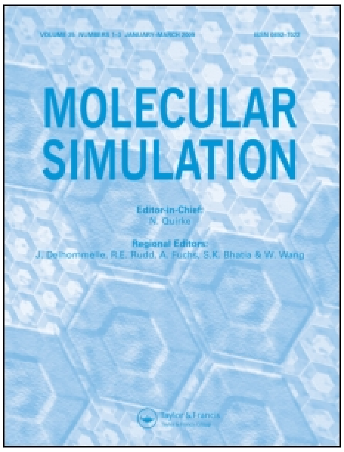

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Computer Simulation of the Liquid-Vapor Interface in Two Dimensions

K. P. Shukla[a]; M. Robert[a]
[a] Department of Chemical Engineering, Rice Quantum Institute, Rice University, Houston, Texas, USA

To cite this Article Shukla, K. P. and Robert, M.(1991) 'Computer Simulation of the Liquid-Vapor Interface in Two Dimensions', Molecular Simulation, 8: 1, 133 — 144

To link to this Article: DOI: 10.1080/08927029108022471

URL: http://dx.doi.org/10.1080/08927029108022471

Molecular Simulation, 1991, Vol. 8, pp. 133–144
Reprints available directly from the publisher
Photocopying permitted by license only

COMPUTER SIMULATION OF THE LIQUID–VAPOR INTERFACE IN TWO DIMENSIONS: TEMPERATURE AND SIZE DEPENDENCES

K.P. SHUKLA and M. ROBERT

Rice Quantum Institute and Department of Chemical Engineering, Rice University, P.O. Box 1892, Houston, Texas 77251, USA

(Received December 1990, accepted January 1991)

Constant-temperature and constant-volume molecular dynamics computer simulation results are reported for the structure of the liquid–vapor interface of two-dimensional fluids. Particles interact via a Lennard-Jones pair potential in the absence of external fields. The effects of temperature and system size on the density profile and the interfacial thickness are investigated, and the exponent describing the divergence of the interfacial thickness at the critical point is determined. The results are used to test the predictions of phenomenological theories and support the view that, in a system of small interfacial area, long-wavelength capillary waves are suppressed and the interfacial thickness is of the form predicted by the nonclassical van der Waals theory.

KEY WORDS: Liquid–vapor interface, density profile, critical behavior, size dependence.

1. INTRODUCTION

Computer simulation methods can play a useful role in the understanding of interfacial properties of fluid systems, in particular for fluids in two dimensions, where experimental results are unavailable and theoretical predictions are contradictory [1]. All previous monte carlo [2] and molecular dynamics [3, 4] simulations of interfaces of two-dimensional fluid phases were performed at a single temperature that lies far from the critical point, close to the triple point, where the thickness of the interface is very small, of the order of the range of the intermolecular forces.

Recently, molecular dynamics simulation results were obtained for the temperature dependence of interfacial properties of two-dimensional fluids, in which particles interact via a truncated Lennard-Jones pair potential in the absence of an external field [5]. The density profile and thickness of the interface were determined over a range of temperatures that lie between the triple point and the critical point temperatures, and the value of the critical exponent ω, which describes the divergence of the interfacial thickness at the critical point, was obtained. For temperatures T close to the critical temperature T_c, the critical exponent ω is defined by:

$$L \sim (T_c - T)^{-\omega} \tag{1}$$

Using the constant number of particles, volume and energy (NVE) molecular dynamics simulation method with $N = 242$ particles, the value of the critical exponent ω was found to be $\omega = 0.91$ [5].

These simulation results for the interfacial thickness were used to test the predictions of the two leading phenomenological theories of fluid interfaces, i.e., the nonclassical van der Waals theory [6] and the capillary wave theory [7].

The nonclassical van der Waals theory assumes that the structure of the interface is independent of both the interfacial area and the presence of external fields, and that the nonzero thickness of the interface arises from fluctuations identical to the spontaneous density or composition fluctuations in the coexisting bulk phases. Such an interface is referred to as an intrinsic interface. In particular, in the critical region, the interfacial thickness L of the intrinsic interface varies with temperature like the bulk correlation length ξ [8] and consequently, in two dimensions of space, one has $\omega = 1$ [9].

