Constant-pressure simulations with dissipative particle dynamics

S. Y. Trofimov
Dutch Polymer Institute, P.O. Box 902, 5600 AX Eindhoven, The Netherlands and Theoretical and Polymer Physics Group, Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

E. L. F. Nies
Laboratory of Polymer Technology, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands and Laboratory of Polymer Science, Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium

M. A. J. Michels
Dutch Polymer Institute, P.O. Box 902, 5600 AX Eindhoven, The Netherlands and Theoretical and Polymer Physics Group, Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

(Received 15 March 2005; accepted 12 August 2005; published online 7 October 2005)

Dissipative particle dynamics (DPD) is a mesoscopic simulation method for studying hydrodynamic behavior of complex fluids. Ideally, a mesoscopic model should correctly represent the thermodynamic and hydrodynamic properties of a real system beyond certain length and time scales. Traditionally defined DPD quite successfully mimics hydrodynamics but is not flexible enough to accurately describe the thermodynamics of a real system. The so-called multibody DPD (MDPD) is a pragmatic extension of the classical DPD that allows one to prescribe the thermodynamic behavior of a system with only a small performance impact. In an earlier paper [S. Y. Trofimov, E. L. F. Nies, and M. A. J. Michels, J. Chem. Phys. 117, 9383 (2002)] we much improved the accuracy of the MDPD model for strongly nonideal systems, which are of most practical interest. The ability to correctly reproduce the equation of state of realistic systems in turn makes simulations at constant pressure sensible and useful. This situation of constant-pressure conditions is very common in experimental studies of (soft) condensed matter but has so far remained unexplored with the traditional DPD. Here, as a proof of concept, we integrate a modified version of the Andersen barostat into our improved MDPD model and make an evaluation of the performance of the new model on a set of single- and multicomponent systems. The modification of the barostat suppresses the “unphysical” volume oscillations after a sudden pressure change and simplifies the equilibration of the system. © 2005 American Institute of Physics. [DOI: 10.1063/1.2052667]

I. INTRODUCTION

Mesoscale modeling focuses on predicting the material properties that are determined by the structures and behavior in between the microscopic (atomistic) and macroscopic (continuum) scales. This scale, typically 10–1000 nm and 1 ns–10 ms, is particularly important for understanding polymeric and other complex-fluid systems.

While conventional computational methods such as molecular dynamics on the microscopic scale and fluid dynamics on the macroscopic scale have met with considerable success, the mesoscale of complex fluids still remains beyond their reach. The reason for this state of affairs must be sought in the very high computer-power requirements for the former and the breakdown of the continuum description for the latter. This situation has triggered the development of specifically mesoscopic methods destined to bridge the gap between the micro- and macroscopic approaches.

Dissipative particle dynamics (DPD) is a mesoscopic simulation method for studying the hydrodynamic behavior of complex fluids. It was introduced by Hoogerbrugge and Koelman in 1992 and has since received theoretical support. The method has proven to be useful in the study of the dynamical properties of a wide variety of systems, including, for example, colloidal suspensions, dilute polymer solutions, block-copolymer melts, surfactants, and biological membranes.

While being a competitive technique in the complex-fluid field, DPD is not completely free from limitations. One important limitation is the rigid thermodynamic behavior of the DPD fluid determined by the form of the employed conservative forces. The (parabolic) soft-core pair potential results in an equation of state (EOS) with fixed quadratic density dependence irrespective of the parameter values, which is quite different from the EOS of a real fluid. The so-called multibody DPD (MDPD) model by Pagonabarraga and Frenkel has been introduced to address this limitation of the traditional DPD. MDPD allows one to prescribe the thermodynamic behavior of the DPD fluid beforehand.
and has been expected to be able to mimic the thermodynamics of an arbitrary realistic fluid. However, the model has been derived under the assumption of no particle correlations and provides at best qualitative accuracy for strongly nonideal systems, which are of most practical interest. In an earlier paper we have presented a modification of the original MDPD model that features an explicit correction for particle correlations allowing one to reproduce the thermodynamic behavior of a strongly nonideal (multicomponent) system with quantitative accuracy.

The ability to correctly reproduce the equation of state of realistic systems with our improved MDPD makes simulations at constant pressure sensible and useful. This is a situation that is very common in experimental studies of (soft) condensed matter but has so far remained unexplored with traditional DPD. In this paper as a proof of concept we introduce a barostat in the improved MDPD model and make an evaluation of the performance of the new model on a set of single- and multicomponent systems.

We choose the simple Andersen barostat initially. More sophisticated barostate available in literature are also more difficult to implement and often couple a thermostat and a barostat in one algorithm. We only need to add a barostat to produce the NPT ensemble, because (M)DPD features a built-in thermostat. We find that the model with the standard Andersen barostat is prone to the “unphysical” volume oscillations after a sudden pressure change. To suppress the spurious volume oscillations and to simplify the equilibration of the system we introduce a practical modification of the barostat along the lines of Feller et al.

We proceed with an evaluation of the performance of the obtained model. For the single-component case we show that in the new MDPD model under the given external pressure the average density of a (coarse-grained) Lennard-Jones fluid just above the critical point is maintained in agreement with the prescribed equation of state. To illustrate the performance of the new MDPD model for multicomponent systems, we accurately reproduce the demixing behavior of a binary mixture of components obeying the compressible Huggins lattice theory under constant-pressure conditions.

The paper is organized as follows: In Sec. II the original DPD method is summarized and the problem with the DPD thermodynamic behavior is identified. In Sec. III the MDPD extension by Pagonabarraga and Frenkel is introduced. In Sec. IV the classical Andersen thermostat is briefly described, the adaptation of the MDPD model for constant-pressure simulations is covered, and then the resulting method is evaluated on a single-component model system: the (coarse-grained) Lennard-Jones fluid. Finally, a practical improvement to the method is suggested and evaluated. In Sec. V the multicomponent generalization of the constant-pressure MDPD method is presented, and its performance is then illustrated by reproducing the demixing behavior of two model systems: symmetric and asymmetric binary mixtures of compressible Huggins fluids. In Sec. VI we summarize the main results presented in the paper. In the Appendix we briefly presented an adaptive local-density approximation approach, which allows one to significantly improve the MDPD accuracy and is extensively used throughout this paper.

