Crystallization of one-dimensional hard rods with a periodic interaction*

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Abstract. A one-dimensional model of hard rods with a long-range cosine interaction is solved exactly in some canonical ensemble cases. It exhibits a crystalline phase at low *temperatures as a result of a spontaneous symmetry breaking of the order parameter which* represents an effective collective mode. When the wavelength of the attractive potential is shorter than and commensurate with the rod length, the rods behave like point particles in a reduced volume; when the wavelength is comparable to the system size, the effective potential is equivalent to a quenched random field.

1. Introduction

The purpose of this paper is to investigate the equilibrium behaviour of an order-disorder transition caused by a long-range potential with non-trivial spatial structure. Without a hard core, this model was first analysed by Percus in 1987 [1] (which continues a line that goes back to Ufford and Wigner (1942) [2] and then used by Dyson (1962) and others (see [3] for more references). With a hard core, the system was proposed to model an effective interfacial dynamics in a long wavelength limit [4]; meanwhile, an exact solution of the model in the case of wavelength = core-length *was found very recently [5] in the grand canonical ensemble. The solution in [5]* appears complicated and it made use of a result of the nonuniform hard rod fluids which was originally derived for decaying potentials. We give here a simpler and straightforward derivation for more generalized short wavelength cases by carrying out an exact calculation in a canonical ensemble. Then, for comparison, we also analyse the long wavelength case approximately. We conclude by making comments about some artifacts of the model and the approximation made in the long wavelength case. We should mention that a hard-rod fluid in a periodic potential has been analysed previously by an approximate density functional method [6] of van der Waals type, where the interplay between hard-rod length and the periodicity of the potential was observed. With a more rigorous density functional method, [4] discussed large fluctuations and phase transitions. These 'inverse' approaches are, in some sense, complementary to our direct method.

2. Model and transformation

Consider N particles of mass m with hard core diameter a, interacting pairwise via a long-range cosine potential on a one-dimensional ring of size L. The total potential energy reads

$$U_N = \frac{1}{2} \sum_{i,j=1}^{N} V_{\text{hc}}(|q_i - q_j|) - \frac{u}{2L} \sum_{i,j=1}^{N} \cos \frac{2\pi}{\lambda}(q_i - q_j) \tag{1}$$

where

$$V_{\text{hc}}(|x|) = \begin{cases} 0 & \text{if } |x|, |L-|x|| > a \\ \infty & \text{otherwise} \end{cases}$$

and $u, \lambda > 0$ are constants (assuming $L = M\lambda$ with M a positive integer).

The canonical partition function at $\beta = 1/k_{\text{B}}T$ may then be written as

$$Z_N(L, \beta) = \frac{\Lambda^{-N}}{N!} \int_0^L dq_1 \ldots \int_0^L dq_N\, e^{-\beta U_N} \tag{2}$$

with $\Lambda \equiv \sqrt{\beta h^2/2\pi m}$.

As pointed out in [1], it is natural to introduce the auxiliary 'mode' variables C and S, and rewrite the long range part in terms of its Gaussian transform (alias Kac [7], Siegert [8] or Hubbard-Stratonovich [10] transformation):

$$\exp\left(\frac{\beta u}{2L} \sum \cos \frac{2\pi}{\lambda}(q_i - q_j) \right)$$

$$= \exp\left[\frac{\beta u}{2L} \left(\sum \cos \frac{2\pi}{\lambda} q_i \right)^2 \right] \exp\left[\frac{\beta u}{2L} \left(\sum \sin \frac{2\pi}{\lambda} q_i \right)^2 \right]$$

$$= \frac{L}{2\pi\beta u} \int_{-\infty}^{\infty} dC \int_{-\infty}^{\infty} dS \exp\left(-\frac{L}{2\beta u}(C^2 + S^2) \right.$$

$$\left. + C \sum \cos \frac{2\pi}{\lambda} q_i + S \sum \sin \frac{2\pi}{\lambda} q_i \right)$$

$$= \frac{L}{2\pi\beta u} \int_0^{\infty} r\, dr \int_0^{2\pi} d\alpha \exp\left[-\frac{L}{2\beta u} r^2 + r \sum \cos\left(\frac{2\pi q_i}{\lambda} - \alpha \right) \right] \tag{3}$$

where we have made a change to polar coordinates (r, α) in the $C - S$ plane. This trick of transforming the soft-part of a pair potential into an effective external field has been used for years by many authors (see [10] for instance).

