

## Duality relations for the Gaussian core model

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On account of self-similarity of the Gaussian function under Fourier transformation, the lattice energy of the Gaussian core model at absolute-zero temperature exhibits duality relations. In the cases of one and two dimensions the duality involves high- and low-density pairs for the single stable lattice structure. In three dimensions lattice energies for the two stable crystal forms (fcc at low density, bcc at high density) are paired. The results demonstrate that lattice energy loses its dependence on structure in the high-density limit, and they suggest (but do not prove) an asymptotic scaling for melting and freezing temperatures in the same limit.

### I. INTRODUCTION

The "Gaussian core model" consists of a set of point particles which interact in pairs by repelling Gaussian potentials. The total potential energy  $\Phi$  for a collection of  $N$  such particles thus has the form

$$\Phi(\vec{r}_1, \dots, \vec{r}_N) = \sum_{i < j=1}^N \exp(-r_{ij}^2), \quad (1.1)$$

upon selecting natural units for energy and length.

Within the regime of classical statistical mechanics this model may be a useful tool for the study of fluid-solid phase transitions. Both analytical studies<sup>1,2</sup> and computer simulation<sup>3</sup> have been employed to establish the behavior of the Gaussian core model. The present paper broadens the scope of the subject by deriving a set of duality relations for the model, one for each value of the space dimension  $D = 1, 2,$  and  $3$ .

The duality relations are basically elementary, and stem in an obvious way from self-similarity of the Gaussian function under Fourier transformation. However, some conclusions that can be drawn from them are not quite obvious.

It is the values of  $\Phi$  in the zero-temperature limit that the duality relations involve. In particular they link high density to low density.

The present situation is analogous to that of the two-dimensional Ising model for which Kramers and Wannier also derived a duality relation.<sup>4</sup> But in that much earlier work the density is fixed (half-filled lattice) and a pair of temperatures, one high and one low, were shown to be related. To the extent that the Kramers-Wannier work may have stimulated Onsager's exact solution to the Ising model,<sup>5</sup> it may be important to display the present results in the hope that the future will reveal an analogous advance for the Gaussian core model.

### II. ONE DIMENSION

By focusing attention on the potential energy per particle, we can eliminate boundary effects by passing to the infinite system limit (with density  $\bar{\rho}$  held fixed). In this limit the one-dimensional system will achieve its lowest potential energy when the repelling particles are equally spaced along the line. Although no phase transition is involved in cooling from high temperature, this one-dimensional "crystal" nevertheless is the configuration adopted by the system at absolute zero of temperature.

Let

$$a = 1/\bar{\rho}, \quad (2.1)$$

be the nearest-neighbor spacing in the regular one-dimensional array. Then defining

$$I_1(a) = 1 + \lim_{N \rightarrow \infty} (2\Phi/N), \quad (2.2)$$

we obviously have

$$I_1(a) = \sum_{j=-\infty}^{+\infty} \exp(-j^2 a^2). \quad (2.3)$$

It will be convenient to rewrite this sum in the trivially equivalent way

$$I_1(a) = \int_{-\infty}^{+\infty} ds \rho(s) \exp(-s^2), \quad (2.4)$$

where  $\rho(s)$  is the discrete density function for the linear array

$$\rho(s) = \sum_{j=-\infty}^{+\infty} \delta(s - ja). \quad (2.5)$$

Owing to the fact that  $\rho(s)$  is periodic over length  $a$  it is natural to represent this function as a Fourier series

$$\rho(s) = \sum_k f(k) \exp(iks), \quad (2.6)$$

with

$$k = 2\pi n/a \quad (n=0, \pm 1, \pm 2, \dots) . \quad (2.7)$$

In order to assure proper convergence of the expressions encountered it is prudent to replace each  $\delta$  function in Eq. (2.5) temporarily by a narrow normalized Gaussian

$$\delta(s - s_0) \cong (\alpha/\pi)^{1/2} \exp[-\alpha(s - s_0)^2] , \quad (2.8)$$

with the understanding that  $\alpha \rightarrow \infty$  at an appropriate stage in the calculation. With this provision one has

$$f(k) = \exp(-k^2/4\alpha)/a . \quad (2.9)$$

Substitute Eq. (2.6) into Eq. (2.4) to obtain

$$\begin{aligned} I_1(a) &= \sum_k f(k) \int_{-\infty}^{+\infty} ds \exp(-s^2 + iks) \\ &= \pi^{1/2} \sum_k f(k) \exp(-k^2/4) . \end{aligned} \quad (2.10)$$

Next utilize expression (2.9) in the  $\alpha \rightarrow \infty$  limit

$$\begin{aligned} I_1(a) &= \frac{\pi^{1/2}}{a} \lim_{\alpha \rightarrow \infty} \sum_k \exp \frac{-k^2(\alpha+1)}{4\alpha} \\ &= \frac{\pi^{1/2}}{a} \sum_k \exp \frac{-k^2}{4} . \end{aligned} \quad (2.11)$$