II. DPD simulation method

We first briefly summarize the original DPD simulation method in the (re)formulation by Español and Warren, which has become standard. In DPD the fluid is composed of a number of point (quasi-) particles in continuous space. A particle \( i \) is characterized by its position \( \mathbf{r}_i \), velocity \( \mathbf{v}_i \), and mass \( m_i \). For simplicity the masses of all particles are normally chosen to be the same and equal to the reduced unit of mass \( m_i = m = 1 \). The motion of the particles is governed by Newton’s equations

\[
\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i, \quad \frac{d\mathbf{v}_i}{dt} = \mathbf{F}_i, \tag{1}
\]

with \( t \) time and \( \mathbf{F}_i \) the force acting on particle \( i \) due to the presence of other particles. One can see the similarity with other particle-based simulation methods, such as molecular dynamics. The definition of the interparticle forces is what makes DPD special. The force is separated into pair-wise contributions from conservative, dissipative, and random forces, respectively,

\[
\mathbf{F}_i = \sum_{j \neq i} \left( \mathbf{F}_i^C + \mathbf{F}_i^D + \mathbf{F}_i^R \right). \tag{2}
\]

All the forces between particles \( i \) and \( j \) vanish beyond some cutoff radius \( r_c \), which is usually also chosen as the reduced unit of length, \( r_c = 1 \).

The conservative force determines the thermodynamics of the DPD system and is defined by the soft repulsion

\[
\mathbf{F}_i^C = \begin{cases} a_{ij}(1 - r_{ij})\hat{\mathbf{r}}_{ij} & (r_{ij} \leq 1) \\ 0 & (r_{ij} > 1) \end{cases}, \tag{3}
\]

where \( a_{ij} \) is the maximum repulsion strength between particles \( i \) and \( j \), and \( \hat{\mathbf{r}}_{ij} = \mathbf{r}_j - \mathbf{r}_i \), \( r_{ij} = ||\hat{\mathbf{r}}_{ij}|| \). The force (3) corresponds to the following pair potential:

\[
u(r_{ij}) = \begin{cases} \frac{(a_{ij}/2)(1 - r_{ij})^2}{(r_{ij} \leq 1)} \\ 0 & (r_{ij} > 1) \end{cases}. \tag{4}
\]

The dissipative and random forces are given by

\[
\mathbf{F}_i^D = -\gamma w^D(r_{ij}) (\hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_j) \hat{\mathbf{r}}_{ij}, \tag{5}
\]

\[
\mathbf{F}_i^R = \sigma w^R(r_{ij}) \theta_{ij} \hat{\mathbf{r}}_{ij}, \tag{6}
\]

where \( \gamma \) is the dissipation strength, \( \sigma \) is the noise strength, \( w^D \) and \( w^R \) are \( r \)-dependent weight functions, \( \mathbf{v}_j = \mathbf{v}_i - \mathbf{v}_j \), and \( \theta_{ij} \) is a Gaussian white-noise term with the following properties:

\[
\theta_{ij} = \theta_{ji}, \quad \langle \theta_{ij}(t) \rangle = 0, \quad \langle \theta_{ij}(t)\theta_{ij}(t') \rangle = \delta_{t-t'} \delta_{t_1} \delta_{t_2} \delta(t-t').
\]

The choice of the weight functions is not specified by the method, but Español and Warren showed that they should be related according to

\[
w^D(r) = (w^R(r))^2 \tag{7}
\]

in order for the DPD system to have a well-defined equilibrium state obeying Boltzmann statistics. If Eq. (7) is satis-
fied, the equilibrium temperature is defined as $k_BT = \sigma^2/(2\gamma)$ ($k_BT$ is usually chosen as the reduced unit of energy). For simplicity (and historical reasons) the weight functions are usually chosen to be similar to the form of the conservative force, so

$$w^a(r) = w^D(r) = \begin{cases} 1-r & (r \leq 1) \\ 0 & (r > 1). \end{cases}$$ (8)

The dissipative and random forces have two effects: they act as a thermostat (an alternative DPD thermostat has been proposed by Lowe\textsuperscript{22}) and they allow transport properties such as the viscosity to be tuned (within certain limits)\textsuperscript{23} without altering the equilibrium thermodynamics. Note that all the forces are pairwise additive, central, and satisfy Newton’s third law thus conserving linear and angular momentum. The forces depend only on relative positions and velocities, making the model Galilean invariant.

A. DPD thermodynamics

It is beneficial if a mesoscopic model can correctly reproduce the thermodynamic properties of a real system beyond certain length and time scales as the thermodynamic behavior can be seen as a driving potential for changes occurring in the system. Let us see how DPD performs in this respect.

The DPD conservative force (3) produces an EOS that can be approximated by the following equation:24

$$p = \rho k_BT + a\rho^2,$$ (9)

where $\rho$ is the number density of the DPD particles, $a$ is the repulsion strength (for a single-component system the repulsion strength is the same for all particle pairs, $a_{ij} = a$), and $\alpha$ is a fitting parameter equal to 0.101±0.001 in DPD reduced units (all the numerical values below are given in these units if not stated otherwise). The approximation (9) is very good for $\rho \approx 3$ and $\alpha = 15$. The DPD EOS has a rigid quadratic density dependence irrespective of the parameter values [note though that $aa$ is not the second virial coefficient, so (9) breaks down for $\rho \to 0$].\textsuperscript{25,26} Such an EOS is quite different from the EOS of a real fluid.

As one can see, the thermodynamics of a DPD system is controlled by a single parameter: the repulsion strength $a$. The value of $a$ is usually obtained by matching the compressibility of the DPD model to that of a real system with an incentive to achieve the correct description of the density fluctuations.24

Unfortunately, if one has mapped a particular thermodynamic property of DPD to that of a real system, the other properties are not guaranteed to have the correct values due to the peculiar quadratic density dependence of the DPD EOS (9). For example, it is impossible to simultaneously map the isothermal compressibility and the pressure.\textsuperscript{16} If we succeed in mapping compressibility, the pressure will have an unrealistically high value, or if we map the pressure, the compressibility will be too low.