In contrast, capillary wave theory assumes that the diffuseness of the interface is caused by purely interfacial fluctuations associated with capillary waves thermally excited on an infinitely sharp interface, and that the nonzero thickness of the interface is not an intrinsic property [7], but depends explicitly on both the interfacial area and the external field. In two dimensions of space, capillary wave theory yields $\omega = 9/32$ for the case of gravity [10] and thus contradicts the above prediction of the nonclassical van der Waals theory of the intrinsic interface. It is currently generally believed that a consistent picture of the fluid interface is one in which both spontaneous density (composition) and capillary wave fluctuations are simultaneously present [11]. In addition, it is reasonable to expect that if the long-wavelength capillary waves are suppressed, as they would be in systems of finite interfacial area, the resulting constrained interface may be related to the intrinsic interface of the nonclassical van der Waals theory [11, 12, 13, 14]. Because of the relatively small interfacial areas used in our previous simulations [5], with only $N = 242$ particles, long-wavelength capillary waves were strongly suppressed, and the values of the interfacial thickness and the critical exponent ω were indeed found to be in accord with the predictions of the nonclassical van der Waals theory.

The purpose of the present study is to systematically investigate the effects of both system size and temperature on the interfacial properties of two-dimensional fluids in the absence of external fields. We shall also use these simulation results to test the contradictory theoretical predictions described above.

2. COMPUTER SIMULATION METHOD

In this work, the constant temperature, volume and number of particles (TVN) molecular dynamics simulation method is used to study the liquid–vapor interface as function of temperature. The temperature lies between the triple point temperature and as close to the critical point temperature as possible, with $N = 242$ or 1024 particles confined in a rectangular cell of width L_x and height $L_z = 4L_x$. The potential energy of interactions between particles is given by a truncated Lennard-Jones pair potential,

$$\begin{aligned} u(r_{ij}) &= 4\varepsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}], \quad r_{ij} \leqslant r_c \\ &= 0 \qquad\qquad\qquad\qquad\quad , \quad r_{ij} > r_c \end{aligned} \tag{2}$$

where ε and σ are energy and size parameters, respectively, and their values are chosen to be $\varepsilon/k_B = 119.8\,\mathrm{K}$ and $\sigma = 3.405\,\text{Å}$, which are typical values for argon; k_B is Boltzmann's constant, r_c is the cut-off distance of the pair potential and r_{ij} is the intermolecular separation between particles i and j.

The equations of motion of N particles are solved using a fifth-order predictor-corrector algorithm [15]. Periodic boundary conditions are imposed in both x and z directions, and a neighbor-list method is applied to improve the efficiency of the simulations.

In order to simulate the liquid–vapor phase equilibrium, the initial slab configurations are taken from a bulk phase simulation of $N/2$ particles at the prescribed temperature, as described by Lee *et al.* [16]. Bulk liquid phase simulations are performed in a cell of width $L_x^B = (N/2\,\rho_L^*)^{0.5}$ and height L_z^B, where $\rho_L^* = \rho_L\,\sigma^2$ is the reduced bulk liquid density. L_x^B is kept fixed at each temperature, to ensure a constant interfacial area, while L_z^B is chosen such that the density of the bulk liquid phase corresponds to that given by the liquid–vapor coexistence curve of Barker *et al.* [17]. Each run is started from a triangular lattice structure with initial velocities randomly assigned from a uniform distribution. The liquid slab is equilibrated for 10^3–10^4 time steps N_t, and velocity scaling is performed at each time step to maintain the desired temperature.

Equilibrated configurations of the bulk liquid phase are then duplicated in the vertical z direction, and placed in the center of a cell of height $L_z = 4\,L_x$ and width $L_x = (N/2\,\rho_L^*)^{0.5}$, as schematically illustrated in Figure 1. The simulation cell thus has two liquid–vapor interfaces and there are initially no particles in either vapor slabs.

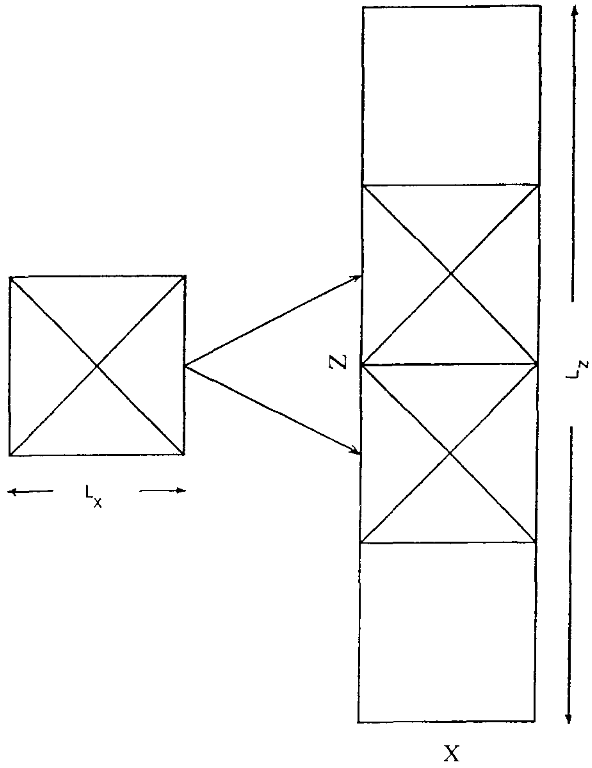

Figure 1 Schematic illustration of construction of liquid–vapor interface from equilibrated bulk liquid slab shown to the left.

