Widom-Rowlinson model (continuum and lattice)

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**Continuum Widom-Rowlinson model:** In the beginning of seventies, a great progress has already been made in understanding equilibrium phase transitions and critical phenomena in classical (i.e. non-quantum) lattice models, where basic elements are localized on vertices of a regular discrete structure and interact with their nearest neighbors. The lattice gas analogy [1] of Onsager’s exact solution of the two-dimensional Ising model enabled one to understand qualitatively as well as quantitatively physical implications of the spontaneous breaking of the particle-hole symmetry on the existence and critical properties of high-density liquid and low-density vapor phases. On the other hand, little was known about the liquid-vapor equilibrium in continuum models (fluids), where the distance between interacting particles is a continuous variable. In 1970 Widom and Rowlinson (WR) introduced a simple model of the classical fluid in thermodynamic equilibrium [2], found a counterpart of the particle-hole symmetry and described implications of this symmetry on a potential liquid-vapor phase diagram. Subsequent studies proved rigorously the existence of liquid-vapor phase transitions in the WR and related models in spatial dimensions \( d \geq 2 \); up to now WR fluids are the only continuum systems with decaying interactions for which on has this kind of rigorous results.

The WR model consists of identical molecules living in an infinite \( d \)-dimensional continuous space of points \( \mathbf{r} \in V \ (V \rightarrow \mathbb{R}^d) \), around the center of each molecule there is a microscopic sphere of radius \( \sigma \) and volume \( v_0 \). The potential energy \( U \) associated with a given configuration \( \mathbf{r}_1, \ldots, \mathbf{r}_N \) of \( N \) molecules is defined by

\[
U(\mathbf{r}_1, \ldots, \mathbf{r}_N) = [W(\mathbf{r}_1, \ldots, \mathbf{r}_N) - Nv_0] \epsilon/v_0, \tag{1}
\]

where \( W \) denotes the volume covered by the corresponding \( N \) (in general interpenetrating) spheres and \( \epsilon > 0 \) is some energy constant. Since \( W \) fulfills the evident inequalities \( v_0 \leq W(\mathbf{r}_1, \ldots, \mathbf{r}_N) \leq Nv_0 \), the potential energy is bounded as follows

\[
-(N-1)\epsilon \leq U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \leq 0; \tag{2}
\]

the lower bound ensures a correct thermodynamics, the upper bound tells us that the short-ranged forces among molecules are purely attractive. The model is usually studied in the grand canonical formalism characterized by the dimensionless inverse temperature \( \theta = \epsilon/(k_BT) \) and particle activity \( z \), the corresponding particle density \( \langle N \rangle/V \) and pressure \( P \) are considered in the dimensionless combinations

\[
\rho(z, \theta) = v_0\langle N \rangle/V, \quad \mathcal{P}(z, \theta) = Pv_0/(k_BT); \tag{3}
\]

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z is normalized so as to be asymptotically equal to ρ in the ideal gas limit ρ → 0.

The symmetry of the WR fluid, whose spontaneous breaking is responsible for the existence of the liquid and vapor phases, is hidden in the original formulation. It becomes transparent after mapping the WR model in a thermodynamic sense onto a two-component WR mixture with non-additive hard-core interactions.

The WR mixture is composed of two kinds of molecules α ∈ {A, B} interacting pairwisely \( U(\{r\}) = \sum_{i<j} u_{\alpha\beta}(|r_i - r_j|) \), where the particles of the same species do not interact whereas the unlike species interact with a hard-core repulsion at distances smaller than 2σ, i.e.

\[
    u_{\alpha\beta}(r) = \begin{cases} 
        \infty & \text{if } \alpha \neq \beta \text{ and } r < 2\sigma, \\
        0 & \text{otherwise.} 
    \end{cases}
\]  

(4)