Additionally, the DPD system is unstable for $a < 0$, so one is restricted to $a \geq 0$ and therefore to strictly repulsive (conservative) interactions. This means that the vapor-liquid coexistence and free-surface simulations are out of the question.\textsuperscript{26}

We have to conclude that the traditional DPD is not flexible enough to mimic the thermodynamic behavior of a real system, and an extension seems necessary to overcome this problem. We focus on one possible solution: the MDPD model introduced by Pagonabarraga and Frenkel\textsuperscript{14,15} that has been specifically developed to address this limitation of the traditional DPD. MDPD allows one to prescribe the thermodynamic behavior of the DPD fluid beforehand and has been expected to be able to mimic the thermodynamics of an arbitrary realistic fluid. A recently developed fully thermodynamically consistent soft fluid-particle model by Español and Revenga\textsuperscript{27} termed smoothed DPD (SDPD) is also worth mentioning in this context. The model conserves energy and allows the desired thermodynamic behavior to be given as input to the simulation but also has the ability to directly specify the transport properties such as viscosity. However, while being conceptually related to the traditional DPD as the name suggests, SDPD is quite different in the technical details. In fact, it is a version of the smoothed particle hydrodynamics (SPH) model,\textsuperscript{28,29} which is a method for solving hydrodynamic equations on a comoving grid introduced more than 20 years ago in astrophysical context.

III. MULTIBODY DPD MODEL

The multibody DPD model\textsuperscript{14,15,30} differs from the original DPD in the definition of the conservative forces acting between the DPD particles. Rather than assuming a force (3) that depends only on the interparticle separation, the force is made additionally dependent on the instantaneous local particle density, which in turn depends on the positions of all the other neighboring particles. This effectively makes the conservative force in MDPD a many-body force, hence the name of the approach. Though generally care must be taken with density-dependent interactions,\textsuperscript{31} the explicit definition of the MDPD local density in terms of the neighboring particle positions is a “safe” way to introduce the density dependence into the interactions.\textsuperscript{26,27}

The precise form of the local-density-dependent conservative forces is chosen on the basis of the desired thermodynamic behavior using the procedure due to Pagonabarraga and Frenkel,\textsuperscript{15} which we will not present here in its entirety, jumping almost directly to the final result: the recipe for the calculation of the interparticle forces given the Helmholtz free energy.

The MDPD conservative force acting on particle $i$ is defined as follows:

$$\mathbf{F}_i^c = -\sum_j \frac{\partial \psi^F(\tilde{\rho}_j)}{\partial \tilde{\rho}_i},$$ (10)

where $\psi^F(\rho)$ is the excess Helmholtz free energy per particle and $\tilde{\rho}_i$ is the approximated local density at the position of particle $j$, which is given by the following expression (we denote it by $n_i$ for further reference):
where \( \bar{\rho}_i = n_i = \sum_{j \neq i} w(r_{ij}) \),

where \( w(r) \) is a weight function vanishing beyond \( r_c \) and normalized so that

\[
\int_0^\infty 4\pi r^2 w(r) dr = 1. \tag{12}
\]

In other words, each particle has a sphere of influence determined by its weight function, and the local-density approximation at a point is a sum of contributions from nearby particles, see Fig. 1. Note that we exclude the contribution of the particle \( i \) itself from the sum in (11), in contrast to the original papers by Pagonabarraga and Frenkel.\(^{14,15}\) Including the self-contribution would not be consistent with the assumption of no particle correlations used by Pagonabarraga and Frenkel (see our earlier paper\(^{16}\) for a more extensive discussion of this issue).

Having specified the form of \( \bar{\rho}_i \), we can derive the final expression for the MDPD conservative forces

\[
F_i^C = - \sum_j \frac{\partial \psi_{\text{ex}}(n, \{r_{ij}\})}{\partial r_{ij}},
\]

\[
\sum_{j \neq i} \left( \psi_{\text{ex}}'(n_i) + \psi_{\text{ex}}'(n_j) \right) w'(r_{ij}) \bar{r}_{ij} = \sum_{j \neq i} F_{ij}^C, \tag{13}
\]

where the primes denote derivatives with respect to the corresponding function arguments.

Using Eq. (13) one can easily calculate the conservative forces acting on the particles for a prescribed free energy. As we can see, although the forces in the MDPD approach are effectively many-body forces, they can be represented as a sum of pairwise components. At the same time the local densities are easily computed by a single additional sweep through the list of the interacting particle pairs. The original DPD with a self-consistent integrator\(^{33}\) already requires several such sweeps, so MDPD does not appear to be much more computationally demanding than the normal DPD method.

The conservative forces (13) depend not only on the free energy but also on the form of the weight function. However, the weight function is not specified by the method. There are no \textit{a priori} arguments for the selection of a particular weight function, apart from that it should vanish beyond \( r_c \) to decrease the computational requirements by limiting the number of particle interactions in the spirit of DPD and be continuous and smooth to avoid spurious jumps in the calculated forces. For simplicity we use a quadratic function related to the weight functions employed in the original DPD (8),

\[
w(r) = \begin{cases} 
\frac{15}{2\pi} (1-r)^2 & (r \leq 1) \\
0 & (r > 1).
\end{cases} \tag{14}
\]

The use of this weight function ensures that DPD is recovered as a special case of MDPD. Indeed, if the free energy per particle is set equal to

\[
\psi^C(n) = \frac{\pi}{30} an, \tag{15}
\]

the original DPD is recovered exactly. This permits one to fall back on the well-tested DPD method in specific cases, which is useful during the implementation stage.

Multibody DPD by Pagonabarraga and Frenkel\(^{14,15}\) is a convenient DPD extension allowing one to prescribe the thermodynamic behavior of a system with small impact on the simulation performance. However, the model has been derived under the assumption of no particle correlations and provides at best qualitative accuracy for strongly nonideal systems, which are of most practical interest. In an earlier paper\(^{16}\) we have presented a modification of the original MDPD model that features an explicit correction for particle correlations allowing one to significantly improve MDPD accuracy. In the Appendix we give a short account of this pragmatic modification, which is extensively used in the following sections of this paper.

**IV. MDPD AT CONSTANT PRESSURE**

Most experimental studies in condensed matter are conducted at constant pressure and constant temperature. The simulations discussed so far were performed at constant volume and temperature. For many experiments the difference between \textit{NVT} and \textit{NPT} can be quite significant. For example, liquid-liquid miscibility under constant \( P \) and \( T \) can be quite different from that under constant \( V \) and \( T \), in particular, when the density of the system changes with composition as it occurs in most experimental systems. Hence it is of importance to be able to conduct constant \( PT \) simulations in order to get direct comparison with experimental conditions.