Table 1 Details of simulations

Number of particles, N	242, 1024
Integration time step, Δt	$0.004\ \sigma\ (m/\varepsilon)^{0.5}$*
Potential cut-off radius, r_c	$3\ \sigma$
Duration of the liquid-vapor phase equilibration, N_t	$5 \times 10^4 - 2 \times 10^5$
Duration of the liquid-vapor phase equilibrium, N_t	$(2\text{–}12) \times 10^5$

*m is the mass of an argon atom.

The two fluid-phase system is equilibrated for several thousand time steps, until the large interfacial fluctuations have relaxed to equilibrium. Relaxation to equilibrium was checked by continuously monitoring temperature, energy, mean-squared displacement and total linear momentum of the center of mass of the system. After the equilibration period, the simulation is continued, the energy fluctuations being always less than 0.1% of the total energy, and the data of interest are finally collected. Technical details of the simulations are summarized in Table 1. We note that the CPU time required for a system of 1024 particles on a vector processing super computer, such as the NEC SX-2 of the Houston Advanced Research Center (HARC), which has been used in the present simulations with vectorized fortran-77 code of the program, was ~0.02 second/time step.

2.1 *Density Profile*

After proper equilibrium is reached, the density profile is computed as the time average of the number of particles in a strip of width Δz centered at z_k and parallel to the x-axis, given by

$$\rho(z_k) = \langle N(z_k)\rangle/(\Delta z . L_x), \tag{3}$$

Table 2 Bulk phase densities and interfacial thickness

T^*	ρ^*_L	ρ^*_V	N_t	L	N
0.424	0.7326	0.0396	20×10^4	4.68	242
	0.7285	0.0330	15×10^4	5.32	1024
0.430	0.7195	0.0421	10×10^5	5.06	242
	0.7201	0.0340	50×10^4	5.95	1024
0.436	0.7214	0.0467	20×10^4	5.29	242
	0.7140	0.0360	15×10^4	6.07	1024
0.446	0.7049	0.0518	90×10^4	5.98	242
	0.7011	0.0480	60×10^4	8.82	1024
0.464	0.6737	0.0712	90×10^4	7.56	242
	0.6473	0.0511	20×10^4	9.22	1024
0.468	0.6505	0.0762	35×10^4	8.06	242
	0.6386	0.0900	20×10^4	11.00	1024
0.474	0.6259	0.0980	12×10^5	8.18	242
	0.5945	0.1077	90×10^4	13.22	1024

with $\Delta z = L_z/200$ for the 242 particle simulations, and $\Delta z = L_z/400$ for the 1024 particle simulations.

2.2 Bulk Phase Densities and Interfacial Thickness

Once the density profile is obtained, bulk phase densities are determined by averaging over the density fluctuations in the respective bulk phases.

The interfacial thickness is determined using 10–90 rule [18], according to which the interfacial thickness is equal to the distance between points in the liquid–vapor interface at densities, respectively, equal to $\rho_V^* + 0.1\ (\rho_L^* - \rho_V^*)$ and $\rho_V^* + 0.9\ (\rho_L^* - \rho_V^*)$.

3. RESULTS AND DISCUSSION

In order to systematically investigate the effects of system size and temperature on the interfacial properties, simulations have been performed at seven reduced temperatures, $T^* = k_BT/\varepsilon = 0.424, 0.430, 0.436, 0.446, 0.464, 0.468$ and 0.474, which lie

