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Abstract. An ensemble of hard-core particles with infinite-range cosine interaction is solved exactly in one dimension. The system exhibits a disordered (high-temperature) and a periodically ordered (low-temperature) state, a classical second-order (high-density) and a first-order (low-density) phase transition, and four regions in the activity-temperature plane.

1. Introduction

The classical infinite-range XY model, in which each spin interacts with each spin equally strongly via a cosine potential, exhibits a classical second-order phase transition [1, 2]. Each spin can be identified with a point on the unit circle; the ensemble of these points can be identified with a gas in one dimension with periodic boundary condition; the volume can be enlarged to a circle of radius $M \in N$. Here we investigate the case in which each particle has, in addition, a hard core. We solve this model exactly in the grand canonical ensemble and find both a classical second-order phase transition at high density, and a first-order phase transition at low density. The disordered (high-temperature) state is a hard-core fluid, while the ordered state is a one-dimensional crystal.

2. The model

Consider N particles of mass m, with hard-core diameter 1, interacting pairwise via a long-range (V_0/M) cosine potential in a uniform external potential μ and a box of size M. The N-particle Hamiltonian has the form

$$H_N = \frac{1}{2m} \sum_{i=1}^{N} p_i^2 - \frac{V_0}{2M} \sum_{i,j}^{N} \cos[2\pi(q_i - q_j)] + \frac{1}{2} \sum_{i,j}^{N} V_{hc}(|q_i - q_j|) \tag{1}$$

$$\equiv T_N + V_N$$

where

$$V_{hc}(x) = \begin{cases} 0 & \text{if } |x| > 1 \\ \infty & \text{if } |x| < 1 \end{cases}$$

and $q_i \in [0, M]$, p_i is momentum. The corresponding grand canonical partition function at the inverse temperature β is

$$\Xi = \sum_{N=0}^{\infty} \lambda^N \int_0^M dq_1 \ldots dq_N \exp(-\beta V_N) \tag{2}$$

where $\lambda = e^{\beta\mu}\sqrt{2m\pi/\beta}/h$ is the activity. We assume $q_i < q_{i+1}$ in the integrations and the $1/N!$ consequently does not appear.

3. The transformation

We begin with the Hubbard–Stratonovich, alias Kac–Siegert, transformation [2] of (2):

$$\Xi = \sum_{N=0}^{\infty} \lambda^N \int dq_1 \dots dq_N \exp\left(-\frac{\beta}{2}\sum_{i,j}^{N} V_{hc}(|q_i - q_j|)\right)\frac{1}{2\pi}\int_{-\infty}^{\infty} d\hat{x}\, d\hat{y}$$

$$\times \exp\left[-\frac{\hat{x}^2}{2} - \frac{\hat{y}^2}{2} - \sqrt{\frac{\beta V_0}{M}}\left(\hat{y}\sum_{i=1}^{N}\cos 2\pi q_i + \hat{x}\sum_{i=1}^{N}\sin 2\pi q_i\right)\right]. \qquad (3a)$$

Consider the substitution $\hat{x}^2 = \beta M(x^2/V_0)$, $\hat{y}^2 = \beta M(y^2/V_0)$, thus

$$\Xi = \frac{\beta M}{2\pi V_0}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \, \exp[-(\beta M/2V_0)x^2 - (\beta M/2V_0)y^2]\Xi_{hc}(x, y, M, \beta, \lambda)$$

where

$$\Xi_{hc}(x, y, \beta, \lambda)$$

$$= \sum_{N=0}^{\infty} \lambda^N \int dq_1 \dots dq_N$$

$$\times \exp\left(-\frac{\beta}{2}\sum_{i,j}^{N} V_{hc}(|q_i - q_j|) - \beta y \sum_{i=1}^{N}\cos 2\pi q_i - \beta_x \sum_{i=1}^{N}\sin 2\pi q_i\right). \qquad (3b)$$

Let us now identify $\Xi_{hc}(x, y, M, \beta, \lambda)$ as the grand partition function of a hard-core (HC) system, each particle of mass m and diameter 1 in the external non-uniform potential

$$u(x, y, q) = y \cos 2\pi q + x \sin 2\pi q. \qquad (3c)$$

This system has been solved [3] in the thermodynamic limit $M \to \infty$. In the following we neglect all finite-size corrections; the limit $M \to \infty$ is obvious.

