Monte Carlo Study of the Widom-Rowlinson Fluid Using Cluster Methods

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The Widom-Rowlinson model of a fluid mixture is studied using a new cluster algorithm that is an adaptation of the invaded cluster method previously applied to Potts models. The algorithm overcomes the difficulties of treating continuum hard-core systems and has almost no critical slowing down. Our estimates of β/ν and γ/ν for the two-component fluid are consistent with the Ising universality class in two and three dimensions. We also present preliminary results for the three-component fluid. [S0031-9007(97)04175-6]

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Some years ago Widom and Rowlinson [1] introduced a simple continuum model that exhibits a phase transition [2]. The two-component version of this model consists of "black" and "white" particles; particles of the same type do not interact, but particles of differing type experience a hard-core repulsion at separations less than or equal to σ [3]. We present a new Monte Carlo method for simulating the Widom-Rowlinson (WR) model and apply the method to study the demixing transition in two and three dimensions.

There have been few Monte Carlo studies of the WR critical point because of the difficulties of treating hard-core systems and critical slowing down using standard Monte Carlo techniques. We discuss a new algorithm that overcomes these difficulties using cluster methods of the type introduced by Swendsen and Wang [4]. The algorithm employs the invaded cluster (IC) approach [5,6] to locate the critical point. We find that the algorithm has almost no critical slowing down and that we can obtain accurate values of the critical density and the exponent ratios β/ν and γ/ν with modest computational effort.

The two-component WR model is expected to be in the Ising universality class. Our results for β/ν and γ/ν are consistent with this assumption, and our value for the critical density of the three-dimensional ($d = 3$) WR model agrees with recent results obtained in Ref. [7].

We also consider a WR model in which there are q components, any two of which interact via a hard-core repulsion [8,9]. Our algorithm easily extends to these q-component WR models, and we present results for the three-component model in $d = 2, 3$.

Graphical representations of the WR model.—A configuration of the WR fluid consists of two sets of points, S and T, corresponding to the positions of the black and white particles. In the grand canonical ensemble, the probability density for finding the configuration (S, T) is

$$P(S,T) = \frac{1}{\mathcal{Z}} \frac{z_1^{N_1}}{N_1!} \frac{z_2^{N_2}}{N_2!} \Gamma(S,T). \tag{1}$$

$\mathcal{Z}$ is the grand partition function, z_1 (z_2) is the fugacity of the black (white) particles, and N_1 (N_2) is the number of black (white) particles. The object Γ, which expresses the hard-core interaction between particles of different types, vanishes if any point in S is within a distance σ of any point in T and is one otherwise. Symmetry considerations ensure that the critical point is along the line $z_1 = z_2$; hereafter we restrict attention to the case $z = z_1 = z_2$.

To motivate and justify our cluster algorithm, we consider a different representation of the WR model. In the "gray" representation [10,11] one considers the particles without reference to color, but with configurations weighted according to the number of allowed colorings. Let W be a list of N points, $W \equiv (\mathbf{r}_1, \ldots, \mathbf{r}_N)$. Clusters of particles can be defined by the condition that every particle in a cluster is within a distance σ of some other particle in the cluster. Particles in a cluster must all be the same color, so if there are $C(W)$ distinct clusters (including single particles), there are $2^{C(W)}$ allowed colorings. Starting with Eq. (1) and working through the combinatorics, we find that the probability density for W is given by

$$p(W) = \frac{1}{\mathcal{Z}} \frac{z^N}{N!} 2^{C(W)}. \tag{2}$$

These densities describe the *gray measures*. The appropriate gray measure for the q-component model is defined by the analog of Eq. (2) with 2 replaced by q. To return to the distribution in Eq. (1) starting from the gray representation, we select one of the $2^{C(W)}$ (or $q^{C(W)}$) allowed colorings with equal probability. It turns out that the gray measures are a special case of the models studied in [12]. The connection with the WR models was discussed in [13] and made precise in [10,11].

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Cluster algorithms.—We start from a configuration of gray particles and identify the clusters. Each cluster is independently labeled black or white with probability $1/2$ and all the white particles are removed. In the next step, white particles are replaced via a Poisson process at fugacity z in the free volume permitted by the black particles. Finally, color identities are erased and we obtain the next gray configuration. The fraction of clusters deleted in the q-component WR model is $1/q$. This algorithm is the generalization of the Swendsen-Wang method to the WR model. It is described in more detail and verified in [14] and independently in [15].

