Rigorous Proof of a Liquid-Vapor Phase Transition in a Continuum Particle System

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We consider particles in $\mathbb{R}^d$, $d \geq 2$, interacting via attractive pair and repulsive four-body potentials of the Kac type. Perturbing about mean field theory, valid when the interaction range becomes infinite, we prove rigorously the existence of a liquid-gas phase transition when the interaction range is finite but long compared to the interparticle spacing. [S0031-9007(98)06167-5]

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An outstanding problem in equilibrium statistical mechanics is to derive rigorously the existence of a liquid-vapor phase transition in particles interacting with any kind of reasonable potential, say Lennard-Jones or hard core plus attractive square well. This is in marked contrast to the situation for lattice systems where proofs of phase transitions abound. Thus for an Ising model with ferromagnetic interactions in dimensions $d \geq 2$ there are known to be two coexisting phases at low temperatures. These are perturbations of the two ground states, namely, the configuration with all spins up or all spins down. At nonzero temperature, there are fluctuations which cause the formation of droplets of the opposite phase, but their energy cost is so high that they remain, at low temperatures, in $d \geq 2$, only small perturbations of the ground state. It was Peierls [1] who first gave a convincing argument of the validity of such a picture; the argument was later made fully rigorous by Dobrushin [2] and Griffiths [3]. Independently of this general argument, Onsager [4] solved the two-dimensional Ising model on $\mathbb{Z}^2$ explicitly, with nearest neighbor interactions, and found the behavior of the system near the critical temperature which marks the end point of phase coexistence. Since that time solutions have been found for many other two-dimensional lattice models [5]. At the same time ferromagnetic and other inequalities as well as the development of the powerful Pirogov-Sinai formalism [6] have resulted in comprehensive rigorous theory of phase transitions in lattice systems, in $d \geq 2$, at sufficiently low temperatures.

The extension of these results to continuum particle systems has proven difficult. The ground states of such systems are not at all easy to characterize; they are presumed to be periodic or quasiperiodic configurations which depend in some complicated way on the interparticles forces. This is however far from proven and hence the analysis of the fluctuations that appear when we increase the temperature above zero is correspondingly harder, indeed very much harder, to study than in the simple lattice systems; moreover key inequalities like the ferromagnetic ones are no longer available. These problems have been overcome so far only for some multicomponent systems with special features. In particular, Ruelle [7] proved that the two component Widom-Rowlinson model [8] has a demixing phase transition. Ruelle's proof strongly exploits the symmetry between the components present in this model: see also later proofs of phase transitions in related models [9–11]. There are also proofs of phase transitions in $d = 1$ for continuum systems with interactions which decay very slowly or not at all. Such models with many particle interactions were analyzed by Felderhof and Fisher [12], while Johansson [13] has considered pair interactions which decay as $r^{-\alpha}$, $1 < \alpha < 2$, proving that at low temperatures the pressure is not differentiable.

In this Letter we report the first proof of a liquid-vapor transition in one-component continuum systems with finite range interactions and no symmetries. The basic idea of our approach is to study perturbations not of the ground state but of the mean field behavior (mfb); i.e., we shall consider situations where the interactions are parametrized by their range γ^{-1} [14,15] and perturb about $\gamma = 0$ which gives mfb. Such scaling potentials were investigated by Kac, Uhlenbeck, and Hemmer (KUH) [16] for a system of one-dimensional hard rods with an added pair potential

$$\phi_\gamma(q_i, q_j) = -\tfrac{1}{2}\,\alpha\,\gamma \exp(-\gamma |q_i - q_j|), \qquad \gamma, \alpha > 0\,. \tag{1}$$

This was later generalized by Lebowitz and Penrose (LP) [17] to d-dimensional systems with suitable short range interactions and general Kac potentials of the form

$$\phi_\gamma(q_i, q_j) = -\alpha\,\gamma^d J(\gamma |q_i - q_j|) \tag{2}$$

with $\int_{\mathbb{R}^d} J(r)\,dr = 1, J(r) > 0$.