4. Local field density relation

The grand partition function Ξ_{hc} of HC has the form [3]

$$\Xi_{hc} = \exp\left(\int_0^M \frac{\rho(z-1)}{1 - \int_{z-1}^{z} \rho(w)\, dw}\, dz\right) \qquad (4)$$

where $\rho(z)$ is the non-uniform density. Because of the periodicity of the potential u, we have

$$\rho(z) = \rho(z+1). \qquad (5a)$$

Thus the integration in (4) can be performed, and yields

$$\Xi_{hc} = \Xi_0^M \qquad (5b)$$

$$\rho_0 := \int_0^1 \rho(z)\, dz \qquad (5c)$$

$$\Xi_0 := \exp\left(\frac{\rho_0}{1 - \rho_0}\right). \qquad (5d)$$

The relation between the density and the external field for HC is given by

$$\beta u(q) + \ln \rho(q) - \ln \lambda = \ln\left(1 - \int_{q-1}^{q} \rho(w)\,dw\right) - \int_{q}^{q+1} \frac{\rho(z)}{1 - \int_{z-1}^{z} \rho(w)\,dw}\,dz. \tag{6a}$$

Using $(5a)$ we have

$$\beta u(q) + \ln \rho(q) - \ln \lambda = \ln(1 - \rho_0) - \frac{\rho_0}{1 - \rho_0}$$

or

$$\rho(q) = \lambda \rho_0 \exp(-\ln \Xi_0 - \ln \ln \Xi_0 - \beta u(q)). \tag{6b}$$

Therefore, the $\rho(q) - u(q)$ relation is local in this special case. Integrating the above equation yields

$$\lambda f = \Xi_0 \ln \Xi_0 \tag{7a}$$

where

$$f = \int_{0}^{1} e^{-\beta u(q)}\,dq.$$

Inserting $(3c)$ shows $f = f(x, y)$, however comparison with $(3a)$ shows that $f = f(\sqrt{x^2 + y^2} = r)$ only, (i.e. the fields x, y are distributed isotropically for any M), in fact integration yields

$$f(r) = I_0(\beta r) \tag{7b}$$

where I_0 is the modified Bessel function. It is convenient to substitute $R = \beta r$, thus

$$f(R) = I_0(R) \tag{7c}$$

and $(3a)$ becomes

$$\Xi = \frac{M}{\beta V_0} \int_{0}^{\infty} dR\, R \exp[-(M/2V_0\beta)R^2]\Xi_{hc}(R, M, \lambda). \tag{7d}$$

Inserting $(5b)$ yields

$$\Xi = \frac{M}{\beta V_0} \int_{0}^{\infty} dR\, R \exp\left[M\left(-\frac{R^2}{2V_0\beta} + \ln \Xi_0(R, \lambda)\right)\right]. \tag{7e}$$

Let us summarise that Ξ is determined implicitly by $(7e)$, $(7a)$ and $(7c)$, where $(7a)$ contains the parameters λ and β.

The integration will be performed by the saddle point method. Therefore it follows that the disordered state exhibits $R = 0$ exactly, and thus this system behaves identically to HC in this case $(R = 0)$. In the next section the highly ordered states will be investigated, and thereby the discussion of the phase transition will be prepared.

5. Highly ordered states

In the limit of large M, the integral in $(7c)$ can be evaluated by the saddle point method. In this section, we consider the possibility of $R \gg 1$. In that case $(7a)$ reduces to

$$\ln \lambda f(R) = \ln \Xi_0(R) \tag{8a}$$

at leading order in $\ln \Xi_0$, which is growing monotonically with R. Therefore

$$\frac{d}{dR} \ln \Xi_0(R) = \frac{1}{f(R)} \frac{d}{dR} f(R) / = \frac{I_1(R)}{I_0(R)}$$

or

$$\frac{d}{dR} \ln \Xi_0(R) \xrightarrow{R \to \infty} 1. \qquad (8b)$$

Thus $R = V_0\beta$, $\ln \Xi_0 \xrightarrow{R \to \infty} \ln \lambda + V_0\beta$,

$$\Xi \xrightarrow[M \to \infty]{R \to \infty} \exp\left(M \frac{V_0\beta}{2} + M \ln \lambda \right)$$

or

$$\beta\Omega = -\ln \Xi = -M \frac{V_0\beta}{2} - M \ln \lambda. \qquad (8c)$$

Without loss of generality, we can choose one direction for the vector (x, y); we choose

$$x = 0 \qquad y = R. \qquad (9a)$$

Thus the potential $(3c)$ is

$$u(r, q) = r \cos(2\pi q). \qquad (9b)$$

With $(6b)$ we find the local density

$$\rho(q) = \lambda\rho_0 \exp[-\ln \Xi_0 - \ln \ln \Xi_0 - \beta V_0 \cos(2\pi q)]. \qquad (9c)$$

Thus the ordered state is periodic, the location of the maxima is determined by the symmetry breaking $(9a)$. The ratio of densities between the minimum and the maximum decays exponentially with $2V_0\beta$. The ordered state is a 'one-dimensional crystal', see [4], stablised by the infinite range of the periodic interaction.

