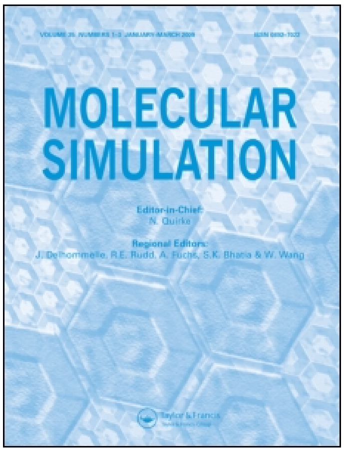
This article was downloaded by:
On: *14 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

The Boundary Condition in the Gibbs Ensemble Simulation of a Stockmayer Fluid under an Applied Field

Kenji Kiyohara[a]; K. J. Oh[b]; X. C. Zeng[b]; Koji Ohta[a]
[a] Department of Optical Materials, Osaka National Research Institute, Osaka, Japan [b] Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE, USA

To cite this Article Kiyohara, Kenji , Oh, K. J. , Zeng, X. C. and Ohta, Koji(1999) 'The Boundary Condition in the Gibbs Ensemble Simulation of a Stockmayer Fluid under an Applied Field', Molecular Simulation, 23: 1, 95 — 107
To link to this Article: DOI: 10.1080/08927029908022114
URL: http://dx.doi.org/10.1080/08927029908022114

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Molecular Simulation, 1999, Vol. 23, pp. 95–107
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

THE BOUNDARY CONDITION IN THE GIBBS ENSEMBLE SIMULATION OF A STOCKMAYER FLUID UNDER AN APPLIED FIELD

KENJI KIYOHARA[a, *], K. J. OH[b], X. C. ZENG[b] and KOJI OHTA[a]

[a] *Department of Optical Materials, Osaka National Research Institute, Ikeda, Osaka, 563-8577, Japan;*
[b] *Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE 68588-0304, USA*

(Received June 1999; accepted June 1999)

We calculate the vapour-liquid coexistence properties of the Stockmayer fluid with reduced permanent dipole $\mu^* = 2.0$ under an applied electrostatic field $E_0^* = 1.0$ for various boundary conditions by the Gibbs ensemble simulation. In contrast to the system under no field, the phase behaviour of the Stockmayer fluid under the applied field calculated in simulation strongly depends on the dielectric constant of the surroundings used in the Hamiltonian. We propose that the value of the dielectric constant of the surroundings for the vapour and the liquid phase used in the simulation should be adjusted to that of the system in the corresponding phase, in order to best represent the thermodynamics of the bulk system under applied field.

Keywords: Vapour–liquid coexistence; polar fluids; applied field

1. INTRODUCTION

Dipolar hard/soft spheres and Stockmayer fluids have been studied as models for polar fluids and there are many studies on the structural [1, 2], thermodynamic [3–8] and dielectric properties [1, 2, 6, 9, 10, 11, 12]. The effect of applied field on the properties of dipolar fluids such as saturation of dielectric constants [1, 2, 9], electrostriction [2, 10], ferroelectricity [13] and phase behaviour [5–7] have also been studied. In this article, we discuss the

---

*Corresponding author.

effect of applied field on the vapour–liquid equilibrium properties of Stockmayer fluids [14] by the Gibbs ensemble simulation [15].

Due to the long range nature, two dipolar molecules are interacting even when they are apart by a macroscopic distance. In order to carry out the energy calculation of a dipolar system with a limited number of molecules, as in simulation, the approximation by Lorentz [16] is used: the interaction of the system is separated into two parts, the direct interaction with neighbouring molecules and the averaged interaction with those far away, which is treated as a continuum [17, 18]. Based on this idea, the reaction field method [19, 20] and the Ewald summation method [21] have been commonly used in computer simulation. The Ewald summation method seems to be the most widely used method because of its small dependence on the size of the simulated system [2, 11]. The boundary condition for the potential used in simulation (in the form of the dielectric constant of the surroundings, ε') must be carefully chosen to calculate the bulk properties of the system.

The relation between the boundary condition, the external field and the Maxwell field of the system is well established [2, 3, 4, 20]. The internal consistency between these three properties has been demonstrated by simulation [21, 10]. Using that relation, the dielectric constant of the system, ε', can be calculated by using any value for ε'. In practice, large values are often used for ε' because less numerical errors are expected than by using small dielectric constants [21].