Let \( z_A \) and \( z_B \) be the dimensionless activities of the two species, normalized so as to be equal to the densities \( \rho_A = v_0 \langle N_A \rangle / V \) and \( \rho_B = v_0 \langle N_B \rangle / V \) in the ideal gas limit, and \( P_{\text{mix}}(z_A, z_B) \) be the dimensionless pressure (independent of the temperature since the only interactions are infinitely strong repulsions) defined in analogy with (3). The mixture possesses the obvious symmetry with respect to the interchange of A and B molecules, \( P_{\text{mix}}(z_A, z_B) = P_{\text{mix}}(z_B, z_A) \). Let us consider the line of equivalent activities \( z_A = z_B = z \). The system behaves like the ideal gas at very low z, i.e. there is just one pure (mixed) phase with equivalent particle densities \( \rho_A = \rho_B \). At very large z, since unlike molecules experience an infinitely strong repulsion, a mixed phase suffers from packing effects, which are substantionally reduced in a demixed phase with a single majority component. Consequently, the A – B symmetry of the WR mixture is broken and the system can exist in two different homogeneous (i.e. translation invariant) pure phases: the A-rich phase with \( \rho_A - \rho_B = \delta \rho > 0 \) and the complementary B-rich phase with \( \rho_B - \rho_A = \delta \rho \). The two phases become equivalent (\( \delta \rho = 0 \)) at the “demixing” critical point \( z_d \).

The two-component WR mixture is exactly solvable in one dimension with no phase transition. For dimensions \( d \geq 2 \), the proof of the existence of more than one pure thermodynamic phase for sufficiently large z was given by Ruelle [3] using the Peierls contour method.

**Theorem 1.** For each dimension \( d \geq 2 \), there exists \( z_d > 0 \) such that the A-B WR model on the line of equivalent activities \( z_A = z_B = z \) has

- A unique homogeneous mixed phase for all \( z < z_d \).
- Multiple homogeneous demixed phases for all \( z > z_d \).

By integrating over the coordinates of one species in the two-component WR mixture, its thermodynamic equivalence with the original WR model is realized via the identity between the dimensionless pressures [2]

\[
P(z, \theta) = -\theta + P_{\text{mix}}(\theta, ze^\theta).
\]  

(5)

The line \( z_A = z_B \) of the A-B mixture is thus transcribed to the line of symmetry

\[
z = \theta \exp(-\theta)
\]  

(6)
in the original WR model and the demixing critical point \( z_d \) has its image at the critical point \( (\theta^* = z_d, z^* = z_d e^{-z_d}) \). For \( \theta > \theta^* \), the line of symmetry \( (6) \) is the coexistence curve of the gas (vapor) phase with particle density \( \rho_g \) and of the liquid phase with density \( \rho_l > \rho_g \). The mapping enables one to deduce, without solving explicitly the WR model, singular behaviors of thermodynamic quantities on the line of symmetry \( (6) \) in the neighborhood of the demixing critical point. Some features of singular behaviors differ from those predicted by the lattice gas model \([1]\), e.g. the temperature derivative of the mean density \( (\rho_g + \rho_l)/2 \) is proportional to the heat capacity at constant volume and goes to \(-\infty\) at the critical point \([2]\).

The multicomponent generalization of the \( A-B \) WR mixture consists in considering molecules of \( M \) different types \( \alpha = 1, 2, \ldots, M \), all having the same activity \( z \). The molecules interact pairwisely, the only interaction is a hard-sphere repulsion \([4]\).

It was shown \([4]\) that for any finite number \( M \) of components the WR model in \( d \geq 2 \) dimensions exhibits the demixing phase transition at some \( z_d(M) \) (Theorem 1); in a pure demixed phase, the homogeneous density of just one of the components is dominant, say \( \rho_1 > \rho_2 = \ldots = \rho_M \).