The Ornstein–Zernike correlation function of HC is [3]

$$c_2(q, s) = \frac{1}{1 - \int_{s-1}^{s} \rho(w)\,dw} - \int_{s}^{q+1} \frac{\rho(z)\,dz}{(1 - \int_{z-1}^{z} \rho(w)\,dw)^2}. \qquad (10a)$$

For the special case $s = q + l$, $l \in \mathbb{N}$, we find

$$c_2(q, q+l) = \frac{-1}{1 - \rho_0} - \frac{\rho_0(l-1)}{(1 - \rho_0)^2} \qquad (10b)$$

which depends on the mean density ρ_0 and the distance l only. Especially the dependence on R enters into ρ_0 only; therefore the form of c_2 (equation $(10b)$) is valid in the whole phase diagram of figure 1; the value of ρ_0 is determined by Ξ_0 via $(5d)$.

For the case of the highly ordered state

$$1 \ll \ln \Xi_0 \xrightarrow{R \to \infty} \ln \lambda + V_0\beta = \frac{\rho_0}{1 - \rho_0} \xrightarrow{R \to \infty} \frac{1}{1 - \rho_0}$$

or

$$\rho_0 \xrightarrow{R \to \infty} 1 - (\ln \lambda + V_0\beta)^{-1}. \qquad (10c)$$

Thus the highly ordered state exhibits almost the maximal density, a feature that one expects in crystals.
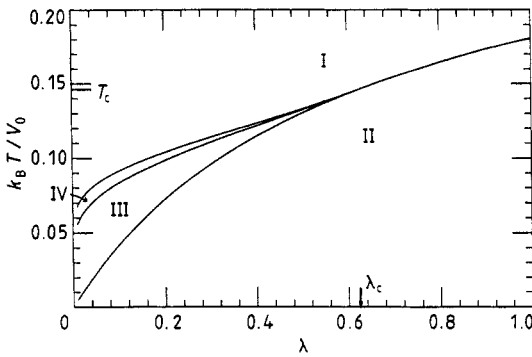
Figure 1. Phase diagram in the $\lambda - T$ plane. I corresponds to disordered states and II the periodically ordered states. III and IV are metastable states. The boundary between them is the coexistence curve. For $\lambda > \lambda_c = 0.626$ or $T > T_c = 0.146 V_0 / k_B$ the phase transition is of second order and classical.
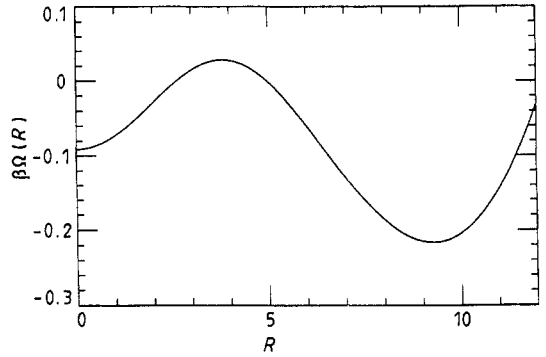

Figure 2. A triple-well shape of the grand potential is shown for $T = 0.08$, $\lambda = 0.1$. The minimum occurs at $R = 0$ and $R = 9.25$.

6. Phase transition

We first take the logarithm of $(7a)$

$$\ln(\lambda I_0(R)) = \ln \Xi_0 + \ln \ln \Xi_0. \tag{11a}$$

Now we expand the left-hand side of $(11a)$ around $R = 0$ up to R^6:

$$\ln[I_0(R)] = \tfrac{1}{4}R^2 - \tfrac{1}{64}R^4 + \tfrac{1}{516}R^6.$$

The same expansion for the right-hand side of $(11a)$ is

$$\ln \Xi_0 = a_0 + a_1 R^2 + a_2 R^2 + a_2 R^4 + a_3 R^6$$

$$\ln(\ln \Xi_0) = \ln a_0 + R^2 \frac{a_1}{a_0} + R^4 \left[\frac{a_2}{a_0} - \frac{1}{2} \left(\frac{a_1}{a_0} \right)^2 \right] + R^6 \left(\frac{a_3}{a_0} - \frac{a_1 a_2}{a_0^2} + \frac{a_1^3}{3 a_0^3} \right). \tag{11b}$$

From comparison of the coefficients it follows that

$$\ln \lambda = a_0 + \ln a_0 \qquad a_1 = \tfrac{1}{4}(1 + 1/a_0)^{-1}$$

$$a_2 = \frac{a_1}{8} \left(\frac{1}{(1 + a_0)^2} - \frac{1}{2} \right) \qquad a_3 = 4 a_1 \left(\frac{1}{516} + \frac{a_1 a_2}{a_0^2} - \frac{a_1^3}{3 a_0^3} \right). \tag{11c}$$