After this transformation and ordering of the particles, (2) takes a new form

$$Z_N = \Lambda^{-N} \int \ldots \int_{0 \leqslant q_1 \ldots q_N \leqslant L} \exp\left(-\frac{\beta}{2} \sum V_{\text{hc}}(|q_i - q_j|) \right) \frac{L}{2\pi\beta u} \int_0^{\infty} r\, dr \int_0^{2\pi} d\alpha$$

$$\times \exp\left(-\frac{L}{2\beta u} r^2 + r \sum \cos\left(\frac{2\pi q_i}{\lambda} - \alpha \right) \right) \tag{4}$$

or

$$Z_N = \frac{\Lambda^{-N} L}{\beta u} \int_0^{\infty} r\, dr \exp\left(-\frac{L}{2\beta u} r^2 \langle Q_N(r; \alpha) \rangle_\alpha \right) \tag{5}$$

where

$$Q_N(r; \alpha) \equiv \int \dots \int_{0 \le q_1 \dots q_N \le L} \mathrm{d}^N q \, \exp\left(-\frac{\beta}{2} \sum V_{\mathrm{hc}}(|q_i - q_j|) + r \sum \cos\left(\frac{2\pi}{\lambda} q_i - \alpha\right)\right)$$

and $\langle . \rangle_\alpha$ denotes the α-averaging.

Physically, this may be interpreted as N hard rods moving in a cosine external potential with an amplitude distributed as a Maxwellian and a uniformly distributed random phase. We write, for N large, that

$$Q_N(r; \alpha) = \int_{(N-1)a}^{L-a} \mathrm{d}q_N \, \exp\left(r \cos\left(\frac{2\pi}{\lambda} q_N - \alpha\right)\right) \int_{(N-2)a}^{q_N - a} \mathrm{d}q_{N-1}$$

$$\times \exp\left(r \cos\left(\frac{2\pi}{\lambda} q_{N-1} - \alpha\right)\right) \dots \int_a^{q_3 - a} \mathrm{d}q_2$$

$$\times \exp\left(r \cos\left(\frac{2\pi}{\lambda} q_2 - \alpha\right)\right) \int_0^{q_2 - a} \mathrm{d}q_1 \, \exp\left(r \cos\left(\frac{2\pi}{\lambda} q_1 - \alpha\right)\right) \tag{6}$$

or in new variables $x_i \equiv q_i - (i-1)a$

$$Q_N(r; \alpha) = \int_0^{L-Na} \mathrm{d}x_N \, \exp\left(r \cos\left[\frac{2\pi}{\lambda}(x_N + (N-1)a) - \alpha\right]\right) \int_0^{x_N} \mathrm{d}x_{N-1}$$

$$\times \exp\left(r \cos\left[\frac{2\pi}{\lambda}(x_{N-1} + (N-2)a) - \alpha\right]\right) \dots \int_0^{x_3} \mathrm{d}x_2$$

$$\times \exp\left(r \cos\left[\frac{2\pi}{\lambda}(x_2 + a) - \alpha\right] \right) \int_0^{x_2} \mathrm{d}x_1 \, \exp\left(r \cos\left[\frac{2\pi}{\lambda} x_1 - \alpha\right]\right)$$

$$= \int_0^{L-Na} \mathrm{d}x_N \dots \int_0^{x_2} \mathrm{d}x_1 \prod_{j=0}^{N-1} \exp\left(r \cos\left[\frac{2\pi}{\lambda}(x_{j+1} + ja) - \alpha\right]\right). \tag{7}$$

We see clearly that, due to the hard core $a \neq 0$, the effective potential is not only inhomogeneous in the particle position, but also inhomogeneous in the particle indexing, the latter adds a further discrete 'phaseshift' to the original continuous potential in (3). The general solution will of course depend on the relative choice of the three length scales a, λ and L.

