PHASE TRANSITION IN A CONTINUUM CLASSICAL SYSTEM WITH FINITE INTERACTIONS*

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Ruelle's proof of the existence of a phase transition in a classical continuum system composed of two kinds of particles with hard core repulsions between them (the Widom-Rowlinson model) is here extended to the case of soft potentials.

In a very interesting recent paper Ruelle [1] proved for the first time the existence of a phase transition in a classical continuum system with finite range potentials** The system consists of a mixture of two types of particles, to be called, A and B, in two dimensions. (The extension to higher dimensions is staightforward.) The interaction potential between two particles of the same species is zero and between two particles of different species, separated by a distance r is $u(r) = \infty$ for $r < R$; $= 0$ for $r > R$, i.e. there is a hard-core exclusion, of diameter R, between an A and a B particle [3]. In view of the fact that this is the only known continuum system with finite range potentials that can be proved to have a phase transition, it is worthwhile to question whether this singular potential is really essential to the proof.

In this note we extend Ruelle's result and prove the existence of a phase transition in this type of system even when the repulsion between the A and B particles is not infinite. We merely require that,

$$u(r) \geqslant W \text{ for } r < R; = 0 \text{ for } r > R, \quad W > 0 \tag{1}$$

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**Previously such proof was available only for continuum systems with very long range, van de Waals type, potentials, c.f. ref. [2] and for the ideal Bose gas.

Ruelle's proof is based on an extension to this continuum system of the Peierls [4] argument for lattice systems: our proof utilizes Ruelle's method. To apply the Peierls argument the system is confined to a box Λ with some boundary conditions which we shall denote by b_Λ. The correlation functions of the system at reciprocal temperature β, and fugacities z_A, and z_B, are obtained in the usual way from the grand canonical ensemble probabilities. In particular the average densities of A and B particles are given by

$$\rho_\alpha(\beta, z_A, z_B; \Lambda, b_\Lambda) = \qquad \alpha = \mathrm{A}, \mathrm{B},$$
$$= z_\alpha \frac{\partial}{\partial z_\alpha} [\ln Z(\beta, z_A, z_B; \Lambda, b_\Lambda)/V(\Lambda)],$$

where Z is the grand partition function and $V(\Lambda)$ is the volume of Λ.

When $\Lambda \to \infty$ in a siutable way, it is well known that

$$\lim_{\Lambda \to \infty} V(\Lambda)^{-1} \ln Z(\beta, z_A, z_B; \Lambda, b_\Lambda) = \beta\pi(\beta, z_A, z_B)$$

exists and is independent of the boundary conditions for *all* positive z_A, z_B and β [5]. Since the limit pressure $\pi(\beta, z_A, z_B)$ is independent of the boundary conditions and since the interparticle potential is symmetric in A and B, the limit pressure is therefore a symmetric function of z_A and z_B. The thermodynamic limit of the densities exists and is equal to

$$\lim_{\Lambda\to\infty} \rho_\alpha(\beta, z_A, z_B; \Lambda, b_\Lambda) = z_\alpha \frac{\partial}{\partial z_\alpha} \beta\pi(\beta, z_A, z_B) \equiv$$
$$\equiv \rho_\alpha(z_A, z_B),$$

whenever $\partial\pi(\beta, z_A, z_B)/z_\alpha$ exists*. *When* this last equality holds (which it always will when z_A and z_B are sufficiently small [7]) then clearly $\rho_A(\beta, z, z') = \rho_B(\beta, z', z)$ and in particular the densities of A and B particles are equal in the thermodynamic limit when $z_A = z_B = z$, *independent* of the boundary conditions. We shall show, however, that for certain intervals of z and β, $\lim_{\Lambda\to\infty}\rho_\alpha(\beta, z_A, z_B; \Lambda, b_\Lambda)$ with $z_A = z_B = z$ does *depend* on the boundary conditions, which implies in turn that the derivatives of the limit pressure with respect to the fugacities have discontinuities as $z_A \to z_B$ and thus the existence of a first order phase transition is established.

To be specific we shall show that for the boundary conditions b_Λ^+, considered by Lebowitz and Gallavotti and by Ruelle, corresponding to the exclusion of B-particles from within a distance R of the boundary of Λ, $\rho_A(\beta, z, z; \Lambda, b_\Lambda^+) - \rho_B(\beta, z, z; \Lambda, b_\Lambda^+) > \epsilon > 0$ uniformly in Λ for some domain, given by eq. (4), of the (z, β) plane. Clearly, the situation would be reserved, and there would be a higher density of B particles, if the boundary conditions were changed to exclude A particles from the vicinity of the walls. Hence if we write generally $z_A = z\exp(\beta h)$ and $z_B = z\exp(-\beta h)$ the thermodynamic pressure $\pi(\beta, z; h)$ will have a discontinuity in its derivative with respect to h at $h = 0$, for the specified range of β and z.