Constant-pressure simulations are certainly technically “possible” with standard DPD as with any similar particle or
molecular-dynamics method, however, only the newly acquired ability to correctly reproduce the equation of state of realistic systems with MDPD makes DPD simulations at constant pressure truly sensible and useful. In this paper we introduce a modified version of the Andersen barostat into the MDPD model and make an evaluation of the performance of the new model on a set of single- and multicomponent systems. Evidently by choosing the appropriate potential for representing DPD our method is equally applicable to traditional DPD simulations. However, the DPD EOS is far from representative for real systems and constant-pressure DPD simulations are not really useful.

A. The Andersen barostat

We choose the simple Andersen barostat initially. More sophisticated barostats available in literature are also more difficult to implement and often couple a thermostat and a barostat in one algorithm. However, we only need to add a barostat to produce the \( NPT \) ensemble, because a thermostat is already realized in DPD by the interplay of dissipative and random forces.

The Andersen barostat is a so-called “extended system” method. This means that the system containing \( N \) particles is coupled to an additional dynamical variable \( V \), the volume of the simulation box, and the simulation of the resulting extended system with \( 3N+1 \) degrees of freedom is carried out. The new variable comes with its own equations of motion, and the equations for the particle positions and velocities are rewritten in a volume-scaled form

\[
\dot{V} = \Pi/M, \\
\dot{p} = p(t) - p_{\text{ext}}, \\
\dot{r}_i = \pi_i, \\
\dot{\pi}_i = V^{1/3} f_i,
\]

where \( M \) is a “piston mass” associated with the volume variable \( V \) (\( M \) has the dimension of \( \text{mass} \times \text{length}^{-3} \)), \( \Pi \) is the momentum conjugate to \( V \), \( p(t) \) is the instantaneous pressure, \( p_{\text{ext}} \) is the externally imposed pressure, and \( \tau_i = V^{1/3} r_i, \pi_i = V^{1/3} p_i \) are the volume-scaled particle positions and momenta.

Andersen has shown that the piston mass \( M \) does not affect the values of the equilibrium properties calculated in a simulation (if \( M \) is finite and positive). However, the actual value of \( M \) is quite important for the dynamics of the simulation because it determines the time scale of the volume fluctuations. The piston mass \( M \) is usually chosen using the following rule. In reality the time scale for the fluctuations of the volume of a small sample of fluid embedded in a much larger sample of fluid is approximately equal to the length of the sample divided by the speed of sound in the sample. Thus, it is desirable to choose the piston mass \( M \) so that the time scale of the fluctuations in the volume variable \( V \) is roughly equal to \( V^{1/3} \) divided by the speed of sound in the fluid. However, one has to keep in mind that the speed of sound depends on density and the compressibility of the fluid and is therefore likely to be different at every point on the EOS. In this case for simplicity we choose a reasonable value from the available interval. To quickly verify that the chosen \( M \) value is reasonable, one can compare the time scale of the volume fluctuations in a constant-pressure simulation with the time scale of pressure fluctuations in the constant-volume case; the two time scales should be of the same order.

We incorporate the rescaling of the variables into a DPD integration algorithm and solve the equations for the volume variable using a leap-frog scheme.

Apart from the inclusion of a barostat no further modifications to the MDPD method and the force derivation procedure are necessary. To illustrate the operation of MDPD under constant-pressure conditions we take the (coarse-grained) Lennard-Jones fluid from our earlier paper.

B. The (coarse-grained) Lennard-Jones fluid

In this subsection we apply the constant \( PT \) simulations to the Lennard-Jones (LJ) model fluid.

The successful use of a mesoscopic simulation method such as (M)DPD always requires some sort of coarse graining, i.e., discarding the excessive detail at smaller length and time scales that presumably have no direct influence on the properties of interest. Coarse-grained models allow one to study larger-scale systems for longer times as compared to purely microscopic approaches such as molecular dynamics, which retain (almost) full atomistic detail.

In our coarse-grained description of the Lennard-Jones fluid a single DPD particle corresponds to a number of LJ particles grouped in some way. The obvious result of such coarse graining is that the number density of the coarse-grained particles \( \rho \) is different from the number density of the real fluid molecules \( \rho^R \) (an \( R \) superscript marks “real” variables) even if both are expressed in the same units. The ratio \( N_m = \rho^R / \rho \) is the number of real fluid molecules associated with one coarse-grained particle and is a measure for the level of coarse graining. Not all of the thermodynamic variables are affected by coarse graining. The volume of the system is obviously not affected. Moreover, it is known that grouping simple molecules into equally sized nonintersecting clusters leaves the average kinetic energy per degree of freedom unchanged. Therefore, it is reasonable to assume that the temperature is also not changed by a coarse-graining procedure.

To apply MDPD we need the expression for the free energy. The exact form of the LJ fluid free energy is unknown. However, highly accurate approximate EOSs obtained by fitting empirical or semitheoretical equations to the LJ simulation data are available in literature.

Fortunately, examination of Eq. (A1) shows that to calculate the conservative forces in a simulation one only needs to know the derivative of the excess free energy per particle with respect to the density, and not the free energy itself. Therefore, for a single-component system these forces can be derived from the EOS directly.

\[
\frac{\partial f^E}{\partial \rho} = p(\rho, T)/\rho^2 - k_B T/\rho.
\]
In fact, the paper\textsuperscript{36} gives the approximate form of the free energy as well, but we follow the EOS route for simplicity.

We mimic the LJ EOS isotherm for a temperature just above the critical one ($T_{\text{LJ}}=1.4$, $T_{\text{LJ}}^{1.31}$ in standard LJ reduced units) to avoid the vapor-liquid heterogeneous region but to retain the complex form of the isotherm. For simplicity, the chosen LJ EOS isotherm is fitted with a fifth-order polynomial (21), which is then used as a target EOS for MDPD,

\[
p(\rho, T_{\text{LJ}}=1.4) = \sum_{i=1}^{5} b_i\rho^i.
\]  

The next task is to choose the level of coarse graining and express the parameter values in DPD units. To the level of coarse graining $N_p=100$ is set and we map the LJ density of 0.5 to the DPD density of 5 (note the change of the unit of length; the LJ particle density is equal to 0.5 in LJ units and to $\rho N_p=500$ in DPD units) and the LJ reduced temperature of 1.4 to the usual DPD reduced temperature of 1. This mapping establishes all the DPD reduced units in terms of the LJ reduced units and allows one to express the target polynomial EOS in DPD units. The parameter values in DPD units are presented in Table I.