3. Short wavelength case

We begin with the study of the short wavelength case (termed 'S-case') which is defined by $a = k\lambda$ for some positive integer k. $k = 1$ was the special case studied in [5] using grand canonical ensemble. Since all the discrete 'phaseshifts' vanish, (7) is actually independent of α and may be reduced to

$$Q_N(r) = \frac{1}{N!}\left((M - Nk) \int_0^\lambda \mathrm{d}x \, \exp\left(r \cos\frac{2\pi}{\lambda} x\right)\right)^N$$

$$= \frac{M^N}{N!}\left(1 - \frac{Nk}{M}\right)^N \lambda^N I_0^N(r) \tag{8}$$

where I_0 is the modified Bessel function and we have changed the integration from the ordered space to the N-dimensional symmetric space. The partition function (5) then becomes

$$Z_N(M, \beta) = \frac{L}{\beta u} \left(\frac{\lambda}{\Lambda}\right)^N \frac{M^N}{N!} \left(1 - \frac{Nk}{M}\right)^N \int_0^\infty r \exp\left(-\frac{L}{2\beta u} r^2\right) I_0^N(r) \, dr. \tag{9}$$

In the thermodynamic limit $M \to \infty$, $N \to \infty$, $Nk/M \to \rho$, the Helmholtz free energy per unit length $f(\rho, \beta)$ is seen to be given by

$$\beta f(\rho, \beta) \equiv -\lim \frac{1}{L} \ln Z_N = \frac{\rho}{k\lambda} \left\{ \ln \frac{\Lambda \rho}{ek\lambda(1-\rho)} + \Phi(\rho\beta) \right\} \tag{10}$$

where

$$\Phi(\rho\beta) = \min_{0 \leqslant r < \infty} \frac{k\lambda}{2u\rho\beta} r^2 - \ln I_0(r). \tag{11}$$

Here r plays the role of an order parameter. Since $d \ln I_0(r)/dr = I_1(r)/I_0(r)$ is monotonic in r and ranges from 0 to 1, it is easy to see from figure 1 that

$$\Phi(\rho\beta) = \begin{cases} 0 & \text{for } \frac{k\lambda}{u\rho\beta} \geqslant \frac{1}{2} \\ \frac{k\lambda}{2u\rho\beta} r_0^2 - \ln I_0(r_0) & \text{for } \frac{k\lambda}{u\rho\beta} < \frac{1}{2} \end{cases} \tag{12}$$
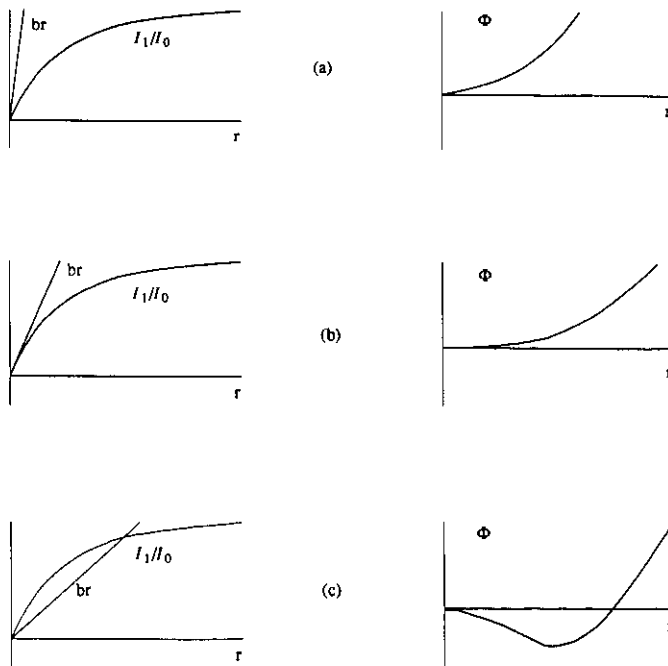