However, the actual interaction of the system under an applied field is determined only after a specific boundary condition or ε' is chosen. Therefore, for calculating the vapour–liquid phase coexistence properties, an appropriate value for ε' should be chosen for both the vapour and the liquid phase. There are some studies on the phase behaviour of Stockmayer fluids under applied field [5, 6, 10]. In those studies, however, ε' was chosen to be infinity and dependence of the simulated thermodynamic properties on the boundary condition was not investigated.

Discussion on the effect of the choice of the boundary condition in simulation of the polar molecules can be found in literature [22, 23, 24]. In particular, dependence of the phase behaviour of Stockmayer fluids on the boundary condition under no applied field has been studied by Garzón *et al.* [23] using the reaction field method. They showed that the vapour–liquid coexistence properties of Stockmayer fluids are insensitive to the choice of ε' in their simulations. On the other hand, Wei and Patey's study [13] on isotropic-to-liquid-crystal transition of soft spheres shows that the boundary condition significantly affects the thermodynamics of dipolar systems.

These results suggest that the interaction of the simulated system strongly depends on the value of ε' when the system can have a non-zero net dipole and that does not when the system cannot have a net dipole. Therefore, for Stockmayer fluids under an applied field, which has a net dipole along the direction of the filed, a strong dependence of the interaction on the value of ε' is expected.

In this study, the vapour–liquid coexistence properties of a Stockmayer fluid under an applied field are calculated by the Gibbs ensemble and a reasonable way to choose the value of ε' is discussed.

2. MODEL AND BOUNDARY CONDITIONS

The potential of Stockmayer fluids is described as a Lennard-Jones interaction site with an embedded point dipole at the center of the molecule [14]. The pair potential of Stockmayer molecules i and j is written as

$$u(i,j) = u_{LJ}(i,j) + u_{dp}(i,j), \tag{1}$$

where

$$u_{LJ}(i,j) = 4\varepsilon_{LJ}\left[\left(\frac{\sigma_{LJ}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{LJ}}{r_{ij}}\right)^{6}\right] \tag{2}$$

and

$$u_{dp}(i,j) = -\boldsymbol{\mu}_i \cdot \mathbf{T}_{ij} \cdot \boldsymbol{\mu}_j \tag{3}$$

In the equations above, ε_{LJ} and σ_{LJ} are the Lennard-Jones parameters, r_{ij} is the separation of the molecules, $\boldsymbol{\mu}_i$ is the dipole vector of the i-th molecule and $\mathbf{T}_{ij}$ is the dipole tensor. If the vector connecting the centers of molecules i and j is denoted by $\mathbf{r}_{ij}$ and the unit tensor by $\mathbf{I}$, the dipole tensor is defined as

$$\mathbf{T}_{ij} = \frac{3\mathbf{r}_{ij}\mathbf{r}_{ij}}{r_{ij}^5} - \frac{\mathbf{I}}{r_{ij}^3}. \tag{4}$$

We used the Ewald summation method for most of the simulations and used also the cut-off potential when comparison was needed.

In the Ewald summation method, the simulation cell is periodically duplicated in a spherical shell in order to represent an infinitely large system. The whole duplicates are surrounded by a continuum of a dielectric constant

ε' [21]. The interaction of the molecules that are in the simulation cell is calculated directly with the periodic boundary condition and the long range interaction is introduced through the interaction with the duplicated cells and that with the surrounding continuum. The total interaction of the system is expressed as

$$H(\varepsilon') = \sum_{i<j} -(\boldsymbol{\mu}_i \cdot \nabla)(\boldsymbol{\mu}_j \cdot \nabla)\Psi_{p.b.c.}(r_{ij}) - \frac{2(\varepsilon' - 1)}{2\varepsilon' + 1} \frac{4\pi}{3} \frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{L^3} \tag{5}$$

where

$$\Psi_{p.b.c.}(\mathbf{r}) = \frac{1}{L}\left[\frac{\mathrm{erfc}(\alpha|\mathbf{r}/L|)}{|\mathbf{r}/L|} + \frac{1}{\pi}\sum_{\mathbf{n}\neq 0} \frac{\exp(2\pi i\mathbf{n} \cdot \mathbf{r}/L - \pi^2|\mathbf{n}|^2/\alpha^2)}{|\mathbf{n}|^2} - \frac{2\pi}{3}|\mathbf{r}/L|^2\right]. \tag{6}$$

α is the convergence factor and L is the box-length of the simulation cell. The interaction calculated in simulation is in general a function of ε' [21, 12]. The first term in the summation of Eq. (5) represents the interaction between the periodically and infinitely duplicated cells and the second term the reaction field from the surroundings.