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LP showed that in the infinite volume limit followed by the limit $\gamma \to 0$ the Helmholtz free energy a takes the form

$$\lim_{\gamma\to 0} a(\rho,\gamma) = \mathrm{CE}\{a_0(\rho) - \tfrac{1}{2}\alpha\rho^2\}. \quad (3)$$

Here ρ is the particle density, a_0 is the free energy density of the reference system, i.e., the system with $\alpha = 0$ in (2), a_0 is convex in ρ (by general theorems), and CE$\{f(x)\}$ is the largest convex lower bound of f. (The dependence of a_0 on the temperature β^{-1} has been suppressed.) For α large enough the term in the curly brackets in (3) has a double well shape and the CE corresponds to the Gibbs double tangent construction. This is equivalent to Maxwell's equal area rule applied to a van der Waals' type equation of state where it gives the coexistence of liquid and vapor phases [17].

Following the work of KUH and LP, various attempts were made to go beyond the $\gamma = 0$ limit [18,19]. It is clear from general arguments, and it follows also explicitly from [14], that in $d = 1$ there is no phase transition for $\gamma > 0$. Straightforward expansions in γ are therefore bound to fail for $d = 1$, in the two phase region. In $d > 1$ these schemes give plausible, but uncontrolled, approximations. The main difficulty comes from the fact that the phase transition is a singular event, whose dependence on the parameter γ is not at all smooth. To overcome this problem requires all the modern machinery of Pirogov-Sinai theory built up in the past twenty-five years [6,20,21] plus considerable additional effort.

It is the success of such an effort which enables us to show for some systems in $d \geq 2$, that their behavior at finite $\gamma > 0$ is close to mfb at $\gamma = 0$, so that a phase transition in the latter yields a phase transition in the former for sufficiently small γ. Such results have been recently obtained for Ising models [20], where one uses a version of the Peierls argument, exploiting the spin flip symmetry of the model. The absence of symmetries in our case requires instead the whole machinery of the Pirogov-Sinai theory [6,21]. To insure stabilization against collapse, which would be induced by a Kac attractive pair potential, the natural choice made by KUH and LP is to replace point particles by hard spheres or similar strongly repulsive pair interactions. Our approach however does not work in such a case, as we need a cluster expansion for the unperturbed reference system (i.e., without the Kac interaction) at values of the chemical potential or density for which it is not proven to hold. Instead we consider point particles and insure stability by introducing a positive four-body potential of the same range as the attractive two-body one. The unperturbed system is then the free, ideal gas for which the cluster expansion holds trivially. The price is a much more involved mean field analysis, which requires a special choice of the form of the interactions.

We now specify the model, state precisely our results, and give a flavor of the proof [22]. Let $q = \{q_i\}$, $i = 1, 2, \ldots$ be a configuration of particles in a domain $\Lambda \subset \mathbb{R}^d$, $d \geq 2$. The energy of the configuration q is

$$H_\gamma(q) = -\frac{1}{2!}\sum_{i_1}\sum_{i_2\neq i_1} J_\gamma^{(2)}(q_{i_1}, q_{i_2}) + \frac{1}{4!}\sum_{i_1} \times \sum_{i_2\neq i_1}\sum_{i_3\neq i_1,i_2}\sum_{i_4\neq i_1,i_2,i_3} J_\gamma^{(4)}(q_{i_1}, q_{i_2}, q_{i_3}, q_{i_4}). \quad (4)$$

Here

$$J_\gamma^{(2)}(q_{i_1}, q_{i_2}) = \gamma^d J^{(2)}(\gamma q_{i_1}, \gamma q_{i_2}), \quad (5)$$

$$J_\gamma^{(4)}(q_{i_1}, q_{i_2}, q_{i_3}, q_{i_4}) = \gamma^{3d} J^{(4)}(\gamma q_{i_1}, \cdots, \gamma q_{i_4}), \quad (6)$$

and

$$J^{(2)}(r_1, r_2) \geq 0, J^{(4)}(r_1, r_2, r_3, r_4) \geq 0, \quad (7)$$

are fixed, bounded, translation invariant functions of finite range: they vanish whenever any of the distances $|r_i - r_j|$ is larger than some fixed length l_d.