Figure 1. The S-case: br, $I_1(r)/I_0(r)$ against r (left) and $\Phi(r)$ against r (right) as one decreases $b \sim T/\rho$ from (a) to (c). $(b = k\lambda/(u\rho\beta))$.

where $r_0(\rho\beta)$ is the unique positive root of

$$\frac{k\lambda}{u\rho\beta}\, r_0 - \frac{I_1(r_0)}{I_0(r_0)} = 0.$$

$(\rho\beta)_c = u/2k\lambda$ is the (second order) critical point. The phase transition is of the classical type with the critical exponent, for instance, $\beta = \frac{1}{2}$ (i.e. $r_0^2 \sim T_c - T$). It should be noticed that the phase diagram depends on the temperature and the density only through the combination T/ρ.

The key to the exact solution of the S-case is the vanishing of the 'phaseshifts' in (8) as opposed to (7). It implies physically that the collective contributions to the effective potential, due to the hard cores, act destructively and get cancelled exactly as a result. Aside from the excluded volume effect in the first term of (10), the rods behave like free point particles ($a = 0$) moving in an external cosine potential. At high T/ρ, the system is in the disordered state—a uniform fluid; at low T/ρ, it crystallizes dues to the spontaneous symmetry breaking $r_0 \neq 0$. The crystalline structure can be best seen from the equivalent (transformed) system in which there exists an effective external potential $-(r_0/\beta)\cos(2\pi x/\lambda)$. It follows that the local density profile (or, two-point correlation function, to be more precise) will be proportional to the corresponding Boltzmann weight

$$g(x) \propto \exp\left(r_0 \cos \frac{2\pi}{\lambda} x \right).$$

4. Long wavelength case

Although the S-case can be solved exactly in a closed form, it seems a bit artificial physically as $\lambda \lesssim a$. It is more interesting to consider the case of long wavelength (L-case) defined by $\lambda = L$. As a matter of fact, this was in the original model [1] which is generalized in [4] to provide an effective interfacial dynamics. But this should not be confused with the Kac–Uhlenbeck limit [11], the latter has an attractive tail with range strictly much smaller than the size of the system (this point will be further discussed at the end of the paper).

For $\lambda = L$, the thermodynamics is again determined by (5) with $Q_N(r)$ given by (7). Due to the correlation between the phaseshift and the particle indexing, the exact solution becomes extremely involved. We make an approximation by ignoring this correlation and write (7) as

$$Q_{N;\alpha}(r) \simeq \frac{1}{N!} \int_0^{L-Na} dx_N \ldots \int_0^{L-Na} dx_1 \prod_{j=0}^{N-1} \exp\left(r \cos\left[\frac{2\pi}{\lambda}(x_{j+1}+ja) - \alpha \right] \right).$$

Numerical tests indicate that this is an approximation when a is small, which translates into a low density approximation (see the end of the last section for more comments).

Within this approximation, it is convenient to rewrite (7) as

$$Q_{N;\alpha}(r) = \frac{1}{N!} \exp\left\{ \sum_{j=0}^{N-1} \ln \int_0^{L-Na} dx \exp\left(r \cos\left[\frac{2\pi}{\lambda}(x+ja) - \alpha \right] \right) \right\}. \tag{13}$$

For L, N large ($N/L \sim \rho$), this becomes

$$Q_N(r;\alpha) = \frac{1}{N!} \exp\left\{ \frac{L}{a} \int_0^{2\pi\rho} \frac{d\phi}{2\pi} \ln\left[L \int_0^{2\pi(1-\rho)} \frac{d\theta}{2\pi} \exp a(r\cos(\theta+\phi-\alpha)) \right] \right\}.$$