Using Eq. (20) we derive the MDPD conservative forces from Eq. (21) and then follow the proposed iterative procedure to determine a good local-density-approximating function:

\[
\bar{\rho}(n) = 1.062n + 1.39.
\]

At the particle density of 6 in a \textit{NVT} simulation the system has an average pressure of 420.36 (DPD units). We set this pressure as the externally imposed desired pressure $p_{\text{ext}}$, set the piston mass to 0.1, switch the barostat on, and run the simulation. The measured pressure and average density are presented in Fig. 2. As we can see both the pressure and the average density fluctuate very closely around the expected values. Changing the externally imposed pressure $p_{\text{ext}}$ to a different value will cause the system to expand or shrink, maintaining the average density dictated by the desired EOS. We test this by letting $p_{\text{ext}}=1000$. The simulation results for the pressure, average density, and temperature are shown in Fig. 3. While the expected pressure and density values are reached eventually, the system exhibits large, slowly decaying volume oscillations. This unphysical "ringing" of the volume is an (unwanted) artifact of the barostat. The oscillations extend the time needed for equilibration and can interfere with the study of dynamical processes. They also have a negative effect on the temperature control as the DPD thermostat is the only sink for energy introduced by the pressure change.

C. Damping the volume oscillations

To minimize the negative influence of the volume oscillations we choose, in line with Feller \textit{et al.}\textsuperscript{23} to add a damping term into Eq. (17) governing the dynamics of the volume variable,

\[
\ddot{\rho} = p(t) - p_{\text{ext}} - \Gamma\ddot{\rho},
\]

where $\Gamma$ is the "piston friction" parameter controlling the strength of the damping force.

The simulation results for the pressure, average density, and temperature obtained with the modified barostat ($\Gamma=10$) are shown in Fig. 4. The large-scale volume oscillations have been suppressed and the overall response of the system to the sudden pressure change has become much more controlled.

Care must be taken with the choice of the value of the piston friction parameter $\Gamma$, so that the dynamics of the system in situations with constant and slowly changing external pressure is not negatively affected, while the ability to suppress the ringing of the volume is retained. Again, to quickly verify that the chosen $\Gamma$ value is reasonable, one can compare the volume fluctuations in a constant-pressure simulation with the chosen $\Gamma$ to the situation with $\Gamma=0$ after the volume ringing has receded. The damping term should not distort the dynamics of the volume fluctuation too much.

We now turn to the constant-pressure simulations with MDPD in the context of multicomponent systems.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_1$</td>
<td>100.0000</td>
</tr>
<tr>
<td>$b_2$</td>
<td>−33.5275</td>
</tr>
<tr>
<td>$b_3$</td>
<td>8.2340</td>
</tr>
<tr>
<td>$b_4$</td>
<td>−1.7641</td>
</tr>
<tr>
<td>$b_5$</td>
<td>0.1952</td>
</tr>
</tbody>
</table>

**TABLE I.** Parameter values in DPD reduced units of the fifth-order polynomial EOS fitted to the chosen Lennard-Jones isotherm ($T_{\text{LJ}}=1.4$).
V. MULTICOMPONENT SYSTEMS

MDPD for multicomponent systems is largely a straightforward generalization\(^\text{16}\) of the single-component MDPD model. We consider a multicomponent system containing \(N\) particles of component \(\alpha\). Greek letters \(\alpha, \beta, \gamma\) are used to denote different components and Latin ones—\(i, j, k\)—to denote individual particles. A term inside the curly brackets having a free index denotes a set, for example, \(\{N_\alpha\}\). Every particle in a system can have neighboring particles of different kinds. To capture this we generalize Eq. \((11)\) and define partial local densities

\[
\bar{n}_i^\alpha = \sum_{j=\alpha, j\neq i} w(r_{ij}).
\]  

The desired free energy has also to be defined as a function of numbers of particles of different components \(F(\{N_\alpha\}, V, T)\). Let us represent the excess free energy in the form

\[
F^\alpha = \sum_\alpha N_\alpha \varphi^\alpha_\alpha (\{\rho_\beta\}),
\]  

where \(\varphi^\alpha_\alpha (\{\rho_\beta\})\) is an equivalent of the excess free energy per particle for a single-component system. Such a function depends on all the partial densities and represents the energy of interaction of a particle of type \(\alpha\) with its local environment consisting of particles of different types.

Given the free energy \((25)\) we can derive the conservative MDPD forces, obtaining analogously to Eq. \((10)\),

\[
F_{ij}^\alpha = -\left( \pd{\phi_{ij}^{\alpha\alpha}(n_{\alpha})}{n_{ij}} + \pd{\phi_{ij}^{\alpha\alpha}(n_{\alpha})}{n_{\tilde{\alpha}ij}} \right) w'(r_{ij}) F_{ij},
\]  

where \(\tilde{\alpha}\) is the component to which particle \(i\) belongs (\(\tilde{\alpha} = \alpha\), if \(i \in \alpha\)), and \(\{n_{\alpha i}\}\) is the set of local densities of different components at the position of particle \(i\). As one can see this is a strict generalization of Eq. \((13)\).
The multicomponent version of our adaptive local-density approximation approach\(^{16}\) is also a generalization of the single-component one and is briefly presented in the Appendix.

A. Compressible Huggins fluid

Let us demonstrate the multicomponent version of MDPD under constant-pressure conditions by attempting to reproduce the demixing behavior of a test system: a compressible analog of the Huggins lattice fluid.\(^{16,37}\) Here the model is restricted to monomeric species. The free energy of coarse graining and subtracting the ideal contribution of components. The third term corresponds to the intersite attraction. Equation (27) can be quite easily represented in the form (25), resulting in the following expression for \(\psi_{\alpha}\):

\[
\begin{align*}
\psi_{\alpha} &= \frac{k_{B}T}{v_{\alpha}}(1 - v_{\alpha}N_{\alpha}^{\beta})\ln(1 - v_{\alpha}N_{\alpha}^{\beta}) \\
&+ k_{B}T\ln(v_{\alpha}N_{\alpha}^{\beta}) - v_{\alpha}N_{\alpha}^{\beta}C(T),
\end{align*}
\]

where \(C(T)\) is an expression only dependent on the temperature.