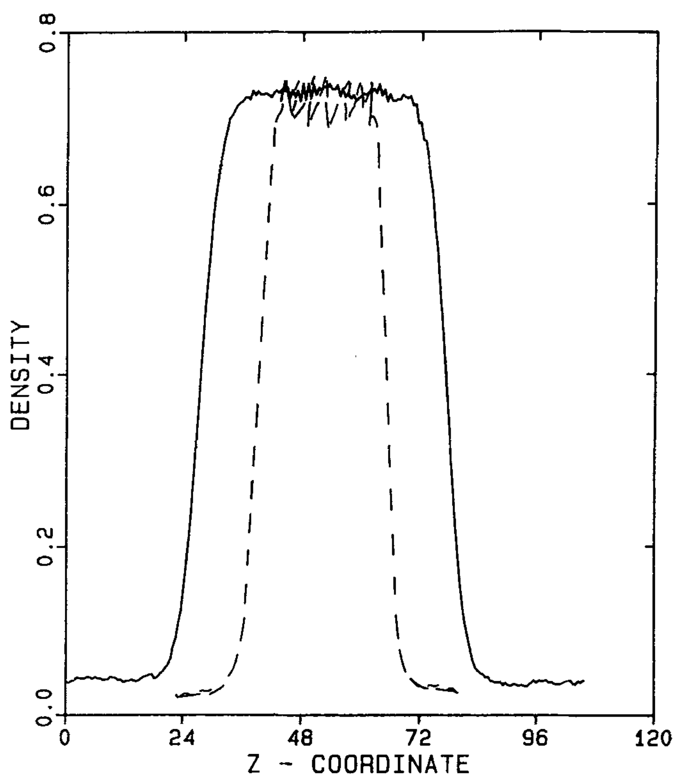

Figure 2 System size dependence of the density profile at $T^* = 0.430$. --- $N = 242$, 350,000 time steps; — $N = 1024$, 500,000 time steps.

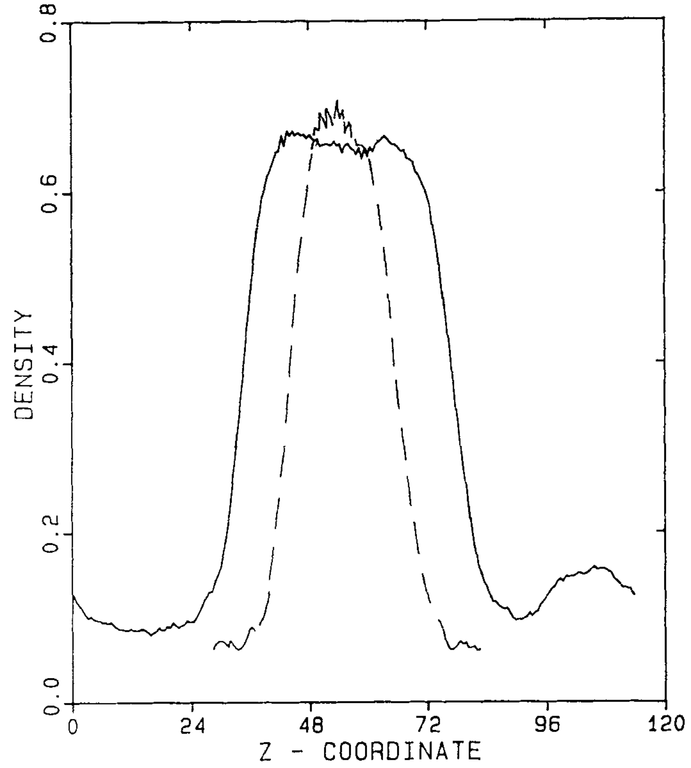

Figure 3 System size dependence of density profile at $T^* = 0.468$. --- $N = 242$, 350,000 time steps; — $N = 1024$, 400,000 time steps.

between the triple point temperature $T_t^* = 0.415$ and the critical point temperature $T_c^* = 0.533$ of the fluid with nontruncated Lennard-Jones potential [17]. At each temperature, the density profile and interfacial thickness are determined for $N = 242$ and 1024. Results for bulk liquid and vapor densities, with statistical uncertainties of 0.5% and 3%, respectively, are given in Table 2. These errors are based on the values of the densities obtained from intermediate results, which are averages over blocks of $5 \times 10^4 - 10^5$ consecutive time steps; they may be higher in the near-critical region. As expected, an increase in temperature amounts to a systematic decrease in the bulk liquid density and a corresponding increase in the bulk vapor density. Also included in Table 2 are the values of the interfacial thickness, which is found to increase as either the temperature or the number of the particles increases. In particular, the system size and temperature effects on the bulk liquid density and on the interfacial thickness are large in the near-critical region of the liquid–vapor phase equilibrium.