In the thermodynamic limit $L \to \infty$, $N \to \infty (Na/L \to \rho)$, the Helmholtz free energy density can be read off as

$$\beta f(\rho, \beta) = \frac{\rho}{a} \left\{ \ln \frac{\Lambda \rho}{ea(1-\rho)} + \Phi(\rho, \beta) \right\} \tag{15}$$

where

$$\Phi(\rho, \beta) \equiv \min_{0 \leqslant r < \infty} \frac{1}{2u\rho\beta} r^2 - \Psi(r; \rho) \tag{16}$$

with

$$\Psi(r; \rho) = \max_\alpha \bar{\Psi}(r; \rho; \alpha) = \bar{\Psi}(r; \rho; 0) \tag{17}$$

and

$$\bar{\Psi}(r; \rho; \alpha) \equiv \int_0^{2\pi} \frac{d\phi}{2\pi} \ln \int_0^{2\pi} \frac{d\theta}{2\pi} \exp\{r \cos[(1-\rho)\theta + \rho\phi - \alpha]\} \tag{18}$$

which has a maximum at $\alpha = 0$ and a minimum at $\alpha = \pi$.

It is obvious that Ψ plays the same role in the L-case as $\ln I_0$ does in the S-case. Despite the remarkable simplicity of its form, it cannot be integrated into a closed form. Nevertheless, it is a rather smooth function of r, and the physical message it carries is quite transparent.

First of all, it is easy to check that if $\rho \ll 1$, $\Psi \sim \ln I_0(r) + O(\rho)$. It means physically that, at low density, it is always possible for particles to arrange themselves into an optimal position as in the S-case. Namely, since $\lambda = L$, all the particles at low temperature tend to squeeze together within the half wavelength interval so that they can interact in phase to maximize the attention.

To analyse Ψ into more detail, it is very instructive to consider Ψ as a free energy of a quenched random system itself. The random external potential $-(r/\beta) \cos[(1 - \rho)\theta + \rho\phi]$ depends upon a uniformly distributed random phase variable ϕ. With the obvious notation '$\langle \rangle$' and '$-$' as the 'thermal' and 'quenched' averages, we can write the derivatives as

$$\Psi'(r) = \overline{\langle \cos[(1-\rho)\theta + \rho\phi]\rangle} \tag{19}$$

and

$$\Psi''(r) = \overline{\langle \cos^2[(1-\rho)\theta + \rho\phi]\rangle - \langle \cos[(1-\rho)\theta + \rho\phi]\rangle^2} \geqslant 0. \tag{20}$$

We suppress the ρ-dependence of Ψ.

The last equation shows the convexity of the function $\Psi(r)$. $\Psi''(r) = 0$ occurs only if (a) r, $\rho = 0$, as in the S-case; (b) $r = \infty$, no thermal fluctuations (also true for the S-case); or (c) $\rho = 1$, $\Psi \equiv 0$. At the origin, we have

$$\Psi(0) = 0 \qquad \text{and} \qquad \Psi'(0) = \frac{\sin^2(\pi\rho)}{\pi^2\rho(1-\rho)} \leqslant 0. \tag{21}$$

Therefore, $\Psi(r)$ starts out from the origin with a negative slope ($\rho \neq 0$ and 1, noticing also that min $\Psi'(0)$ occurs at $\rho = \frac{1}{2}$). This is because the attractive strength is not strong enough to overcome the entropy effect (represented by the random initial positions or the quenched randomizations), the latter effect makes the particles interact off-phase which results in a net effective repulsion. According to (16), locally $r = 0$ is always a

minimum of $\Phi(r)$. The question now becomes whether there exists another lower minimum (where Φ is negative).

Asymptotically, we found $\Psi(r) \sim c(\rho)r$ as $r \to \infty$ with $c(\rho) \geq 0$ a decreasing function of $\rho(c(0_+) = 1, c(1_-) = 0)$. Since the two terms in (16) are both convex, at a fixed $\rho \neq 0$ and 1, there are five possibilities as shown below.