The equilibrium properties of this system are specified by a grand canonical ensemble with reciprocal temperature β, chemical potential λ, and suitable boundary conditions (bc), i.e., by the Gibbs measure $\mu^{\mathrm{bc}}_{\Lambda,\gamma,\beta,\lambda}$. To prove coexistence of liquid and vapor phases for some β and λ we have to show that by choosing two different bc, one favoring the liquid and another the vapor phase, call them $+$ and $-$, the Gibbs measures obtained in the limit $\Lambda \nearrow \mathbb{R}^d$ describe two phases differing primarily by their densities, the appropriate order parameter for this transition. We do this in detail [22] for a particular choice of the interactions

$$J^{(2)}(r_1, r_2) = |B(r_1) \cap B(r_2)|, \quad (8)$$

$$J^{(4)}(r_1, r_2, r_3, r_4) = |\cap_{j=1}^4 B(r_j)|, \quad (9)$$

where $B(r)$ is the ball in $\mathbb{R}^d$ of volume 1 and center r, i.e., $J^{(2)}(r_1, r_2)$ is equal to the overlap volume of the two balls [of radius $\pi^{-1/2}$ and $(4/3\pi)^{-1/3}$ in $d = 2, 3$] centered at r_1 and r_2. Similarly $J^{(4)}(r_1, r_2, r_3, r_4)$ is equal to the overlap volume of four such balls.

Theorem.—Let $\beta_c = (\frac{3}{2})^{\frac{3}{2}}$ and $\beta_0 > \beta_c$ (as below), then, for any $\beta \in (\beta_c, \beta_0)$ there exist functions $\gamma_0(\beta)$ and $\lambda(\gamma, \beta)$ such that for $0 < \gamma < \gamma_0(\beta)$ the model with $J^{(2)}$ and $J^{(4)}$ as in (9) has at least two distinct infinite volume Gibbs measures $\mu^{\pm}_{\gamma,\beta}$. These measures are translation invariant and ergodic (with respect to space translations), with an exponential decay of correlations. They have particle densities, respectively, equal to $\rho_{\gamma,\beta,-} > 0$ and $\rho_{\gamma,\beta,+} > \rho_{\gamma,\beta,-}$. In the limit $\gamma \to 0$, $\lambda(\gamma,\beta) \to \lambda(\beta)$, $\rho_{\gamma,\beta,\pm} \to \rho_{\beta,\pm}$ and there exist positive constants c and δ such that $|\lambda(\gamma,\beta) - \lambda(\beta)| + \sum_{s=\pm}|\rho_{\gamma,\beta,s} - \rho_{\beta,s}| \leq c\gamma^\delta$.

The reason for the particular choice of the interactions (9) as well as for the appearance of β_0 in the theorem are related to the mfb of the system (4) valid when $\gamma \to 0$ (following the limit $\Lambda \nearrow \mathbb{R}^d$). The mean field equilibrium profiles are functions $\rho^\star(r)$ that minimize the mean field Gibbs free energy functional,

$$\mathcal{F}_{\beta,\lambda}(\rho) = \int dr \frac{\rho(r)}{\beta}[\ln \rho(r) - 1] - \int dr\, \lambda\rho(r) - \frac{1}{2!}\int dr_1\, dr_2\, J^{(2)}(r_1, r_2)\rho(r_1)\rho(r_2) + \frac{1}{4!}\int dr_1 \cdots dr_4 J^{(4)}(r_1, \ldots, r_4)\rho(r_1)\cdots\rho(r_4), \tag{10}$$

where $\rho(r)$ is a test density profile and the first integral gives the entropy contribution to the free energy.

The minimizers $\rho^{\star}(r)$ satisfy the mean field equation $\delta\mathcal{F}_{\beta,\lambda}/\delta\rho(r) = 0$. The resulting equation is highly nonlinear and not very much is known about its solutions for general $J^{(2)}$ and $J^{(4)}$. For the particular choice (9) Eq. (10) simplifies to

$$\mathcal{F}_{\beta,\lambda}(\rho) = \int dr\left[\frac{\rho(r)}{\beta}[\ln\rho(r) - 1] - \lambda R(r,\rho) - \frac{1}{2!}R^2(r,\rho) + \frac{1}{4}R^4(r,\rho)\right], \tag{11}$$

where $R(r,\rho)$ is the average density over a ball of unit volume in $\mathbb{R}^d$ centered at r. It is now easy to show, using the convexity of the first term, that the minimizers are always spatially homogeneous i.e., they correspond to a constant density $\rho \geq 0$. For such a density, the Gibbs free energy per unit volume given in (10) takes the form

$$f(\rho) = \beta^{-1}\rho(\ln\rho - 1) - \lambda\rho - \rho^2/2 + \rho^4/24. \tag{12}$$