When an external field is applied on the system the total Hamiltonian becomes

$$H(\mathbf{E}_0, \varepsilon') = H(\varepsilon') - \sum_i \boldsymbol{\mu}_i \cdot \mathbf{E}_0 \tag{7}$$

where $\mathbf{E}_0$ is the applied field and $H(\varepsilon')$ is from Eq. (5). We use this Hamiltonian to calculate the phase coexistence properties for different ε' under applied field.

There has been criticism of using the Ewald summation method [22, 24, 25]. However, we do not intend to discuss in this article the inherent problems of the method itself. We rather focus on how to choose the dielectric constant of the surroundings, ε', which is necessary to describe the reaction field. Many simulation studies use $\varepsilon' = \infty$ or $\varepsilon' = 1$. In fact, this particular choice of ε' is justified for the calculation of thermodynamic properties of the system under no field. Boresch and Steinhauser [24] showed that the value of ε' does not significantly affect the internal energy of the simulated water system, although it does significantly affect the structure. The study of Garzón *et al.* [23], as already mentioned in the preceding section, more directly shows that the choice of ε' is not important for calculating the thermodynamics of polar systems. We investigate if the same rule applies for the system under applied field in the following sections.

3. SIMULATION DETAILS

Throughout this study, data are presented in the reduced units, denoted by the superscript (*). The units of energy and length are reduced by the Lennard-Jones parameters ε_{LJ} and σ_{LJ}, respectively. Reduced temperature is $T^* = k_B T/\varepsilon_{LJ}$, reduced electric field is $\mathbf{E}^* = \mathbf{E}/(\varepsilon_{LJ}/\sigma_{LJ}^3)^{1/2}$ and reduced dipole moment is $\mu^* = \mu/(\varepsilon_{LJ}\sigma_{LJ}^3)^{1/2}\cdot$ k_B is the Boltzmann constant. We studied the Stockmayer fluid with permanent dipole moment $\mu^* = 2.0$, where μ^* denotes the magnitude of the dipole vector of a molecule.

We performed the Gibbs ensemble simulations of the Stockmayer fluid with different boundary conditions and with and without an applied field of $E_0^* = 1.0$, where E_0^* denotes the magnitude of the field, $\mathbf{E}_0^*$. We used the total of 300 molecules, the convergence factor $\alpha = 5$, and 514 reciprocal lattices (vectors **n** in the second term in Eq. (6)) throughout this study.

First, we calculated the vapour-liquid coexistence properties of the Stockmayer fluid of $\mu^* = 2.0$ with three different boundary conditions, the Ewald summation with $\varepsilon' = 1$, the Ewald summation with $\varepsilon' = \infty$, and the cut-off potential under no applied field. For the cut-off potential, the interaction between molecules that are apart more than half the box-length of the simulation cell is neglected.

Next, an external field of $E_0^* = 1.0$ was applied on the system and the vapour-liquid coexistence properties were calculated and were compared with the results for no applied field. For the simulation with applied field, we used not only the three boundary conditions as above but also the boundary condition in which ε' is set equal to the dielectric constant of the system, ε, which we shall call the self-consistent boundary condition. This way of choosing ε' allows us to represent molecules in a simulation cell that is placed in the bulk of the same kind of molecules. This is intuitively the most reasonable choice of the boundary condition. Discussion on this choice is given in the next section.

The method to calculate ε is described in the following. We define ε by

$$\varepsilon \equiv 1 + 4\pi\frac{P}{E}, \tag{8}$$

where P is the polarization and E is the Maxwell field of the system. Thus defined ε should be understood as a measure of polarization rather than the proportionality constant relating the electric field and the electric displacement for infinitesimally small field. Suppose there is an external field E_0 in a sphere of vacuum in a continuum of dielectric constant ε'. If the sphere is filled with a substance with polarization P, the electric field in the sphere E is given by [9, 10, 22]

$$E = E_0 - \frac{4\pi P}{2\varepsilon' + 1}. \tag{9}$$

From Eqs. (8) and (9), we obtain the formula to calculate ε,

$$\frac{(\varepsilon - 1)(2\varepsilon' + 1)}{2\varepsilon' + \varepsilon} = \frac{4\pi P}{E_0} \tag{10}$$

or

$$\varepsilon = \frac{1 + 2\varepsilon' + 2\varepsilon' \frac{4\pi P}{E_0}}{1 + 2\varepsilon' - \frac{4\pi P}{E_0}}. \tag{11}$$