The Peierls-Ruelle argument. We shall use the geometric definitions and constructions given by Ruelle. The reader should regard Ruelle [1] p. 1040 as being inserted here verbatim except for one change; Ruelle's upper bound for the probability of a contour γ is replaced by

$$\rho(\gamma) \leqslant \exp\{\tfrac{1}{2} z l d^2 [(36\pi + 25)\exp(-\beta W) - 1]\}. \quad (2)$$

To prove (2), let X be any configuration of A and B particles producing a contour $\Gamma(X)$ and let γ be an outer piece of $\Gamma(X)$. Also, let G_γ be the union of all $\frac{1}{2}d\sqrt{2}$ by $\frac{1}{2}d\sqrt{2}$ squares ($d = R/3\sqrt{2}$) which have as their diagonals the segments of γ of length d. Let $G'_\gamma = \{x{:}x \in \text{Interior}(\gamma), d(x; G_\gamma) \leqslant R\}$ where $d(\cdot\,;\cdot)$ is the Euclidean distance.

The problem we face in proving (2) is that when $W = \infty$ (Ruelle's case) one could be sure of the following fact: (*) both G_γ and G'_γ contain no A particles. Otherwise there would be an A-B overlap and the energy would be infinite. In our case (*) is false, but we can conclude (**): of $x \in G''_\gamma \equiv G_\gamma \cup G'_\gamma$ then $d(x; B) \leqslant R$, where B is the set of coordinates of the B particles in X.

Define $C_\gamma = \{X{:}\gamma \text{ is an outer contour of } \Gamma(X)\}$. Given $X \in C_\gamma$ we define the configuration X' in which all A and B coordinates are the same as in X except that all A particles in G''_γ are removed. We write $X' = \Psi_\gamma(X)$ and note that Ψ_γ is a many to one mapping. Now define $D_\gamma = \{X{:}X \in C_\gamma \text{ and } \Psi_\gamma(X) = X\}$ and, for $Y \in D_\gamma$, define $E_\gamma(Y) = \{X{:}X \in C_\gamma \text{ and } \Psi_\gamma(X) = Y\}$. Clearly $\Sigma_{X\in C_\gamma} = \Sigma_{Y\in D_\gamma}\Sigma_{X\in E_\gamma}(Y)$. If $U(X)$ is the total potential energy of a configuration, X, and if $\eta_\gamma(X)$ is the number of A particles of X in G''_γ, then, for $X \in E_\gamma(Y)$, $U(X) \geqslant U(Y) + W\eta_\gamma(X)$ because of (**). Thus,

$$Z(\gamma) \equiv \Sigma_{X\in C_\gamma} \exp[-\beta U(X)] \leqslant \quad (3)$$
$$\leqslant \exp[zV(G''_\gamma)\exp(-\beta W)]\,\Sigma_{X\in D_\gamma}\exp[-\beta U(X)],$$

where $V(G''_\gamma)$ is the volume (area) of G''_γ. The sum over $X \in D_\gamma$ in (3) will be denoted by $Z'(\gamma)$.

For $X \in D_\gamma$ we follow Ruelle and define a class X^* of configurations: (a) All A particles in Interior (γ) are changed to B particles and vice versa; (b) A particles are placed in an arbitrary manner in G_γ. The essential new point to notice is that no new B particle is within a distance R of the new A particles in G_γ because X had no A particles (which are converted to B particles) in G''_γ. Thus $Z'(\gamma)/Z \leqslant \exp[-zV(G_\gamma)]$ by Ruelle's proof and

$$p(\gamma) = Z(\gamma)/Z \leqslant \exp\{z[V(G''_\gamma)\exp(-\beta W) - V(G_\gamma)]\}.$$

A very crude estimate gives $V(G'_\gamma) \leqslant l\,[\pi R^2 + 2\sqrt{2}Rd + \frac{1}{2}d^2]$ where l is the length (number of segments) of γ, while $V(G_\gamma) = \frac{1}{2}ld^2$. Thus, (2) is proved.

To complete the proof of the existence of the phase transition we again refer the reader to Ruelle who shows that for these boundary conditions $\rho_A - \rho_B \geqslant \epsilon > 0$ uniformly when the argument of this exponential in (2) is small enough at the minimum value of l (=12). Thus if z_R is Ruelle's upper bound for the critical z, we obtain a phase transition in the (z, β) domain defined by

*We are using here the fact that $\ln Z$ is a convex function of β, $\ln z_A$, and $\ln z_B$ [6].

$$z[1-(36\pi + 25) \exp(-\beta W)] > z_R . \quad (4)$$

Remarks: (1) Eq. (4) shows that there is always a phase transition for sufficiently large z if $\beta W > \ln(36\pi + 25)$. In other words, there is a temperature above which our method does not yield a proof of a phase transition. It is not implausible, however (as mean field theory indicates), that there is a phase transition for all values of β provided z is sufficiently large. We have been unable to settle this question rigorously.

(2) Ruelle's remark, that his proof can be extended to include small (compared to R) hard cores between all the particles is valid here as well.

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