The system size dependence of the density profile is shown in Figure 2 at the temperature $T^* = 0.43$, which is just above the triple point temperature. As can be seen, an increase of the number of particles from 242 to 1024 yields a more symmetric density profile and smaller density fluctuations in the bulk phases. Similar results are shown in Figure 3 at the higher temperature $T^* = 0.468$. However, the curves start to deviate from the symmetrical case; this deviation is substantial for the $N = 242$

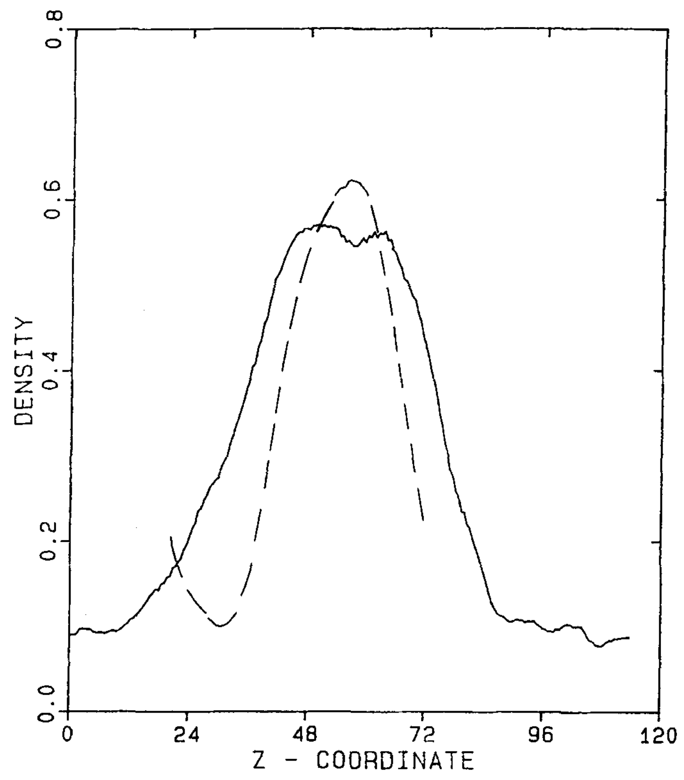

Figure 4 System size dependence of density profile at $T^* = 0.474$. --- $N = 242$, 1,200,000 time steps; — $N = 1024$, 800,000 time steps.

system. At near-critical temperatures, the system size largely affects the width of the density profile, as is clear from Figure 4, corresponding to the temperature $T^* = 0.474$. On the other hand, properties in the bulk phases far from the critical point are found to be independent of the system size, as shown by previous simulations for $N = 256$ particles [19].

Figure 5 illustrates the explicit temperature dependence of the density profile for $N = 1024$ particles. The density profile is seen to gradually become asymmetric as the temperature increases, and in the critical region the thickness of the interface is largely affected. As a result, sufficiently large system sizes and long enough simulation runs are required to obtain smooth density profiles and accurate values of the bulk phase densities and of the interfacial thickness.

The temperature dependence of the bulk correlation length ξ, which can be approximately estimated from the size of the bubbles present in the bulk liquid, is another interesting property worthy of being investigated. In particular, as described in the introduction, it is generally believed that the thickness of the interface becomes proportional to the correlation length of the spontaneous density fluctuations in either bulk phase as the critical point is approached [8]. Figures 6–7 show snapshots of the particle positions at two different temperatures $T^* = 0.430$ and 0.468, respec-