For the self-consistent boundary condition, ε is calculated during simulation and the value of ε' is iteratively adjusted to ε, separately for the vapour and the liquid phase. In practice, the simulation is divided into several blocks of Monte Carlo steps and ε is calculated in one block of steps and the obtained value is put in ε' of the next block of Monte Carlo steps. In this way, ε' is self-consistently adjusted to ε after certain number of blocks of simulation. It is important to choose a block length that is long enough to accurately calculate the average polarization. From our preliminary simulations, we found that the average value of the polarization calculated from a block of 100,000 Monte Carlo steps is essentially the same as that from a block of 1,000,000 Monte Carlo steps. Therefore, we used a block-length of 100,000 steps for calculating the average value of the polarization. Also, we found that the value of ε' converges within 500,000 steps or 5 blocks of equilibration runs, whether the initial value of ε' is chosen to be unity or infinity. This fast convergence for the dielectric constant contrasts with the calculation of ε by simulation under no field, in which much longer simulation is required because the fluctuation of the polarization needs to be calculated.

The typical ratio of different Monte Carlo moves in the Gibbs ensemble simulation we used are 35–40% of the Monte Carlo moves for displacement of a molecule, 35–40% for rotation, 19–29% for transfer, and 1% for volume change. The average values and the error-bars are calculated from

10 block averages. Each block length of 1 million steps and the total of 10 million steps were used for each simulation for calculation of error-bars.

4. RESULTS AND DISCUSSION

First, the Gibbs ensemble simulations of the Stockmayer fluid of $\mu^* = 2.0$ under no applied field were performed for three different boundary conditions: the Ewald summation with $\varepsilon' = \infty$, the Ewald summation with $\varepsilon' = 1$, and the cut-off potential. The results are shown in Figure 1 and Table I. As it is seen, the results for all the three boundary conditions agree well and no significant difference was observed in the coexistence properties. This is consistent with Garzón *et al.*'s calculation with the reaction field method [23].

Next, the external field of $E_0^* = 1.0$ was applied parallel to the z-coordinate of the system and the vapour–liquid coexistence properties were calculated. The Gibbs ensemble simulations were performed with the four boundary conditions described in the preceding section. The results are shown in Figure 2 and Table II. For the boundary condition $\varepsilon' = 1$ as well as for the cut-off potential, the liquid density is lower, the vapour density is

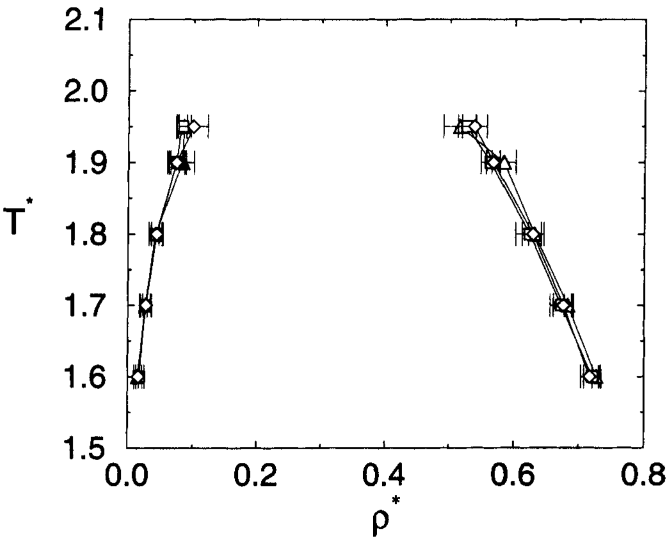


FIGURE 1 Comparison of the vapour–liquid coexistence density of the Stockmayer fluid of dipole moment $\mu^* = 2.0$ for different boundary conditions: the cut-off potential (up-triangles), the Ewald summation method with "$\varepsilon' = \infty$" (squares), and the Ewald summation method with "$\varepsilon' = 1$" (diamonds). T^* and ρ^* denote temperature and density, respectively.