In figure 2, (a), (b) and (c) correspond to high temperature disordered phases where the core repulsion and the quenched randomness dominate (the 'roton' phenomenon as indicated by (c) can only be observed in a finite system); (d) corresponds to a low temperature crystalline phase where the net in-phase attractions among the particles dominate; (d) corresponds to a 'phase coexistence', of course only in the sense of the ensemble average. $\rho = 1$ is the singular point where $\Psi(r) \equiv 0$, even though
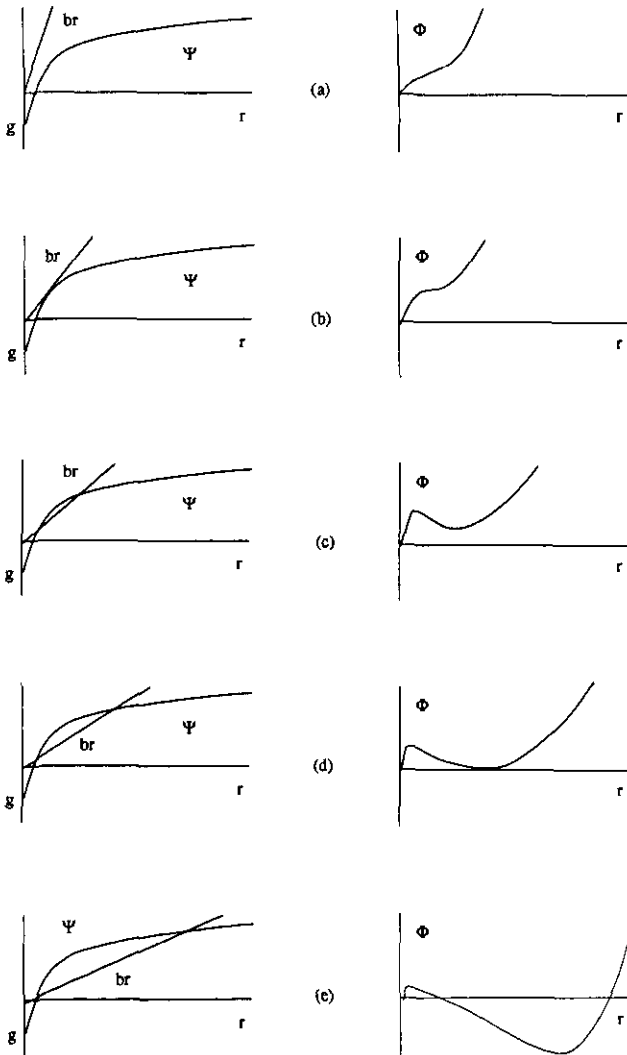

Figure 2. The L-case: br, $\Psi(r)$ against r (left) and $\Phi(r)$ against r (right) as one decreases $b \sim T/\rho$ at a fixed $\rho \neq 0, 1$ from (a) to (e). $(b = k\lambda/(u\rho\beta))$.

it corresponds to disorder for the quenched random system, it is actually an extremely ordered state for the original system because it coincides with the close packing.

5. Final comments

To summarize, we see in both cases, the phase diagram consists of disordered and ordered regions as shown in figure 3.

The major differences are: (1) In the S-case, the phase diagram depends only on T/ρ; in the L-case, it depends on both ρ and T/ρ. (2) The phase dividing point c in the S-case is a second order transition point; the phase dividing line c in the L-case is a first order coexistence curve. The order parameter r_0 (or, better, tanh r_0) against T for a fixed ρ is depicted in figure 4 for both cases.

The gap g in figure 2 and figure 4 are proportional to ρ for small ρ, therefore L-case is more general in the sense that it will reduce to S-case as $\rho \to 0$. It can also be seen from figure 3 that the phase diagram of the S-case is the sub-diagram of the L-case.

In comparison with the grand canonical approach for the special S-case (i.e. $\lambda = a$), we see the canonical one is far more straightforward and the analysis is simpler and more transparent. We notice that the spontaneous symmetry broken should be referred to the order parameter r_0, the symmetry of the angle α in (3) which corresponding to the translational invariance cannot be broken without an external potential (i.e. $\rho =$ constant).

