcal{L}^{\dagger\epsilon}\varphi \tag{19}$$

where the superscript ϵ indicates that all variables that are *odd* under time reversal are to have their signs reversed. In the case of DPD, this means that the velocities attract an additional minus sign. The function φ can be any function of the phase space variables.

The appropriate operators for the energy-conserving version of DPD are

$$\mathcal{L}_{\mathrm{C}}^{\dagger\epsilon} = -\sum_i \boldsymbol{v}\cdot\frac{\partial}{\partial \boldsymbol{r}_i} - \sum_{j\neq i}\frac{\boldsymbol{F}_{ij}^{\mathrm{C}}}{m}\cdot\frac{\partial}{\partial \boldsymbol{v}_i} = \mathcal{L}_{\mathrm{C}} \tag{20}$$

$$\mathcal{L}_{\mathrm{VH}}^{\dagger\epsilon} = \frac{1}{2}\sum_{j\neq i} w_{\mathrm{D}}(r_{ij})\left[-\gamma_{ij}(\boldsymbol{v}_{ij}\cdot\boldsymbol{e}_{ij}) + L_{ij}\frac{\sigma_{ij}^2}{2}\right]L_{ij} \tag{21}$$

$$\mathcal{L}_{\mathrm{HC}}^{\dagger\epsilon} = -\sum_{j\neq i} A_{\mathrm{D}}(r_{ij})\kappa_{ij}\left[\frac{1}{\theta_j} - \frac{1}{\theta_i} + \frac{\partial}{\partial \epsilon_i} - \frac{\partial}{\partial \epsilon_j}\right]\frac{\partial}{\partial \epsilon_i}. \tag{22}$$

We can then show that

$$\begin{aligned}\mathcal{L}_{\mathrm{C}}P_{\mathrm{eqm}}\varphi &= P_{\mathrm{eqm}}\mathcal{L}_{\mathrm{C}}\varphi + \varphi\mathcal{L}_{\mathrm{C}}P_{\mathrm{eqm}} \\ &= P_{\mathrm{eqm}}\mathcal{L}_{\mathrm{C}}^{\dagger\epsilon}\varphi\end{aligned} \tag{23}$$

$$\begin{aligned}\mathcal{L}_{\mathrm{VH}}P_{\mathrm{eqm}}\varphi &= \frac{1}{2}\sum_{j\neq i} w_{\mathrm{D}}(r_{ij})L_{ij}\left\{\gamma_{ij}(\boldsymbol{e}_{ij}\cdot\boldsymbol{v}_{ij}) + L_{ij}\frac{\sigma^2}{2}\right\}P_{\mathrm{eqm}}\varphi \\ &= \frac{1}{2}\sum_{j\neq i} w_{\mathrm{D}}(r_{ij})L_{ij}P_{\mathrm{eqm}}L_{ij}\frac{\sigma^2}{2}\varphi \\ &= \frac{1}{2}\sum_{j\neq i} w_{\mathrm{D}}(r_{ij})L_{ij}P_{\mathrm{eqm}}\left[-\gamma_{ij}(\boldsymbol{e}_{ij}\cdot\boldsymbol{v}_{ij}) + L_{ij}\frac{\sigma^2}{2}\right]L_{ij}\varphi \\ &= P_{\mathrm{eqm}}\mathcal{L}_{\mathrm{VH}}^{\dagger\epsilon}\end{aligned} \tag{24}$$

and

$$\begin{aligned}
\mathcal{L}_{\mathrm{HC}} P_{\mathrm{eqm}}\varphi &= \sum_{j\neq i} A_{\mathrm{D}}(r_{ij})\frac{\partial}{\partial\epsilon_i}\left[\frac{1}{\theta_i}-\frac{1}{\theta_j}+\frac{\partial}{\partial\epsilon_i}-\frac{\partial}{\partial\epsilon_j}\right]\kappa_{ij}P_{\mathrm{eqm}}\varphi \\
&= \frac{1}{2}\sum_{j\neq i} A_{\mathrm{D}}(r_{ij})\kappa_{ij}\left[\frac{\partial}{\partial\epsilon_i}-\frac{\partial}{\partial\epsilon_j}\right]\left[\frac{1}{\theta_i}-\frac{1}{\theta_j}+\frac{\partial}{\partial\epsilon_i}-\frac{\partial}{\partial\epsilon_j}\right]P_{\mathrm{eqm}}\varphi \\
&= \frac{1}{2}\sum_{j\neq i} A_{\mathrm{D}}(r_{ij})\kappa_{ij}\left[\frac{\partial}{\partial\epsilon_i}-\frac{\partial}{\partial\epsilon_j}\right]P_{\mathrm{eqm}}\left[\frac{\partial}{\partial\epsilon_i}-\frac{\partial}{\partial\epsilon_j}\right]\varphi \\
&= \frac{1}{2}\sum_{j\neq i} A_{\mathrm{D}}(r_{ij})\kappa_{ij}P_{\mathrm{eqm}}\left[\frac{1}{\theta_i}-\frac{1}{\theta_j}+\frac{\partial}{\partial\epsilon_i}-\frac{\partial}{\partial\epsilon_j}\right]\left[\frac{\partial}{\partial\epsilon_i}-\frac{\partial}{\partial\epsilon_j}\right]\varphi \\
&= \sum_{j\neq i} A_{\mathrm{D}}(r_{ij})\kappa_{ij}P_{\mathrm{eqm}}\left[\frac{1}{\theta_i}-\frac{1}{\theta_j}+\frac{\partial}{\partial\epsilon_i}-\frac{\partial}{\partial\epsilon_j}\right]\frac{\partial}{\partial\epsilon_i}\varphi \\
&= P_{\mathrm{eqm}}\mathcal{L}^{\dagger\epsilon}_{\mathrm{HC}}\varphi
\end{aligned} \tag{25}$$