TABLE I Comparison of the vapour–liquid coexistence density and potential energy of the Stockmayer fluid of $\mu^* = 2.0$ for different boundary conditions (b.c.). T^*, ρ^*, U^* denote temperature, density, and potential energy, respectively. The subscripts indicate the liquid phase (l) or the vapour phase (v). "Cutoff" denotes the cutoff potential and ε' is the dielectric constant of the surroundings. The numbers in parentheses are the errors in the last digits

T^*	*b.c.*	ρ_l^*	ρ_v^*	U_l^*	U_v^*
1.6	cutoff	0.7273(61)	0.0156(17)	−10.332(81)	−0.85(20)
	$\varepsilon' = \infty$	0.7200(45)	0.0157(19)	−10.171(47)	−0.80(11)
	$\varepsilon' = 1$	0.717(14)	0.0168(59)	−10.13(15)	−0.88(35)
1.7	cutoff	0.6835(56)	0.0269(34)	−9.712(54)	−1.17(20)
	$\varepsilon' = \infty$	0.673(17)	0.0276(96)	−9.54(18)	−1.16(41)
	$\varepsilon' = 1$	0.677(16)	0.0279(77)	−9.58(16)	−1.19(34)
1.8	cutoff	0.6314(99)	0.0423(59)	−9.04(10)	−1.59(25)
	$\varepsilon' = \infty$	0.624(22)	0.044(11)	−8.93(22)	−1.57(40)
	$\varepsilon' = 1$	0.629(17)	0.0446(86)	−8.97(18)	−1.64(34)
1.9	cutoff	0.584(18)	0.084(18)	−8.41(17)	−2.52(39)
	$\varepsilon' = \infty$	0.563(15)	0.074(11)	−8.20(14)	−2.36(34)
	$\varepsilon' = 1$	0.568(11)	0.075(14)	−8.24(10)	−2.30(35)
1.95	cutoff	0.516(25)	0.085(11)	−7.69(23)	−2.46(29)
	$\varepsilon' = \infty$	0.526(14)	0.0828(72)	−7.77(13)	−2.39(17)
	$\varepsilon' = 1$	0.539(19)	0.100(22)	−7.89(18)	−2.76(40)

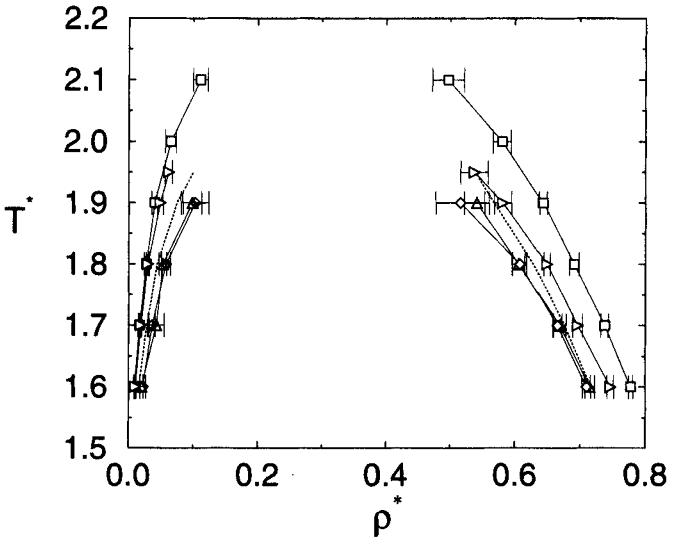


FIGURE 2 Comparison of the vapour–liquid coexistence density of the Stockmayer fluid of $\mu^* = 2.0$ under an applied of $E^* = 1.0$ for different boundary conditions. Up-triangles, squares, and diamonds denote the same as in Figure 1. Right-triangles denote the self-consistent boundary condition. The results without applied field are indicated by dotted-lines.

TABLE II The vapour–liquid coexistence density, potential energy, and average dipole moment of the Stockmayer fluid of $\mu^* = 2.0$ under an applied field of $E^* = 1.0$ for different boundary conditions (b.c.). T^*, ρ^*, U^*, and m^* denote temperature, density, potential energy, and average dipole moment per molecule in z-direction (the direction of the applied field), respectively. The subscripts indicate the liquid phase (l) or the vapour phase (v). "Cutoff" denotes the cut-off potential and ε' is the dielectric constant of the surroundings. "$\varepsilon' = \varepsilon$" denotes the self-consistent boundary condition. The numbers in parentheses are the errors in the last digits