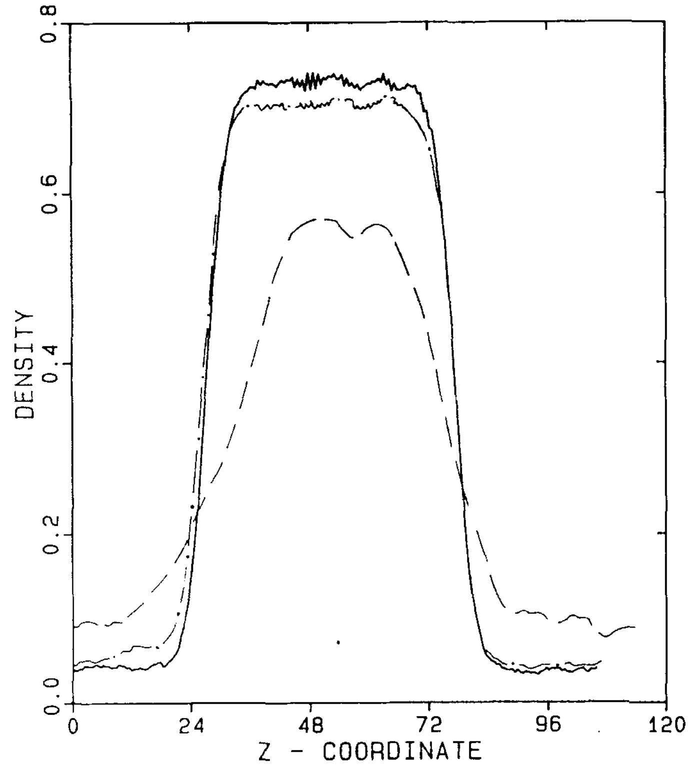

Figure 5 Temperature dependence of density profile for $N = 1024$ particles. --- $T^* = 0.474$, 800,000 time steps; -.-.- $T^* = 0.446$, 600,000 time steps; — $T^* = 0.4430$, 500,000 time steps.

tively, for the $N = 1024$ system, and show that the size of the bubbles increases with increasing temperature. When the temperature approaches its critical value, the size of the bubbles becomes comparable to the size of the system. Consequently, the bulk liquid phase tends to break into several pieces and the two distinct stable liquid–vapor interfaces no longer exist. This sets up an upper limit on the value of temperature in the present simulations. Accordingly, reliable values of the density profile and interfacial thickness can be obtained only up to approximately $T^* = 0.474$, which is taken as the limiting temperature for the liquid–vapor phase equilibrium for $N = 242$ and for $r_c = 3\sigma$. However, for the $N = 1024$ system and for a larger cut-off distance r_c of the pair potential, this limit may be higher, and is currently being investigated.

Finally, Figure 8 shows the variation of the interfacial thickness L with reduced temperature $t = (T_c^* - T^*)/T_c^*$. The slopes obtained by the least-squared regression method yield the values of the critical exponent $\omega = 0.96$ for $N = 242$ and $\omega = 0.97$ for $N = 1024$. Note that the value of $\omega = 0.96$ for $N = 242$ differs slightly from that of $\omega = 0.91$, which was determined using the less accurate *NVE* molecular dynamics simulation [5]. Within statistical uncertainties, these values of the critical exponent ω are found to agree with the prediction of the nonclassical van der Waals theory of the intrinsic interface ($\omega = 1$). These results are in close agreement with the exact

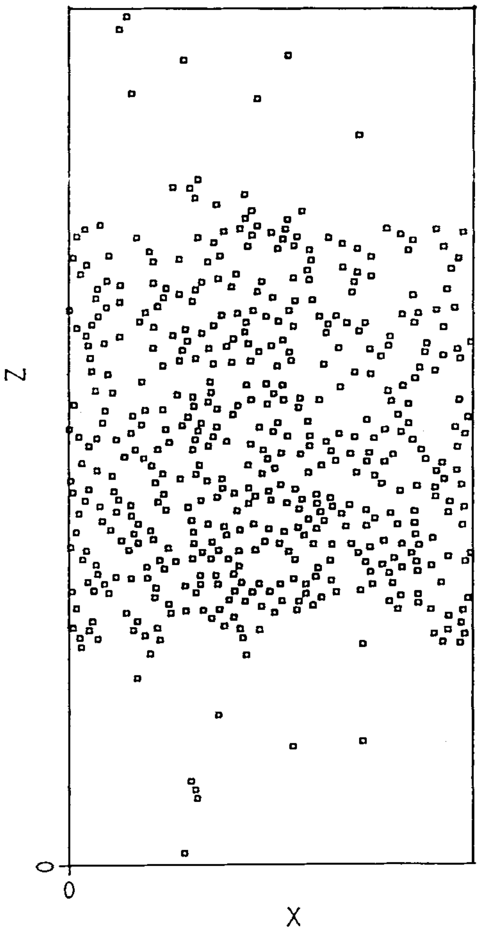

Figure 6 Snapshot of particle positions at $T^* = 0.430$; $N = 1024$, 500,000 time steps.

calculations [12] for the interface of the two-dimensional lattice gas (Ising) model of finite interfacial area in the absence of an external field.

This study suggests that systems much larger than those investigated here are needed to determine the full effects of capillary waves on critical interfaces and to test the predictions of theory.