We should emphasize that the double minima ('coexistence') is an artifact of the long-range model. It is well known that this occurs when the range of the interaction depends on the size of the system. It is, in some sense, analogous to the van der Waals loop in many mean field theories. In more realistic models where the range of interaction
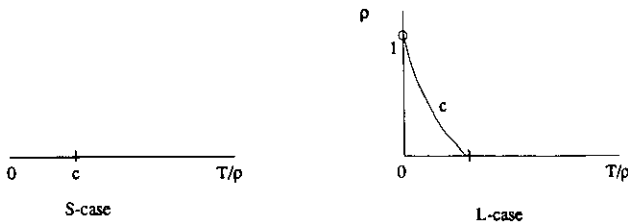

Figure 3. The phase diagrams. For the S-case, the crystalline phase is to the left of the second order transition point c; for the L-case, it is below the first order 'coexistence' curve c.
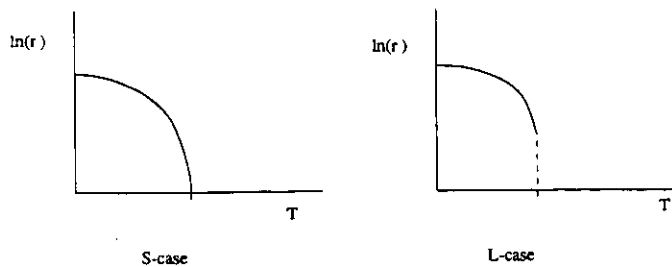

Figure 4. The order parameter r_0 (actually tanh r_0 is depicted) against T at a fixed $\rho \neq 0, 1$.

may be controlled separately, one should let the range of interaction go to infinity after the thermodynamic limit has been taken [12]. This is the case of Kac–Uhlenbeck limit and it is very different from our current situation ($\lambda = L \to \infty$). Even if λ remains finite, the periodicity of the cosine potential still guarantees the range of interaction to be L.

We should emphasize again the approximation made in the solution of the long wavelength case and the phase diagram is based on this approximation. It is interesting to mention that the exact solution in the general case is equivalent to a 1D homogeneous sos model. The relation may be briefly indicated as follows: let us define as integral $\bar{Q}_N$ by

$$\bar{Q}_N(L-Na) = \int_0^{L-Na} dx_{N-1} \int_0^{x_N} dx_{N-2} \ldots \int_0^{x_2} dx_1 \exp\left(r \sum_{j=0}^{N-1} \cos[k(x_{j+1}+ja)-\alpha]\right)$$

which is the essential part of Q in (7). $\bar{Q}$ can be regarded as a partition function for N hard-core particles moving in an inhomogeneous external field. Taking the Laplace transform with respect to $L-Na$ (which gives the partition function of the isoparic ensemble), using the (modified) Bessel function expansion for the integrand, we have

$$\hat{Q}(p) = \sum_{\{m\}} \prod_j I_{m_j}(r) \exp\left(-i\alpha \sum_j m_j + ika \sum_j jm_j\right) \frac{1}{p} \frac{1}{p-ikm_N} \ldots \frac{1}{p-ik(m_N+\ldots+m_1)}$$

where m_j run over all integers Z. Or, using n_j defined by $m_j = n_{j+1} - n_j$ with $n_{N+1} \equiv 0$

$$\hat{Q}(p) = \sum_{\{n\}} \frac{1}{p} T(n_{N+1}, n_N) \ldots T(n_2, n_1)$$

where the nearest neighbour transfer matrix T is given by

$$T(n, n') = I_{n-n'}(r) \frac{e^{-i\alpha(n-n')+ikan'}}{p-ikn'}$$

again n_j run over all integers (one may also construct Hermitian transfer matrices by changing the signs of all other n_j). This partition describes manifestly an interface model with integer interfacial heights. The thermodynamics is determined by the largest real eigenvalue and phase transitions may be related to the degeneracies. Although the sos transfer matrix is homogeneous, its structure is still very complicated. We hope to report its investigation later in a separate paper.

Acknowledgment

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