A version of the \( M \)-component WR model, in which the hard-sphere interaction between unlike species is slightly modified to that of parallel hard (hyper-)cubes, was studied in the limit of infinite dimensionality \( d \to \infty \) \([5]\). In that limit, the calculation of thermodynamic functions within the second virial coefficient is exact. It turns out that for \( M \geq 31 \) the transition from the mixed phase at small values of \( z \) to the demixed phase at large values of \( z \) is preempted by solidification at intermediate values of \( z, z_c(M) < z < z_d(M) \). In the corresponding crystal phase, all species are equivalent \( (\rho_1 = \rho_2 = \ldots = \rho_M = \rho/M \) with \( \rho \) being the total density of molecules), but the density \( \rho \equiv \rho(r) \) varies periodically in space, i.e. the translation symmetry is broken. The origin of this phenomenon is purely entropic: for a large number of component \( M \) it pays the system to create a periodic structure of alternating dense and sparse regions, where the particles in the dense regions are less restricted by the hard-core repulsions coming from particles in the sparse regions.

**Lattice Widom-Rowlinson model:** The lattice version of the two-species WR model was introduced by Lebowitz and Gallavotti \([6]\). The model is defined on a regular \( d \)-dimensional integer lattice \( Z^d \), each lattice site \( i \) can be either empty \{local state \( \sigma_i = 0 \), the corresponding activity \( z(0) = 1 \)\} or singly occupied by a particle of type \( A \) \{\( \sigma_i = 1, z(1) = z \)\} or \( B \) \{\( \sigma_i = 2, z(2) = z \)\}. The only interaction is an infinite repulsion between unlike particles on nearest-neighbor pairs of lattice sites, i.e. the potential energy associated with a given state configuration \( \sigma \) of all sites is formally expressible as \( U(\sigma) = \sum_{\langle i, j \rangle} u(\sigma_i, \sigma_j) \), where the interaction potential between nearest-neighbor pair of lattice sites \( \langle i, j \rangle \) is given by

\[
    u(\sigma_i, \sigma_j) = \begin{cases} 
    \infty & \text{if } \sigma_i \neq \sigma_j \text{ and } \sigma_i \neq 0, \sigma_j \neq 0, \\
    0 & \text{otherwise.}
    \end{cases} 
\]

A relatively simple proof of the demixing phase transition (Theorem 1) in the lattice WR model was done using standard Peierls methods \([6]\). Moreover, in dimensions
In the multicomponent lattice generalization of the two-component WR model, each lattice site \(i \in \mathbb{Z}^d\) can be either empty \(\{\sigma_i = 0, z(0) = 1\}\) or singly occupied by a particle of type \(\sigma_i = 1, 2, \ldots, M\), all having the same activity \(z\). The potential energy of a state configuration \(\sigma\) reads \(U(\sigma) = \sum_{\langle i,j \rangle} u(\sigma_i, \sigma_j)\), where the interaction potential between nearest-neighbor sites \(\langle i,j \rangle\) is given by relation (7). Note that if one replaces \(\infty\) in (7) by some finite \(U \neq 0\), the system is equivalent to a dilute Potts model. The number density of species \(\sigma = 1, \ldots, M\) at site \(i\) will be denoted by \(\rho_i(\sigma)\), the total density of particles at site \(i\) by \(\rho_i = \sum_{\sigma=1}^{M} \rho_i(\sigma)\).

The exact solution of the multicomponent WR model on the Bethe lattice of coordination number \(q\) gives \(M_0 = [q/(q-2)]^2\) for the square lattice \(\mathbb{Z}\), which would suggest more realistic \(M_0 \sim 4\) for the square lattice with \(q = 4\). The Monte-Carlo (MC) simulations for the square lattice \(\mathbb{Z}\) imply \(M_0 = 7\). The MC simulations indicate that the transition at \(z_{d}(M)\) is of second order for \(M \leq 4\) and of first order for \(M \geq 5\), putting the \(M\)-component lattice WR model in the \(M\)-state Potts model universality class. For asymptotically large \(M\), \(z_d(M) \sim M - 2 + 1/M + \cdots\).
The consideration of hard-core exclusion to next-to-nearest-neighbors leads to analogous phases which numbers and characters depend on the specific geometry of the model [9].

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