The \(\psi\)-function derivatives needed for the force computation have the form

\[
\frac{\partial\psi_{\alpha}^{\beta}}{\partial\rho_{\beta}} = \frac{k_{B}T}{v_{\alpha}}\ln(1 - v_{\alpha}N_{\alpha}^{\beta}) - N_{\alpha}^{\beta}C(T),
\]

B. Symmetric binary mixture in NPT

As the first test case a symmetric binary mixture is considered, in which the interactions between particles of the same component are favored (\(e_{AA} = e_{BB}\) and \(e_{AB} = e_{AA}/4\)). We set the temperature equal to 1 and examine the behavior of the system for different effective temperatures by the rescaling of interaction parameters. The parameters, expressed in DPD units and summarized in Table II, are as follows: \(v_{0}\) is equal to 0.001, the level of coarse-graining \(N_{m}\) is the same for the two components and equal to 50. The pressure is equal to \(-969.44\), which corresponds to the pressure of the system with \(\rho = 16\), \(x_{A} = 0.5\), and \(e_{AA} = 1.6\) in the NVT ensemble.

To determine the local-density-approximating functions \(\bar{\rho}_{\alpha\beta}\) we require that condition (A7) be satisfied in the (pressure, composition, and temperature) region of interest, which is defined as follows. The pressure is fixed at \((-969.44\). To prevent the unwanted phase separation during the \(\bar{\rho}_{\alpha\beta}\) function determination procedure the interaction parameter \(e_{AA}\) is set to 1.6. This value corresponds to a temperature in the homogeneous region slightly above the critical point, just outside the demixing region we are interested in. Using the automated routine described in the Appendix we obtain the self-consistent local-density shifts \(n_{\text{shift}}\) (A4) for a number of points in the region of interest (see Fig. 5). The mole fraction of component \(A\), \(x_{A}\), changes from 0.2 to 0.8 (or rather from 0.2 to 0.5 due to the symmetry). Figure 5 suggests that a linear fitting function should be more than sufficient as a good \(\bar{\rho}_{\alpha\beta}\). After fitting we obtain the following set of the density-approximating functions:

\[
\bar{\rho}_{\alpha\beta} = \begin{cases} 
1.0123n_{\text{shift}} + 1.4972, & \alpha = \beta \\
1.0159n_{\text{shift}} + 0.0015, & \alpha \neq \beta .
\end{cases}
\]

To prevent \(\bar{\rho}_{\alpha\beta}\) from taking unphysical negative values,
which is possible with Eq. (31), and to avoid huge forces stemming from the pseudoidal contribution term proportional to $\bar{\rho}_{\alpha\beta}^{-1}$ we set the minimum $\bar{\rho}_{\alpha\beta}$ value: $\bar{\rho}_{\alpha\beta}:=\max(\bar{\rho}_{\alpha\beta},0.01)$.

As the pressure is fixed by the barostat the average density will change with the composition at constant temperature. In Fig. 6 we present a comparison of the $\rho(x_A)$ dependence measured in a simulation and the exact theoretical results. A very good agreement between the desired and obtained behaviors is observed. The increased error at the point $x_A=0.9$ (which is actually beyond our declared region of interest) is related to the low partial density of the second component. In this situation the typical number of nearby component-$B$ particles sampled by the weight function during the calculation of the partial local densities (24) is rather small, and thus the quality of the local-density approximation suffers.

With the appropriate expression we are now in a position to simulate the phase behavior at constant pressure. Simulations are performed at values of the interaction parameter $e_{BB}=e_{AA}$ and $e_{AB}=e_{AA}/4$. The system with $x_A=0.5$ is initially prepared at $e_{AA}=1.6$ by equilibration from a random (uniformly distributed) particle configuration. In accordance with the prescribed behavior the components mix freely. The system is then brought into the two-phase region of the phase diagram by scaling up the interaction energies, whereupon the phase separation is observed. The periodic-boundary conditions and the elongation of the simulation box in the $z$ direction lead in the end to the formation of two phase layers, perpendicular to the $z$ axis, containing predominantly particles of component $A$ or $B$. When the equilibrium is reached the $z$-density profile is sampled and the bulk compositions of the phases are measured. The obtained phase diagram is shown in Fig. 7. Excellent agreement with the prescribed behavior is achieved.

C. Asymmetric binary mixture in NPT

The second CHF test case is the asymmetric binary mixture with the following interaction parameters: $e_{BB}=e_{AA}/2$, $e_{AB}=e_{AA}/4$, where $e_{AA}$ is the only remaining independent variable playing the role of the inverse temperature, while the kinetic temperature of the system is fixed to 1 by the DPD thermostat.

The pressure of the system is again fixed to 969.44, which corresponds to the pressure in the homogeneous mixture with $\rho=16$, $x_A=0.5$, and $e_{AA}=2$ in the NVT ensemble. The self-consistent local-density shifts $n_{shift}$ (A4), for the mole fraction of component $A$ going from 0.15 to 0.85 and at $e_{AA}=2$, are determined with the iterative procedure described in the Appendix (Fig. 8). The fit of the obtained data to linear $\tilde{\rho}_{\alpha\beta}$'s results in

\begin{align}
\tilde{\rho}_{A|A} &= 1.0089n_{A|A} + 1.5106, \\
\tilde{\rho}_{A|B} &= 1.0205n_{A|B} - 0.0344, \\
\tilde{\rho}_{B|A} &= 1.0083n_{B|A} + 0.037, \\
\tilde{\rho}_{B|B} &= 1.0164n_{B|B} + 1.5065.
\end{align}

FIG. 6. A comparison of the average density as a function of the composition measured in a simulation and the exact theoretical results for the symmetric CHF mixture in NPT ($\rho=969.44$, $e_{AA}=1.6$).

FIG. 7. The phase diagram of the symmetric CHF system in NPT (●: composition of coexisting phases obtained from the MDPD simulation at given values of $e_{AA}$; solid line: theoretical binodal).