where we choose the strengths of the dissipative and random forces to satisfy the following relations:

$$\sigma_{ij} = \sigma \qquad \gamma_{ij} = \frac{m\sigma^2}{4}\left[\frac{1}{\theta_i}+\frac{1}{\theta_j}\right]. \tag{26}$$

It is therefore apparent that

$$[\mathcal{L}_{\mathrm{C}}+\mathcal{L}_{\mathrm{VH}}+\mathcal{L}_{\mathrm{HC}}]P_{\mathrm{eqm}}\varphi = P_{\mathrm{eqm}}[\mathcal{L}^{\dagger\epsilon}_{\mathrm{C}}+\mathcal{L}^{\dagger\epsilon}_{\mathrm{VH}}+\mathcal{L}^{\dagger\epsilon}_{\mathrm{HC}}]\varphi \tag{27}$$

and therefore that the energy-conserving DPD algorithm satisfies detailed balance. The equilibrium distribution associated with this detailed balance condition satisfies the following relations:

$$\left[L_{ij}+(\boldsymbol{e}_{ij}\cdot\boldsymbol{v}_{ij})\frac{m}{2}\left(\frac{1}{\theta_i}+\frac{1}{\theta_j}\right)\right]P_{\mathrm{eqm}} = 0 \tag{28}$$

$$\left[\frac{1}{\theta_j}-\frac{1}{\theta_i}+\frac{\partial}{\partial\epsilon_i}-\frac{\partial}{\partial\epsilon_j}\right]P_{\mathrm{eqm}} = 0. \tag{29}$$

Therefore the equilibrium distribution consistent with $[\mathcal{L}_{\mathrm{C}}+\mathcal{L}_{\mathrm{VH}}+\mathcal{L}_{\mathrm{HC}}]P_{\mathrm{eqm}} = 0$ has the following form:

$$P_{\mathrm{eqm}} = \frac{1}{Z_{\mathrm{EC}}}\exp\left\{\sum_i s(\epsilon_i)\right\} \tag{30}$$

where Z_{EC} is the normalization constant.

6. H-theorem for energy-conserving DPD

The H-theorem for energy-conserving DPD can now be formulated. We first define the following H-functional:

$$S[P(\boldsymbol{\Gamma})](t) = \int \mathrm{d}\boldsymbol{\Gamma}\, P(\boldsymbol{\Gamma},t)\left[\left\{\sum_i s(\epsilon_i)\right\} - \ln P(\boldsymbol{\Gamma},t)\right]. \tag{31}$$

Then, with the aid of the appropriate Fokker–Planck equation (14), it is possible to show that the time-evolution of this functional is

$$\frac{\mathrm{d}S[P(\mathbf{\Gamma})](t)}{\mathrm{d}t} = \frac{\sigma^2}{4}\int \mathrm{d}\mathbf{\Gamma} \sum_{j\neq i} \frac{w_{\mathrm{D}}(r_{ij})}{P}\left[\left\{L_{ij} + (\boldsymbol{e}_{ij}\cdot\boldsymbol{v}_{ij})\frac{m}{2}\left(\frac{1}{\theta_i}+\frac{1}{\theta_j}\right)\right\}P\right]^2$$
$$+\frac{1}{2}\int \mathrm{d}\mathbf{\Gamma} \sum_{j\neq i} \frac{A_{\mathrm{D}}(r_{ij})}{P}\left[\left\{\frac{1}{\theta_j}-\frac{1}{\theta_j}+\frac{\partial}{\partial\epsilon_i}-\frac{\partial}{\partial\epsilon_j}\right\}P\right]^2 \kappa_{ij}. \tag{32}$$