Because we are interested in efficiently sampling the transition point of WR models, we will forsake a Swendsen-Wang approach in favor of an IC-type algorithm. The steps involving the coloring and discarding of clusters are essentially the same, but rather than repopulating the free volume by a fixed fugacity process, particles are sequentially added with a uniform distribution throughout the free volume until a *stopping condition* is fulfilled. For example, one could add particles until a fixed particle number is reached. If a stopping rule is chosen that enforces a condition that is characteristic of criticality, then a critical state of the system is sampled automatically. In a finite volume the IC method samples an ensemble that differs from the canonical ensemble, but it presumably converges to the correct infinite volume distribution for all local observables. The validity of the IC method and its relation to the Swendsen-Wang method is discussed briefly below and in detail in Ref. [6].

The signature of the phase transition in the WR model is percolation of a gray cluster [10,11]. Thus an appropriate stopping rule for the IC algorithm is the spanning of a gray cluster—particles are added at random in the allowed volume until a cluster spans the system. (In our case, we use periodic boundary conditions and spanning is said to occur when a cluster wraps the torus.) The other modification is that the spanning cluster is erased on each deletion move, thereby ensuring that a new spanning cluster can form in the repopulation move.

If N_{tot} is the total number of points that are needed to satisfy the stopping condition, $z = N_{\mathrm{tot}}/V$ is an estimator for the critical fugacity z_c. For $V \to \infty$, we assume that the distribution for z becomes sharp. If this assumption is valid, each move is identical to a move of the Swendsen-Wang-type algorithm at the peak value of z. It follows that this peak value is z_c—no other value of the fugacity would exhibit a critical cluster. Hence, if the distribution for z is very narrow in a finite volume, the IC algorithm is essentially the Swendsen-Wang-type algorithm with small fluctuations in the fugacity.

Results.—We collected statistics for the following quantities: the average number of particles in the spanning cluster, M; the normalized autocorrelation function $\Gamma_M(t)$ of the number of particles in the spanning cluster as a function of "time" t as measured in Monte Carlo steps; the compressibility χ defined by

$$\chi = \frac{1}{V}\sum_i s_i^2 , \tag{3}$$

where the spanning cluster is included in the sum and s_i is the mass of the ith cluster; the estimator for the critical fugacity $z = \langle N_{\mathrm{tot}}\rangle/V$; the fluctuations in z, $\sigma_z^2 = [\langle N_{\mathrm{tot}}^2\rangle - \langle N_{\mathrm{tot}}\rangle^2]/V^2$; and the average number of gray particles per unit area (volume) ρ which is an estimator of the critical density. System size is measured in units of the particle diameter σ.

The exponents that depend on the magnetic exponent y_h can be obtained from the fractal dimension of the spanning cluster via $M \sim L^D$ or from $\chi \sim L^{\gamma/\nu}$. The exponents are related by $D = y_h$, $\gamma/\nu = 2y_h - d$, and $\beta/\nu = d - y_h$. The dynamical properties of the algorithm can be measured by the integrated autocorrelation time defined by $\tau_M = \frac{1}{2} + \sum_{t=1}^{\infty} \Gamma_M(t)$. This time is roughly the number of Monte Carlo steps between statistically independent samples and enters into the error estimate for M. In practice, it is necessary to cut off the upper limit of the sum defining τ_M when Γ_M becomes comparable to its error. The increase in τ_M defines a dynamic exponent z_M via $\tau_M \sim L^{z_M}$.

Our results for the two-component, $d = 2$ WR fluid are summarized in Table I. From the log-log plot of M versus L shown in Fig. 1, we find that $y_h = d - \beta/\nu = 1.873 \pm 0.002$, and hence $\beta/\nu \approx 0.127$, a value consistent with the exact Ising result of $\beta/\nu = 1/8$. A log-log plot of χ versus L yields $\gamma/\nu = 1.743 \pm 0.003$, consistent with the Ising value, $\gamma/\nu = 7/4$. These results support the hypothesis that the two-component $d = 2$ WR fluid is in the Ising universality class [16]. The quoted errors are associated with the least squares fitting and are two standard deviations. We also estimated the statistical

TABLE I. Dependence of M, ρ, χ, z, σ_z, and τ_M on L for the two-component, $d = 2$ WR fluid. The error estimates represent one standard deviation. The averages are over 10^5 spanning clusters.