These coefficients can be determined recursively. It is easy to see that $a_0 > 0$, $a_1 > 0$. The sign of a_2 determines the order of the phase transition; namely, it is first order if $a_2 > 0$ and second order if $a_2 < 0$. The critical activity λ_c is determined by setting $a_2 = 0$. Therefore λ_c and the corresponding T_c are given by

$$\lambda_c = (\sqrt{2} - 1) \exp(\sqrt{2} - 1) \approx 0.626 \qquad k_B T_c = V_0(\tfrac{1}{2} - 2^{-3/2}). \tag{11d}$$

The saddle point integration implies the grand potential

$$\beta \Omega = -M \max_R \left[a_0 + R^2 \frac{1}{2 V_0} \left(2 V_0 a_1 - \frac{1}{\beta} \right) + a_2 R^4 + a_3 R^6 + O(R^8) \right]. \tag{11e}$$

The maximum of $\beta \Omega$ is taken at $R = \bar{R}$. $\bar{R}$ can be interpreted as an order parameter.

6.1. Second-order phase transition

For $\lambda \in [\lambda_c, 1]$ there occurs a classical second-order phase transition (figure 1) at $V_0\beta(\lambda) = (2a_1(\lambda))^{-1}$, i.e.

$$k_B T = \tfrac{1}{2} V_0 \rho_0. \tag{12}$$

6.2. Spinodal line

This line separates regions II and III in figure 1. For $\lambda \in [0, \lambda_c]$, the disordered state ($R = 0$) becomes unstable with respect to infinitesimal density fluctuations at the inverse temperature

$$V_0\beta_{sp}(\lambda) = \frac{1}{2a_1(\lambda)}. \tag{13}$$

6.3. Limit $\lambda \to 0$

There are two possibilities, namely $\lambda_0(R) \ll 1$, implying $\Xi_0 \to 1$, therefore

$$\bar{R} = 0 \tag{14a}$$

or $\lambda I_0(R) \gg 1$, implying $\bar{R} = \ln \Xi_0$. This case has been investigated in section 5, thus

$$\bar{R} = \beta V_0. \tag{14b}$$

The boundary marks the first-order phase transition at the inverse coexistence temperature

$$V_0\beta_{coex} = \bar{R} = -\ln \lambda$$

or

$$V_0\beta_{coex} \xrightarrow{\lambda \to 0} \infty. \tag{14c}$$

If in the interaction, the cosine would be multiplied by a factor which decreases with distance, there may be a tendency to form clusters of high and low density in the two-phase region. This tendency does not exist here, because a particle can be shifted by a multiple of the wavelength without change of energy, provided the respective space is available.

6.4. Coexistence curve

Unlike that in region II, where $\beta\Omega$ is a symmetrical double well, the shape of $\beta\Omega$ in regions III and IV is a triple well (figure 2). In region IV, the disordered state corresponds to the global minimum of $\beta\Omega$, while it is only metastable in region III. The boundary is determined by

$$\Omega(R_\pm) = \Omega(0) \tag{15}$$

where $R_\pm$ and 0 are the locations of three local minima of $\beta\Omega$.

6.5. Second part of the spinodal line

There is a third phase boundary for $\lambda < \lambda_c$, which plays a similar role as the usual spinodal line, (6b), which separates a one-phase region (I or II) from a two-phase region (IV or III) in the phase diagram. On the line, the ordered state becomes unstable with respect to infinitesimal perturbations.

7. Discussion

Although our calculation was carried out in a very special and rather artificial case, i.e. the wavelength of the cosine interaction being equal to the HC size, the amazing phase diagram (figure 1) seems qualitatively true in other situations. Fesjian and Percus investigated the same system when the wavelength is equal to the size of the system [5]. Using local density approximations which is supposed to be good there, they discovered the same structure in the phase diagram. The previous calculation has a trivial extension when the HC size is a multiple K of the wavelength. K is equal to 1 in this paper. This change reduces the activity λ to λ/K and all our conclusions are still true. Therefore, if we reasonably assume the phase diagram changes continuously when wavelength changes, figure 1 should be true for any wavelength.

Zhang studied H_N in (1) in a canonical ensemble [6]. The result is somehow different. He discovered a second-order phase transition in the short-wavelength case (K = integer), and a first-order transition in the long-wavelength limit. The former can be understood easily by mapping it into a classical infinite-range XY model, where a second-order phase transition is well known.

Finally, we comment on the possible applications of this calculation. In [4] the qualitative applications of this model to 3D crystallisation are discussed. Høye used a 3D cosine interaction as a perturbation to calculate the melting temperature of argon [7]. With a few further approximations, he obtained a result very close to the experimental data.

Acknowledgment

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