T^*	*b.c.*	ρ_l^*	ρ_v^*	U_l^*	U_v^*	m_l^*	m_v^*
1.6	cutoff	0.7150(74)	0.0206(24)	−10.363(77)	−1.89(16)	0.3066(69)	0.776(25)
	$\varepsilon' = 1$	0.7101(66)	0.0228(42)	−10.258(65)	−2.04(26)	0.3125(65)	0.771(24)
	$\varepsilon' = \infty$	0.7781(32)	0.0099(12)	−12.730(41)	−1.37(13)	1.4759(71)	0.760(48)
	$\varepsilon' = \varepsilon$	0.7471(51)	0.0112(10)	−11.959(52)	−1.40(11)	1.3301(88)	0.767(33)
1.7	cutoff	0.6692(98)	0.043(13)	−9.755(88)	−2.58(43)	0.3208(60)	0.762(25)
	$\varepsilon' = 1$	0.6655(70)	0.0368(45)	−9.674(70)	−2.36(24)	0.3192(50)	0.737(28)
	$\varepsilon' = \infty$	0.7380(57)	0.0173(23)	−12.077(64)	−1.65(15)	1.411(11)	0.772(40)
	$\varepsilon' = \varepsilon$	0.6967(74)	0.0190(18)	−11.165(85)	−1.64(10)	1.228(16)	0.744(25)
1.8	cutoff	0.6063(98)	0.0533(58)	−9.011(91)	−2.63(19)	0.3431(50)	0.705(21)
	$\varepsilon' = 1$	0.608(11)	0.0579(71)	−8.992(97)	−2.77(23)	0.339(11)	0.699(18)
	$\varepsilon' = \infty$	0.6915(74)	0.0276(30)	−11.370(93)	−1.91(18)	1.344(14)	0.742(34)
	$\varepsilon' = \varepsilon$	0.6496(51)	0.0299(27)	−10.470(58)	−1.89(14)	1.157(19)	0.706(24)
1.9	cutoff	0.541(19)	0.099(14)	−8.25(17)	−3.43(32)	0.362(12)	0.647(13)
	$\varepsilon' = 1$	0.516(38)	0.103(22)	−7.99(32)	−3.64(42)	0.373(21)	0.651(23)
	$\varepsilon' = \infty$	0.6435(59)	0.0404(43)	−10.664(60)	−2.20(15)	1.280(11)	0.740(33)
	$\varepsilon' = \varepsilon$	0.582(14)	0.0491(46)	−9.50(12)	−2.36(18)	1.047(11)	0.681(33)
1.95	$\varepsilon' = \infty$	0.613(10)	0.0531(78)	−10.24(10)	−2.55(27)	1.245(12)	0.747(31)
	$\varepsilon' = \varepsilon$	0.537(21)	0.0623(57)	−8.95(21)	−2.68(16)	0.985(21)	0.696(17)
2.0	$\varepsilon' = \infty$	0.580(14)	0.0655(84)	−9.77(15)	−2.81(27)	1.187(16)	0.746(32)
2.1	$\varepsilon' = \infty$	0.497(25)	0.112(12)	−8.67(26)	−3.72(27)	1.087(22)	0.777(24)

higher than that when there is no applied field. The average dipole moment per molecule in the z-direction ($\langle m \rangle$) is larger in the vapour phase than in the liquid phase (see Tab. II). This indicates that the potential energy is lowered more significantly in the vapour phase when the applied field is turned on. A molecule in the vapour phase almost freely responds to the applied field while the response of a molecule in the liquid phase is hindered by the presence of other molecules nearby. Only this effect determines the average dipole moment per molecule since there is no reaction field for these boundary conditions: Note that the reaction field term in Eq. (5) vanishes for $\varepsilon' = 1$.

On the other hand, for the boundary condition of $\varepsilon' = \infty$, the coexistence curve shifted to the opposite direction: the liquid density shifts to a higher value, the vapour density to a lower value than that when there is no field. These results are consistent with those obtained by Stevens and Grest [5] and Boda *et al.* [6], who also used the boundary condition $\varepsilon' = \infty$. The average dipole moment per molecule in the z-direction is larger in the liquid phase than in the vapour phase (see Tab. II). This is understood in terms of the effect of the reaction field. Because ε' is infinity, the reaction field takes the maximum value for the given polarization of the system and that increases the field and lowers the energy of the system (see Eq. (7)). The effect of reaction field is more significant in the liquid phase than in the vapour phase due to the larger polarization. For the boundary condition $\varepsilon' = \infty$, the effect of the reaction field is the major driving force for the change of the phase behaviour when an external field is applied on the system.