L	M	ρ	χ	z	σ_z	τ_M
40	1511(1)	1.5247(4)	1584(2)	1.7201(7)	0.212	0.58
60	3233(3)	1.5379(3)	3217(5)	1.7247(6)	0.170	0.60
80	5527(5)	1.5450(3)	5289(9)	1.7267(6)	0.150	0.72
120	11 836(12)	1.5516(3)	10 760(20)	1.7265(5)	0.120	0.78
160	20 282(20)	1.5552(2)	17 752(30)	1.7262(4)	0.101	0.77

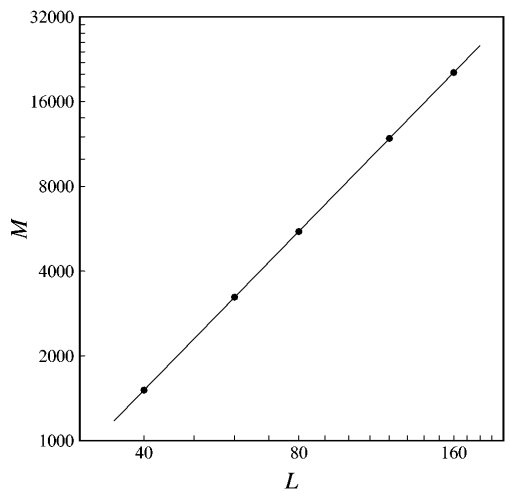

FIG. 1. Log-log plot of M, the average mass of the spanning cluster, versus L, the linear dimension of the lattice, for the two-component, $d = 2$ WR fluid. A least squares fit yields $D = 2 - \beta/\nu = 1.873$.

errors in y_h and γ/ν by generating synthetic data sets consistent with the estimated errors in the measured values of M and χ and found similar results.

From the data of Table I we have estimated the infinite volume critical values of the density ρ_c and fugacity z_c. A linear fit for $\rho(L)$ versus $1/L$ yields $\rho_c = 1.5652$. A three parameter fit of the form

$$\rho(L) = \rho_c - A/L^x \tag{4}$$

yields $\rho_c = 1.5662$ with $x = 0.96$. Because the biggest source of error is the uncertainty in the fitting form rather than the statistical errors in the raw data, we estimate the error in ρ_c as several times the difference between these two fits. Hence, we conclude that $\rho_c = 1.566 \pm 0.003$.

Within the statistical error the fugacity z is unchanged for the three largest system sizes. We take these values and several times the statistical error to estimate the critical fugacity, $z_c = 1.726 \pm 0.002$. To our knowledge, there are no independent estimates of ρ_c and z_c for the two-component, $d = 2$ WR fluid.

The autocorrelation function $\Gamma_M(t)$ decreases rapidly and oscillates about zero after $t \approx 10$. Our results for τ_M for various system sizes are summarized in Table I. The slow increase of τ_M with L indicates that z_M is small or zero ($\tau_M \sim \ln L$). Because of its small value and our limited data, we cannot make a more precise statement. Fitting $\Gamma_M(t)$ to a single exponential leads to decorrelation times similar to τ_M.

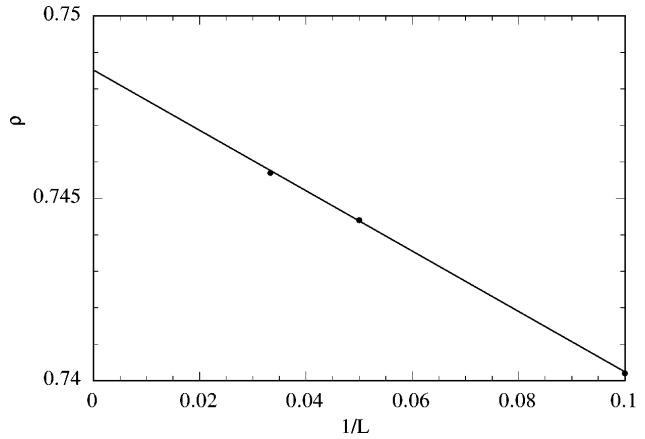

FIG. 2. Plot of ρ versus $1/L$ for the two-component, $d = 3$ WR fluid. A least squares fit yields $\rho_c = 0.7484$.

Our results for the two-component, $d = 3$ WR fluid are summarized in Table II. Power law fits of M and χ versus L yield $y_h = 3 - \beta/\nu = 2.479 \pm 0.001$ and $\gamma/\nu = 1.961 \pm 0.003$, respectively. These values are consistent with each other and with the recent estimate of $y_h = 2.4815(15)$ obtained in Ref. [17]. The results confirm the expectation that the two-component, $d = 3$ WR model is in the $d = 3$ Ising universality class.

In Fig. 2 we show ρ versus $1/L$. A linear fit yields $\rho_c = 0.7484$. A three parameter fit of the form given in Eq. (4) yields $\rho_c = 0.7478$ with $x = 1.16$. We estimate the error in ρ_c as several times the difference between these two fits and conclude that $\rho_c = 0.748 \pm 0.002$. This value of ρ_c is in agreement with and improves upon the recent result in Ref. [7], $\rho_c = 0.762 \pm 0.016$. These values for ρ_c are much higher than older estimates of ρ_c which were in the range of 0.41 to 0.57 [18].

From the estimates of τ_M shown in Table II, we see that τ_M does not appear to increase with L. It may be that there is no critical slowing for IC dynamics for the two-component, $d = 3$ WR model as is the case for the $d = 3$ Ising model under IC dynamics [6,19].