FIG. 8. The self-consistent local-density shifts $n_{shift}$ (A4) obtained for the asymmetric binary CHF mixture in NPT conditions.
The comparison of the $\rho(x_A)$ dependence obtained in a simulation with the theoretical results is shown in Fig. 9. Again the agreement between the set and obtained overall density is excellent except at the lowest overall density and lowest partial density of component $A$, where again the local-density approximation becomes less accurate.

Once more the system can now be studied in the miscibility gap, where liquid-liquid phase separation will occur. The phase diagram is shown in Fig. 10. Again the theoretical prescription and simulations are in agreement, although a slight deviation exists approaching the critical condition, especially for the right $(x_A>0.5)$ branch of the binodal. We attribute this discrepancy to the increased relative width of the interfaces in comparison to the size of the coexisting phases and the resulting difficulty in sampling the true bulk compositions. The fact that the $A$-rich phase is smaller than the $B$-rich phase (for the overall mole fraction $x_A=0.5$) and is more likely to be affected by these finite-size effects supports this explanation (see Fig. 11, where a typical $z$-density profile after phase separation is shown). Note also that the asymmetry of the upper critical solution temperature (UCST) gap is captured accurately. Furthermore, we are able to investigate the lower critical solution temperature (LCST) miscibility equally well with our simulation method.

VI. CONCLUSION

Multibody DPD proposed by Pagonabarraga and Frenkel\textsuperscript{14,15} is a convenient DPD extension allowing one to prescribe the thermodynamic behavior of a system (at constant temperature) with small impact on the simulation performance. A MDPD modification presented in an earlier paper\textsuperscript{16} by the authors greatly improves the accuracy of the MDPD model for strongly nonideal (multicomponent) systems. The ability to correctly reproduce the equation of state of realistic systems with MDPD in turn makes simulations at constant pressure sensible and useful. This is a situation that is very common in experimental studies of (soft) condensed matter but has so far remained unexplored with traditional DPD.

We have integrated a modified version of the Andersen barostat into the MDPD model and have made an evaluation of the performance of the new model on a set of single- and multicomponent systems. The introduced modification of the barostat suppresses the “unphysical” volume oscillations after a sudden pressure change and simplifies the equilibration of the system. In a single-component case we have shown that in a new model under the given external pressure the average density of a (coarse-grained) Lennard-Jones fluid just above the critical point is maintained in good agreement with the prescribed equation of state. No modification to the local-density approximation procedure\textsuperscript{16} was necessary for the constant-pressure situation and the local-density approximation function, obtained in the constant-volume case, has
been successfully used. To illustrate the performance of the model for multicomponent systems, we have reproduced with the new MDPD model the demixing behavior of a binary mixture of compressible Huggins fluids under constant-pressure conditions. The obtained binodals for the NPT ensemble both for the symmetric and the asymmetric model fluid are in excellent agreement with the prescribed behavior.

ACKNOWLEDGMENTS

The use of supercomputer facilities for this work was sponsored by the National Computer Facilities Foundation (Stichting Nationale Computerfaciliteiten, NCF), with financial support from the Netherlands Organization for Scientific Research (Nederlandse Organisatie voor Wetenschappelijk Onderzoek, NWO). This work forms a part of the research programme of the Dutch Polymer Institute (Project No. 181).

APPENDIX: IMPROVING MDPD ACCURACY

In an earlier paper\textsuperscript{16} we have presented a modification of the original MDPD model that features an explicit correction for particle correlations, allowing one to significantly improve MDPD accuracy. Here we give a short account of this pragmatic modification.

1. Single-component systems

We assume that the local density \( n_i \) defined in Eq. (11) provides at least a reasonable starting point to improve on the density approximation. Further, we define the local-density approximation \( \tilde{\rho}_i \) as a function dependent on \( n_i \) but not necessarily equal to it. Substituting the new form of \( \tilde{\rho}_i \) into Eq. (10) we obtain the corresponding MDPD conservative force expression

\[
\mathbf{F}_{ij}^c = -(\psi_{ex}(\tilde{\rho}_i)\tilde{\rho}'(n_i) + \psi_{ex}(\tilde{\rho}_j)\tilde{\rho}'(n_j))w'(r_{ij})\hat{r}_{ij},
\]

where \( \rho_0 = \rho(n_0) \). To determine an appropriate form for \( \tilde{\rho}(n) \) we require that to the very least this function must be able to recover approximately the average density value, based on the information about the values of \( n_i \) calculated during simulation, that is,

\[
\langle \tilde{\rho}(n_i) \rangle = \rho
\]

for all densities within the region of interest. Assuming that \( \tilde{\rho}(n) \) is almost linear in the range where \( n_i \) is found most of the time during simulation, we can rewrite condition (A2) in the following way:

\[
\tilde{\rho}(n) = \rho.
\]

This expression allows us to determine the form of \( \tilde{\rho}(n) \). As \( \langle n \rangle \) is in turn dependent on \( \tilde{\rho}(n) \), it must be determined self-consistently. We obtain \( \tilde{\rho}(n) \) using the following iterative procedure. The approximate local density \( \tilde{\rho}(n) \) is represented by a low-order polynomial (in most cases linear). During each iteration \( \langle n \rangle (\tilde{\rho}) \) is measured in a simulation and the values of parameters in \( \tilde{\rho}(n) \) are obtained by fitting. If the newly measured \( \langle n \rangle (\rho) \) substantially disagrees with condition (A3) the procedure is repeated.

We use \( \tilde{\rho}(n) = n \) or \( \tilde{\rho}(n) = \rho \) as first guesses. The former is the original MDPD density approximation. The latter is more peculiar; it means replacing the approximated local density by the known average density. While this substitution leads to an incorrect value for the compressibility, it often allows one to obtain the actual \( \langle n \rangle (\rho) \) dependency fast. It is questionable to use this form of local-density approximation in production runs, because the information about the actual average density is not available locally in a simulation, but it works well as a first guess. Simulations with the constant \( \tilde{\rho}(n) = \rho \) are also convenient for initial equilibration of the system. Note, however, that in this case it is necessary to provide some dummy value for \( \tilde{\rho}(n_i) \) as well, usually 1.