The minimizing density will therefore be a solution of the equation

$$f'(\rho) = \beta^{-1}\ln\rho - \lambda - \rho + \rho^3/6 = 0. \tag{13}$$

This equation has a unique solution for all λ when $\beta \leq \beta_c = (3/2)^{3/2}$, while for $\beta > \beta_c$ there exists a $\lambda(\beta)$ such that there are two minimizing solutions $\rho_{\beta,+} > \rho_{\beta,-}$ with $\lambda(\beta)$ and $\rho_{\beta,\pm}$ the same as in the last statement of the theorem. In other words, $f(\rho)$ is convex for $\beta \leq \beta_c$ and has a double well shape of equal height for $\beta > \beta_c$, $\lambda = \lambda(\beta)$. Moreover, there is a $\beta_0 > \beta_c$, given by the smallest value of $\beta > \beta_c$ for which $f''(\rho_{\beta,\pm}) = 2(\beta\rho_{\beta,\pm})^{-1}$, such that the diagonal part of $\frac{\delta^2\mathcal{F}_{\beta,\lambda(\beta)}}{\delta\rho(r)\delta\rho(r')}|_{\rho=\rho_{\beta,\pm}}$ is positive and dominates the nondiagonal ones. When $\beta > \beta_0$ the second variational derivative of $\mathcal{F}_{\beta,\lambda(\beta)}$ is still positive at $\rho = \rho_{\beta,\pm}$ but the diagonal part no longer dominates. The former case is much simpler to analyze and we have so far worked out all the details only for that case.

To prove our theorem we carry out a controlled Pirogov-Sinai cluster expansion about the $\gamma = 0$ mean field state. The first step in this analysis is a "coarse graining," in which we partition space into cubes of size l, with l very large compared to the interparticle spacing but small compared to γ^{-1}. Given a particle configuration q we call $\{\rho_x\}$, x the centers of the cubes, the particle densities in each cube. We then show that the measure over the $\{\rho_x\}$, obtained by integrating out all the other variables is, to within controllable errors, a Gibbs measure with an effective Hamiltonian which is essentially a discrete version of the mean field free energy functional (10) with $\rho(r)$ there replaced by ρ_x, and balls replaced by "lattice balls." The important effect of this procedure is that the new effective inverse temperature is βl^d. For γ small enough and l correspondingly large enough, we are now in the right setup for the Pirogov-Sinai theory. The remainder terms are exponentially decaying multibody interactions.

The "ground states" of our "lattice system" corresponding to the vapor and liquid states are now defined by ensembles of configurations having the ρ_x "close" to the mean field vapor and liquid densities $\rho_{\beta,+}$ and $\rho_{\beta,-}$. The analysis of this system is conceptually close to the one used in the extension of Pirogov-Sinai theory to continuous (unbounded) spin systems developed in [21]. Our analysis is actually simpler than that in [21]. Instead of using a cluster expansion which requires dealing with interactions among many Peierl's type contours separating "bubbles" of one ground state inside another, brought about by the extended range of the potentials, we use a more analytic approach. We show in particular that the restricted effective Hamiltonian giving the Gibbs measures of the lattice system corresponding to the + or − ground state ensembles satisfy the Dobrushin uniqueness condition. We then show that this remains true even after the addition of contours to the ground states. From this follows the exponential decay of correlations in the liquid and vapor phases, for $\beta_c < \beta < \beta_0$, stated in the theorem. We expect to prove that similar results will hold even at lower temperatures, $\beta \geq \beta_0$, but, as already mentioned, the proof is now more difficult: technically, the equation satisfied by the stationary points of the free energy functional (10) is no longer a contraction and the criteria for Dobrushin uniqueness is no longer satisfied by the lattice system.

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