For the self-consistent boundary condition, we found that the coexistence curve shifts to the same direction as those for the boundary condition of $\varepsilon' = \infty$, but with relatively small magnitude. The dielectric constants of the systems at vapour–liquid coexistence are shown in Table III. The average dipole moments in x- and y-directions were found to be zero within the error-bars for all the boundary conditions used here.

TABLE III Dielectric constant (ε) of the Stockmayer fluid of dipole moment $\mu^* = 2.0$ at vapour–liquid coexistence for the boundary condition "$\varepsilon' = \varepsilon$". T^* is temperature. The subscripts indicate the liquid phase (l) or the vapour phase (v). The numbers in parentheses are the errors in the last digits

T^*	ε_l	ε_v
1.6	19.35(31)	1.117(15)
1.7	16.68(35)	1.188(21)
1.8	14.71(29)	1.287(35)
1.9	11.88(54)	1.453(61)
1.95	10.47(68)	1.623(73)

As we have shown, the Gibbs ensemble simulation of the Stockmayer fluid under the applied field gives different results depending on the boundary condition. This contrasts with the simulation under no applied field, which shows practically no dependence on the boundary condition. Although we cannot directly compare our results with the "true" calculation by simulating a macroscopically large system, due to the limitation of computational power, we nevertheless recommend the self-consistent boundary condition among the boundary conditions used in this study for the following reason.

The reaction field for a sub-volume of a macroscopic system containing a few hundred molecules is determined by the interaction between the polarization of the sub-volume and the surroundings composed of the same kind of molecules with dielectric constant ε. Therefore, it is most reasonable to adjust the dielectric constant of the surroundings to that of the system itself in order to represent the thermodynamics of a macroscopic system by a few hundred molecules. It is especially important to use this condition in the Gibbs ensemble simulation because the dielectric constant in the vapour phase and that in the liquid phase are usually quite different.

The reason why the value of ε does not significantly affect the thermodynamics of the system under no applied field would be probably that the system has no net dipole and the reaction field has a minor contribution to the interaction. When the system is under applied field and has a net dipole, however, the reaction field gives a significant contribution to the interaction and the calculated thermodynamics is sensitive to the boundary condition used in the simulation.

5. CONCLUSIONS

We performed the Gibbs ensemble simulations of a Stockmayer fluid under an applied field for different boundary conditions. We found that, when there is no applied field, the coexistence properties are insensitive to the boundary condition, which is consistent with Garzón *et al.*'s results. However, when an external field is applied on the Stockmayer fluid, the results for coexistence properties qualitatively differ depending on the boundary condition. When the boundary condition $\varepsilon' = 1$ or the cut-off potential is chosen, the liquid density decreases, the vapour density increases as compared to the results for no applied field. On the other hand, when ε' is chosen to be infinity, the coexistence densities shifted toward the opposite direction: the liquid density increases and the vapour density decreases.

Considering the small size of the simulated system, it is most reasonable to use the dielectric constant of the system for that of the surroundings. To this end, we used an algorithm to self-consistently adjust the dielectric constant of the surroundings to the same values as that of the system. When the external field is applied with this boundary condition, the coexistence densities shift in the same direction as the case where the dielectric constant of the surroundings is chosen to be infinity, although the degree of the shift is much smaller.

To summarize, we found that it is important to use an appropriate boundary condition for calculating the phase behaviour of Stockmayer fluids under applied field, unlike for the system under no field. Our results, those by Garźon [23] and those by wei and Patey [13] all indicate that using the appropriate boundary condition is essential for the simulation of systems that have a net dipole, although it is not of practical importance for the systems that have no net dipole. In order to represent the thermodynamics of a macroscopic system by a few hundred molecules, we recommend that the dielectric constant of the surroundings should be adjusted to that of the system itself.

Acknowledgements

This work is supported by US National Science Foundation, New Energy Industrial Technology Development Organization of Japan, Japan Industrial Technology Association and Japan High Polymer Center. The authors thank Dr. G. T. Gao for assistance and helpful discussions.

References

[1] Pollock, E. L. and Alder, B. J. (1980). "Static dielectric properties of Stockmayer fluids", *Physica A*, **102**, 1.

[2] Adams, D. J. and Adams, E. M. (1981). "Static dielectric properties of the Stockmayer fluid from computer simulation", *Mol. Phys.*, **42**, 907.

[3] Smit, B., Williams, C. P., Hendriks, E. M. and de Leeuw, S. W. (1989). "Vapour–liquid equilibria for Stockmayer fluids", *Mol. Phys.*, **68**, 765.