The iterative procedure converges quite rapidly and the obtained local-density approximation functions (most of the time linear) prove sufficient to achieve quantitative \((<1\% \text{ error in pressure})\) accuracy in a MDPD simulation.\textsuperscript{16}

2. An alternative ("transposed") iterative procedure

The iterative procedure\textsuperscript{16} described in Appendix A 1 requires a set of simulations at different densities and a polynomial fit of the calculated \( \langle n \rangle (\rho) \) dependence during each iteration. Practice shows that an alternative iterative procedure\textsuperscript{23} is more convenient as it can be readily automated. This procedure is in a way a "transposition" of the one above; it requires a number of simulation runs (iterations) at each density point and a single fit at the end. The local-density approximation used at each density point is a simple shift in density

\[
\tilde{\rho}(n) = n + n_{\text{shift}}^k,
\]

where \( n_{\text{shift}}^k \) is a density shift at the iteration \( k \). At each iteration the average predicted density \( \langle \rho(n) \rangle \) is calculated and compared with the true average density. If the discrepancy is still significant the new density shift is calculated according to the following formula:

\[
n_{\text{shift}}^{k+1} = \lambda n_{\text{shift}}^k + (1 - \lambda)(\rho - \langle n \rangle),
\]

where \( \lambda \in [0, 1) \) is the parameter controlling the mixing in of the old density shift into the new one. For the (single-component) systems discussed here the convergence of this iterative procedure is guaranteed and is very fast, so the \( \lambda \) parameter can be set to zero.

The algorithm presented above is very simple, and the density shift can be automatically adjusted at regular intervals even within a single simulation. In such a way the self-consistent density shifts are obtained after convergence.

After the self-consistent density shifts \( n_{\text{shift}}(\rho_i) \) and thus the desired self-consistent local densities \( \langle n \rangle (\rho_i) = \rho_i - n_{\text{shift}}(\rho_i) \) have been calculated for every density point \( i \), we can obtain the final local-density approximation \( \tilde{\rho}(n) \) by fitting in the same way as in Appendix A 1.

One has to keep in mind that the self-consistently calculated dependence between the average and the local density corresponds to the local-density-approximating function \( \tilde{\rho}(n) \) (A4) with the derivative equal to 1. After fitting, on the other hand, especially at high particle densities \( \tilde{\rho}'(n) \) can be substantially larger than 1 (1.05 < \( \tilde{\rho}' < 1.25 \)), which will lead to
the increase of the interparticle forces (A1) and the overestimation of the pressure as a result. However, in this way the pressure is overestimated by a constant factor for all the density points and this situation can be easily corrected for by scaling the interparticle forces down by this factor.

3. Multicomponent systems

The local-density approximation for a multicomponent system is also an extension of the one discussed in Appendix A. In general for an $m$-component system one can identify $m(m+1)/2$ “partial” radial distribution functions $g_{\alpha\beta}(r)$ \times \left[ g_{\alpha\beta}(r) \right] g_{\beta\alpha}(r)$. Analogously, there will be $m^2$ local densities $(n_{\alpha\beta}) = \rho_{\alpha} \rho_{\beta} d\mathbf{r}$ with the term $(n_{\alpha\beta})$ is the averaged approximated density of particles of type $\alpha$ measured at the position of a particle of type $\beta$. This means that to approximate $m$ partial local densities $\rho_{\alpha}$ we need $m^2$ functions $\tilde{\rho}_{\alpha\beta}(n_{\alpha\beta})$ (here for simplicity we make $\tilde{\rho}_{\alpha\beta}$ depend only on the corresponding $n_{\alpha\beta}$ and not on the whole set of $(n_{\alpha\beta})$). Consequently, in the general binary-mixture case we need $2^m=4$ functions: $\tilde{\rho}_{AB}, \tilde{\rho}_{AB}, \tilde{\rho}_{AB}, \tilde{\rho}_{AB}$ (note that $\tilde{\rho}_{AB}$ is not necessarily equal to $\rho_{AB}$). In the case of a symmetric system, in the sense that $g_{AA}(\rho_A, \rho_B, r) = g_{BB}(\rho_B, \rho_A, r) = g_{same}$ and $g_{AB}(\rho_A, \rho_B, r) = g_{AB}(\rho_B, \rho_A, r) = g_{diff}$, only two functions remain: $\tilde{\rho}_{same} = \rho_{AB}$ and $\tilde{\rho}_{diff} = \rho_{AB}$.

The procedure for the determination of the local-density-approximating functions $\tilde{\rho}_{\alpha\beta}$ remains largely unchanged, while conditions (A2) and (A3) become, respectively,

$$\langle \tilde{\rho}_{\alpha\beta}(n_{\alpha\beta}) \rangle = \rho_{\alpha},$$

$$\tilde{\rho}_{\alpha\beta}(n_{\alpha\beta}) = \rho_{\alpha},$$

(A6)

(A7)

A single iterative procedure can be used to determine all $\tilde{\rho}_{\alpha\beta}$ simultaneously.

The updated expression (A1) for the interparticle forces in a multicomponent case reads

$$F_{ij}^C = \left( \frac{\partial \Psi_{\alpha\beta}^C}{\partial \tilde{\rho}_{\alpha\beta}} \right)_{\tilde{\rho}_{\alpha\beta}(r)} \tilde{\rho}_{\alpha\beta} \left( \frac{\partial \Psi_{\alpha\beta}^C}{\partial \tilde{\rho}_{\alpha\beta}} \right)_{\tilde{\rho}_{\alpha\beta}(r)} \rho_{\alpha \beta} \left( \frac{\partial \Psi_{\alpha\beta}^C}{\partial \tilde{\rho}_{\alpha\beta}} \right)_{\tilde{\rho}_{\alpha\beta}(r)} w' (r_{ij}) \hat{r}_{ij}. $$

(A8)

Equation (A8) looks rather complicated, but, in fact, it is a straightforward combination of Eqs. (A1) and (26). One may be tempted to simplify it by inserting the local-density approximations $\tilde{\rho}_{\alpha\beta}$ directly into (26). However, such practice is quite dangerous, because it can violate the potential nature of the interparticle forces (in the sense that they will no longer correspond to any potential energy), and as a consequence lead to energy generation in the system. This uncontrolled inflow of energy will bias the DPD thermostat and, if rapid enough, can even destabilize the system.

13. P. Español, SIMU Newsletter 4, 59 (2002); http://simu.ulb.ac.be
30. As reported by P. B. Warren (Ref. 26) the method was also invented independently by R. D. Groot.