We note that the time derivative of the functional S consists of sums of two types of terms, each of which is positive definite. Therefore $S[P(\mathbf{\Gamma})]$ is monotonically increasing in time and the equilibrium is reached when this time-evolution stops. It is easy to show that this can only be achieved when the equilibrium distribution satisfies the following relations:

$$\left[L_{ij} + (\boldsymbol{e}_{ij}\cdot\boldsymbol{v}_{ij})\frac{m}{2}\left(\frac{1}{\theta_i}+\frac{1}{\theta_j}\right)\right]P_{\mathrm{eqm}} = 0 \tag{33}$$

$$\left[\frac{1}{\theta_j}-\frac{1}{\theta_i}+\frac{\partial}{\partial\epsilon_i}-\frac{\partial}{\partial\epsilon_j}\right]P_{\mathrm{eqm}} = 0 \tag{34}$$

and therefore that the equilibrium distribution consistent with $[\mathcal{L}_{\mathrm{C}}+\mathcal{L}_{\mathrm{VH}}+\mathcal{L}_{\mathrm{HC}}]P_{\mathrm{eqm}} = 0$ will be

$$P_{\mathrm{eqm}} = \frac{1}{Z_{\mathrm{EC}}}\exp\left\{\sum_i s(\epsilon_i)\right\}. \tag{35}$$

This is naturally the same equilibrium distribution already recognized as being a stationary point of the Fokker–Planck evolution equations (28) and (29). The N-body H-theorem provides additional information because it guarantees that the system approaches this equilibrium state monotonically.

The H-functional (31) may be interpreted as the total entropy of the system. We see that the first term in the functional represents the microscopic entropy of each DPD particle while the second term represents the normal macroscopic entropy $-P\ln P$. That the relevant functional is in this case the total system entropy, rather than a free energy, could be expected from the fact that the system is now energy conserving.

For notational ease, the detailed balance property and H-theorem for energy-conserving DPD have been presented for the single component case. However, their extension to the multicomponent case can be achieved in a similar manner to the isothermal H-theorem result presented here.

7. Conclusions

We have shown that the desirable statistical mechanical properties of detailed balance and the existence of H-theorems may be extended to general multicomponent interacting DPD systems, whether maintained at constant temperature or at constant energy. Of course, such properties are rigorously valid in the continuous time limit, and are only approximately true for discrete-time implementations of these algorithms. The approximations improve as the size of the timestep is decreased. Detailed balance makes possible the theoretical analysis of models based on the DPD equations of motion, while the H-theorem provides a means to control numerical instabilities in computer simulations.

Acknowledgments

CAM acknowledges support from EPSRC (UK) and Unilever Research (UK). PVC is grateful to the Department of Theoretical Physics and Wolfson College, University of Oxford, for a Visiting Fellowship.

References

[1] McLeish T 1997 *Theoretical Challenges in the Dynamics of Complex Fluids (NATO ASI Series)* vol 339 (Dordecht: Kluwer)
[2] Boghosian B M, Alexander F J and Coveney P V 1997 Proceedings of the 1996 conference on discrete models for fluid mechanics *Int. J. Mod. Phys.* C **8**
[3] Hoogerbrugge P J and Koelman J M V A 1992 *Europhys. Lett.* **19** 155
[4] Español P and Warren P 1995 *Europhys. Lett.* **30** 191
[5] Koelman J M V A and Hoogerbrugge P J 1993 *Europhys. Lett.* **21** 363
Boek E S, Coveney P V and Lekkerkerker H N W 1996 *J. Phys.: Condens. Matter* **8** 9509
[6] Schlijper A G, Hoogerbrugge P J and Manke C W 1995 *J. Rheol.* **39** 567
Madden W G, Kong Y, Manke C W and Schlijper A G 1994 *Int. J. Thermophys.* **15** 1093
[7] Coveney P V and Novik K E 1996 *Phys. Rev.* E **54** 5134
[8] Novik K E and Coveney P V 1997 *Int. J. Mod. Phys.* C **8** 909
[9] Marsh C A, Backx G and Ernst M H 1997 *Phys. Rev.* E **56** 1676
[10] Marsh C A, Backx G and Ernst M H 1997 *Europhys. Lett.* **38** 411
[11] Marsh C A and Yeomans J M 1997 *Europhys. Lett.* **37** 511
[12] Español P 1997 *Europhys. Lett.* **40** 631
[13] Coveney P V and Español P 1997 *J. Phys. A: Math. Gen.* **30** 779
[14] Risken H 1989 *The Fokker–Planck Equation* (Berlin: Springer)