The quantity σ_z decreases with L as $\sigma_z \sim L^{-a}$ with $a \approx 0.5$ for $d = 2$ and $a \approx 0.8$ for $d = 3$. The $d = 2$ value of a is the same as was found for the $d = 2$ Ising model in the IC ensemble while for $d = 3$ it is somewhat larger than the results obtained for the $d = 3$ Ising model [19], where $a = 0.69 \pm 0.01$. The fact that $\sigma_z \to 0$ as L increases ensures that the IC ensemble is close to the canonical ensemble.

Our results for the three-component WR fluid in $d = 2$ are summarized in Table III. Using the same finite size

TABLE II. Dependence of M, ρ, χ, z, σ_z, and τ_M on L for the two-component, $d = 3$ WR fluid. The averages are over 10^6 spanning clusters.

L	M	ρ	χ	z	σ_z	τ_M
10	313.0(1)	0.740 22(7)	119.5(2)	0.9387(1)	0.138	0.59
20	1745.4(6)	0.744 40(4)	466.1(9)	0.940(1)	0.077	0.57
30	4768(2)	0.745 67(2)	1031(2)	0.9403(1)	0.056	0.57

TABLE III. Dependence of M, ρ, χ, z, σ_z, and τ_M on L for the three-component, $d = 2$ WR fluid. The averages are over 10^5 spanning clusters.

L	M	ρ	χ	z	σ_z	τ_M
40	1480(2)	1.6124(8)	1543(4)	1.965(3)	0.364	0.88
80	5325(7)	1.6352(6)	4987(13)	1.960(1)	0.280	1.2
120	11 211(18)	1.6418(6)	9810(30)	1.953(1)	0.237	1.7
160	19 013(32)	1.6455(6)	15 869(50)	1.949(1)	0.213	1.9

TABLE IV. Dependence of M, ρ, χ, z, σ_z, and τ_M on L for the three-component, $d = 3$ WR fluid. The averages are over 10^5 spanning clusters.

L	M	ρ	χ	z	σ_z	τ_M
10	299.6(3)	0.7914(2)	109.8(2)	1.1789(8)	0.230	0.58
20	1639(2)	0.7947(2)	409.1(9)	1.1717(6)	0.145	0.74
30	4407(6)	0.7947(1)	874(2)	1.1670(5)	0.117	0.83

scaling analysis we used for the two-component WR fluid, we find that $D = y_h = 1.842 \pm 0.004$ and hence $\beta/\nu \approx 0.16$. This result for y_h is consistent with our observed value of $\gamma/\nu = 1.681 \pm 0.008$. These results are *not* consistent with the corresponding value for the three-state, $d = 2$ Potts model where $y_h = 28/15$. Even more surprising, our estimated value of y_h for the WR fluid is less than the minimum value of y_h for any $d = 2$ Potts model with a continuous transition ($y_h \approx 1.86603$ for $q = 3.332$). A full scale study including additional q values and larger systems should be undertaken to determine the relation between the q-state Potts and q-component Widom-Rowlinson universality classes. We also find that ρ approaches ρ_c as $1/L$ and find $\rho_c = 1.657 \pm 0.001$; similarly, $\sigma_z \sim L^{-0.4}$. A log-log plot of τ_M versus L yields the estimate $z_M = 0.58$; for this case z is sufficiently large for us to conclude that $z > 0$.

Our results for the three-component, $d = 3$ WR fluid are summarized in Table IV. The corresponding three-state, $d = 3$ Potts model is believed to have a first-order transition, and it is likely that this behavior holds for the three-component $d = 3$ WR fluid. On the other hand, both the observed values of M and χ are well described by power laws. This situation also holds for the three-state Potts model for computationally accessible system sizes and reflects the fact that the transition is very weakly first order. More study is needed to determine the order of the transition for this case of the WR model. The IC method finds the transition temperature for Potts models independently of whether the transition is first order or continuous [6]. Hence, we believe that extrapolated values of z yield the transition value of the fugacity, $z_c \approx 1.16$, and that $\rho \approx 0.795$ lies between the density of the two coexisting phases at the transition. We also find $\sigma_z \sim L^{-0.25}$ and $z_M = 0.62$.

We have shown that cluster methods may be effectively used to study the Widom-Rowlinson model. To our knowledge, the IC algorithm is the first example of an algorithm that performs efficiently near the critical point of a continuum system with hard-core interactions. We have obtained accurate values of the critical density and fugacity for Widom-Rowlinson models in $d = 2$ and 3. The two-component Widom-Rowlinson model appears to be in the Ising universality class. However, the three-component $d = 2$ model deserves further study and might not be in the three-state Potts universality class.

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