4. SUMMARY

The present molecular dynamics simulation results show that the interfacial thickness is found to increase as temperature and system size increase, in accord with intuition. For a relatively large system size ($N = 1024$), the thickness of the interface is seen to increase strongly as the critical temperature is approached. However, because of the

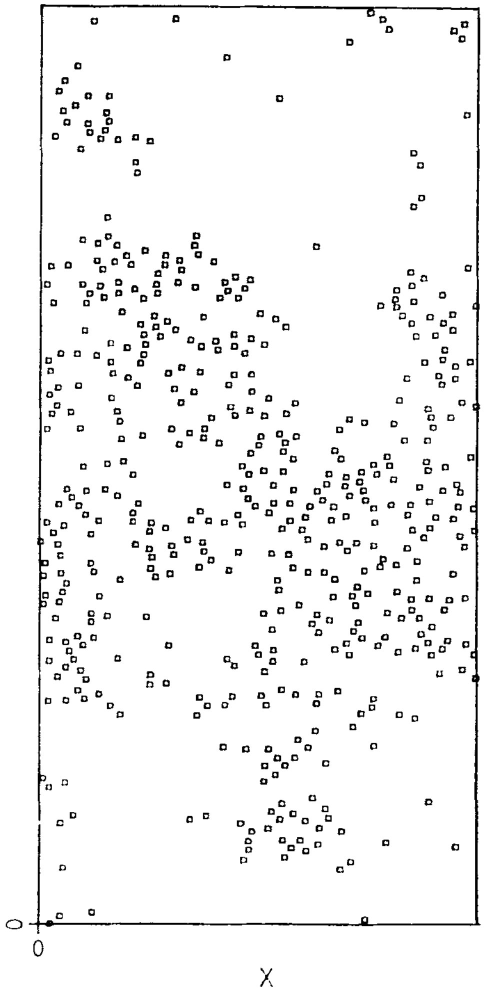

Figure 7 Snapshot of particle positions at $T^* = 0.468$; $N = 1024$, 400,000 time steps

small interfacial areas used in these simulations, long-wavelength capillary waves are strongly suppressed, particularly in the near-critical region. Consequently, the contribution of the capillary waves is not fully accounted for, and within statistical uncertainty, results for the interfacial thickness and its critical exponent are found to be consistent with the prediction of the nonclassical van der Waals theory.

In future studies, we will investigate effects of various macroscopic external fields on the critical behavior of the interfacial thickness, in order to test the general theory of fluid interfaces in external fields [20]. This will enable us to test recent theoretical predictions on two-dimensional fluids, according to which the nature of the increase of the interfacial thickness near the critical point depends strongly on the form of the external field [20].

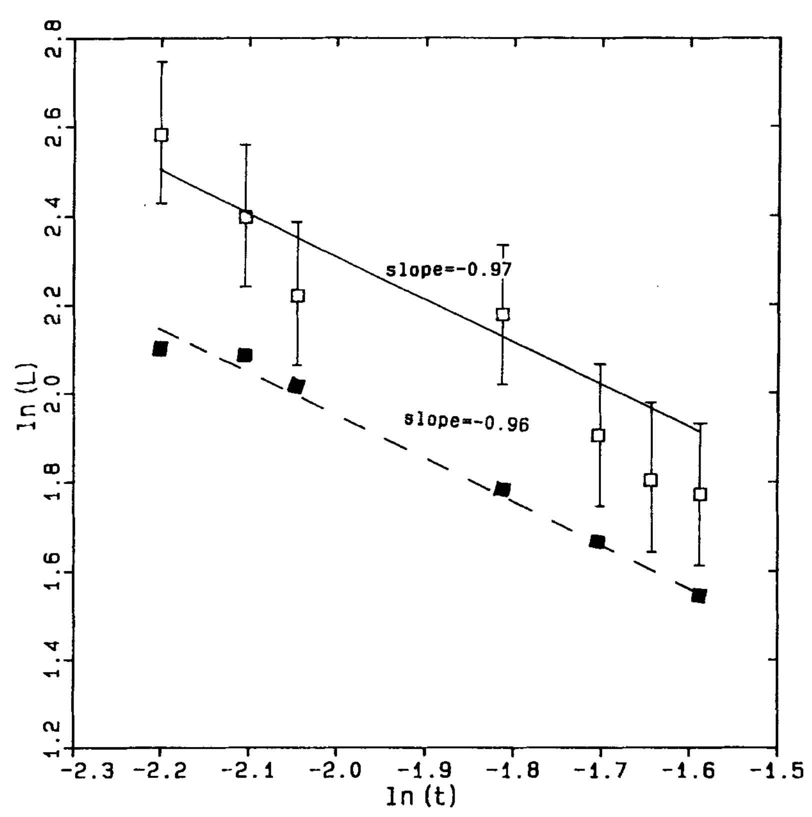

Figure 8 Variation of interfacial thickness with temperature --- $N = 242$; — $N = 1024$.