[4] van Leeuwen, M. E., Smit, B. and Hendriks, E. M. (1993). "Vapour–liquid equilibria for Stockmayer fluids Computer simulations and perturbation theory", *Mol. Phys.*, **78**, 271.

[5] Stevens, M. J. and Grest, G. S. (1995). "Phase coexistence of a Stockmayer fluid in an applied field", *Phys. Rev. E*, **51**, 5976.

[6] Boda, D., Winkelmann, J., Liszi, J. and Szalai, I. (1996). "Vapor–liquid equilibrium of Stockmayer fluids in applied field: Application of the NpTE plus test particle method and perturbation theory", *Mol. Phys.*, **87**, 601.

[7] Kriebel, C. and Winkelmann, J. (1997). "Vapour–liquid equilibria for Stockmayer fluids with rigid and polarizable dipoles", *Mol. Phys.*, **90**, 297.

[8] Kiyohara, K., Gubbins, K. E. and Panagiotopoulos, A. Z. (1997). "Phase coexistence properties of polarizable Stockmayer fluids", *J. Chem. Phys.*, **106**, 3338.

[9] Petersen, H. G., de Leeuw, S. W. and Perram, J. W. (1989). "Applied field simulation of Stockmayer fluids", *Mol. Phys.*, **66**, 637.

[10] Kusalik, P. G. (1994). "Computer simulation study of a highly polar fluid under the influence of static electric fields", *Mol. Phys.*, **81**, 199.

[11] Neumann, M. (1983). "Dipole moment fluctuation formulas in computer simulations of polar systems", *Mol. Phys.*, **50**, 841.

[12] Neumann, M., Steinhauser, O. and Pawley, G. S., "Consistent calculation of the static and frequency-dependent dielectric constant in computer simulations", *Mol. Phys.*, **52**, 97.

[13] Wei, D. and Patey, G. N. (1992). "Orientational order in simple dipolar liquids: computer simulation of a ferroelectric nematic phase", *Phys. Rev. Lett.*, **68**, 2043; Wei, D. and Patey, G. N., "Ferroelectric liquid-crystal and solid phases formed by strongly interacting dipolar soft spheres", *Phys. Rev. A*, **46**, 7783.

[14] Stockmayer, W. H. (1941). "Second virial coefficients of polar gases", *J. Chem. Phys.*, **9**, 398.

[15] Panagiotopoulos, A. Z. (1987). "Direct determination of phase coexistence properties of fluids by Monte Carlo simulation in a new ensemble", *Mol. Phys.*, **61**, 813.

[16] Lorentz, H. A. (1909). *The Theory of Electrons*, Teubner.

[17] Fröhlich, H. (1958). *Theory of Dielectrics*, Oxford.

[18] Onsager, L. (1936). "Electric moments of molecules in liquids", *J. Am. Chem. Soc.*, **58**, 1486.

[19] Barker, J. A. and Watts, R. O. (1973). "Monte Carlo Studies of the dielectric properties of water-like models", *Mol. Phys.*, **26**, 789.

[20] Adams, D. J. (1980). "Computer simulation of highly polar liquids: The hard sphere plus point dipole potential", *Mol. Phys.*, **40**, 1261.

[21] de Leeuw, S. W., Perram, J. W. and Smith, E. R., "Simulation of electrostatic systems in periodic boundary conditions. I. Lattice sums and dielectric constants", *Proc. R. Soc. Lond., A*, **373**, 27.

[22] de Leeuw, S. W., Perram, J. W. and Smith, E. R. (1986). "Computer simulation of the static dielectric constant of systems with permanent electric dipoles", *Ann. Rev. Phys. Chem.*, **37**, 245.

[23] Garzón, B. Lago, S. and Vega, C. (1994). "Reaction field simulations of the vapour–liquid equilibria of dipolar fluids. Does the reaction field dielectric constant affect the coexistence properties?", *Chem. Phys. Lett.*, **231**, 366.

[24] Boresch, S. and Steinhauser, O. (1997). "Presumed *versus* real artifacts of the Ewald summation technique: The importance of dielectric boundary conditions", *Ber. Bunsenges. Phys. Chem.*, **101**, 1019.

[25] Valleau, J. P. and Whittington, S. G. (1977). "A guide to Monte Carlo for statistical mechanics" in *Statistical Mechanics*, *A*, Plenum, New York.