Acknowledgements

We thank the National Science Foundation, the Welch Foundation and the Donors of the Petroleum Research Fund administered by the American Chemical Society for financial support.

The computations reported here were performed on the supercomputer NEC SX-2 through a grant from Houston Advanced Research Center (HARC), the Woodlands, Texas, which is gratefully acknowledged.

References

[1] For a review, see: F.P. Buff and M. Robert, "Equilibrium Structure of the Fluid Interface", in *New Trends in Physics and Physical Chemistry of Polymers*, L.H. Lee, ed, Plenum Publishing Corporation, 1989, p. 19.

[2] F.F. Abraham, "Evidence for Two-Dimensional Liquid-Vapor Coexistence: a Monte Carlo Computer Simulation", *J. Chem. Phys.*, **72**, 1412 (1980).

[3] S. Toxvaerd, "Molecular Dynamics Calculations of the Liquid-Gas Interface for a Two-Dimensional Fluid", *J. Chem. Phys.*, **62**, 1589 (1975).

[4] J.H. Sikkenk, H.J. Hilhorst and A.F. Bakker, "A Molecular Dynamics Simulation of Liquid-Vapor Interfaces in Two Dimensions", *Physica*, **131A**, 587 (1985).

[5] L.J. Chen, M. Robert and K.P. Shukla, "Molecular Dynamics Study of the Temperature Dependence of the Interfacial Thickness in Two-Dimensional Fluid Phases", *J. Chem. Phys.*, **93**, 8254 (1990).

[6] For a review, see: J.K. Percus, "Non-Uniform Fluids", in *Studies in Statistical Mechanics*, E. Montroll and J.L. Lebowitz, eds, North-Holland, Amsterdam, 1982, p. 31.

[7] F.P. Buff, R.A. Lovett and F.H. Stillinger, "Interfacial Density Profile for Fluids in the Critical Region", *Phys. Rev. Lett.*, **15**, 621 (1965).

[8] B. Widom, "Surface Tension and Molecular Correlations Near the Critical Point", *J. Chem. Phys.*, **43**, 3892 (1965).

[9] L. Onsager, *Nuovo Cimento, Supplement*, **6**, 261 (1949).

[10] M. Robert, "Critical Behavior of Fluid Interfaces in Two Dimensions", *J. Stat. Phys.*, **41**, 1037 (1985); F.P. Buff and M. Robert, "Some Considerations of Fluid Interfaces in Two Dimensions", *J. Stat. Phys.*, **41**, 1037 (1985).

[11] B. Widom, "Surface Tension of Fluids", in *Phase Transition and Critical Phenomena*, C. Domb and M.S. Green, eds, Academic Press, New York, 1972, Vol. 2, Ch. 3.

[12] D.B. Abraham, "Intrinsic Structure and Long-Ranged Correlations in Interfaces", *Phys. Rev.*, **29B**, 525 (1984).

[13] D.A. Huse, W. van Saarloos and J.D. Weeks, "Interface Hamiltonians and Bulk Critical Behavior", *Phys. Rev.*, **32B**, 233 (1985).

[14] J.D. Weeks, "Structure and Thermodynamics of the Liquid-Vapor Interface", *J. Chem. Phys.*, **67**, 3106 (1977).

[15] C.W. Gear, *Numerical Initial Value Problems in Ordinary Differential Equations*, Prentice Hall, Englewood Cliffs, NJ, 1971.

[16] J.K. Lee, J.A. Barker and G.M. Pound, "Surface Structure and Surface Tension: Perturbation Theory and Monte Carlo Calculations", *J. Chem. Phys.*, **60**, 1976 (1974).

[17] J.A. Barker, D. Henderson and F.F. Abraham, "Phase Diagram of the Two-Dimensional Lennard-Jones System; Evidence for First-Order Transition", *Physica*, **106A**, 226 (1981).

[18] J. Lekner and J.R. Henderson, "Theoretical Determination of the Thickness of a Liquid-Vapor Interface", *Physica*, **94A** 545 (1978).

[19] C. Bruin, A.F. Bakker and M. Bishop, "Molecular Dynamics Study of the Two-Dimensional Lennard-Jones Equation of State", *J. Chem. Phys.*, **80**, 5859 (1984).

[20] M. Knackstedt and M. Robert, "Nonuniversal Field Dependence of the Critical Behavior of the Interface Between Fluid Phases in Two Dimensions", *J. Chem. Phys.*, **89**, 3747 (1988); "External Field Effects on the Critical Behavior of the Interface Between Fluid Phases", *Inter. J. Thermophys.*, **10**, 321 (1989).