The remaining sum over  $k$  has the same form as that appearing in Eq. (2.3), the definition of  $I_1$ . However,  $a$  in that previous equation has now been replaced by  $\pi/a$ . We conclude

$$I_1(a) = (\pi^{1/2}/a) I_1(\pi/a) . \quad (2.12)$$

Equation (2.12) is the one-dimensional duality relation. It links the lattice energies at two different densities (provided  $a \neq \pi^{1/2}$ ). At high density (small  $a$ ) the sum in Eq. (2.3) converges slowly, but Eq. (2.12) immediately offers an alternative evaluation in terms of the rapidly converging sum for low density. In this way we use Eq. (2.12) to derive the following high-density asymptotic expression for  $I_1$ :

$$I_1(a) \sim (\pi^{1/2}/a) [1 + 2 \exp(-\pi^2/a^2) + \dots] . \quad (2.13)$$

The leading term here is the estimate that would be made on the basis of uniform relative distribution of particles, i.e.,  $\rho(s)$  replaced by  $\bar{\rho}$ . We see that correction terms to this estimate go to zero exponentially as  $a \rightarrow 0$ .

It is elementary to show that the most general family of functions satisfying Eq. (2.12) for real positive  $a$  is given by the formula

$$I_1(a) = (\pi^{1/2}/a)^{1/2} \exp\{F_e[\ln(a/\pi^{1/2})]\} , \quad (2.14)$$

where  $F_e$  is an arbitrary even function.

### III. TWO DIMENSIONS

When its particles are confined to the plane, the Gaussian core model achieves its minimum potential energy in the regular triangular lattice. This structure surrounds each particle with six others at a common nearest neighbor distance  $a$ . The relationship of this distance to the density  $\bar{\rho}$  is given by

$$\bar{\rho} = 2/(3^{1/2}a^2) . \quad (3.1)$$

As was the case for  $D = 1$ , we shall be concerned with twice the limiting interaction energy per particle plus unity, now to be denoted by  $I_2$ ,

$$\begin{aligned} I_2(a) &= 1 + \lim_{N \rightarrow \infty} (2\Phi/N) \\ &= \int d\bar{s} \bar{\rho}(\bar{s}) \exp(-s^2) . \end{aligned} \quad (3.2)$$

$\rho(\bar{s})$  is the discrete density function for the two-dimensional crystal under consideration

$$\begin{aligned} \rho(\bar{s}) &= \lim_{\alpha \rightarrow \infty} \bar{\rho}(\bar{s}, \alpha) , \\ \bar{\rho}(\bar{s}, \alpha) &= (\alpha/\pi) \sum_j \exp[-\alpha(\bar{s} - \bar{s}_j)^2] . \end{aligned} \quad (3.3)$$

Here  $j$  indexes particles in the crystal, and the  $\bar{s}_j$  denote their respective positions.

The doubly periodic function  $\rho(\bar{s}, \alpha)$  may be represented as a Fourier sum

$$\rho(\bar{s}, \alpha) = \sum_{\bar{k}} f(\bar{k}) \exp(i\bar{k} \cdot \bar{s}) , \quad (3.4)$$

where the  $\bar{k}$ 's are  $2\pi$  times the vectors from the reciprocal lattice. By employing the standard construction for the reciprocal lattice,<sup>6</sup> one finds that the  $\bar{k}$ 's also form a regular triangular lattice (although rotated by  $\frac{1}{6}\pi$  radians). The nearest-neighbor distance in this  $\bar{k}$  lattice is  $4\pi/(3^{1/2}a)$ .

Upon multiplying both sides of Eq. (3.4) by  $\exp(-i\bar{k} \cdot \bar{s})$  and integrating over a unit cell, one finds

$$f(\bar{k}) = \bar{\rho} \exp(-k^2/4\alpha) . \quad (3.5)$$

Therefore one has, from Eqs. (3.4) and (3.5),

$$\begin{aligned} I_2(a) &= \lim_{\alpha \rightarrow \infty} \int d\bar{s} \bar{\rho}(\bar{s}, \alpha) \exp(-s^2) \\ &= \pi \bar{\rho} \sum_{\bar{k}} \exp(-k^2/4) . \end{aligned} \quad (3.6)$$

The last summation is just the type which defines  $I_2$  itself, but with lattice spacing  $2\pi/(3^{1/2}a)$ . This leads to the two-dimensional duality relation

$$I_2(a) = \frac{2\pi}{3^{1/2}a^2} I_2\left(\frac{2\pi}{3^{1/2}a}\right) . \quad (3.7)$$

Just as was the case with  $I_1$ , this two-dimensional duality relation links lattice energies at high and at low

densities. Evidently it is necessary only to compute  $I_2$  directly in the density range

$$0 < \bar{\rho} \leq 1/\pi, \quad (3.8)$$

since Eq. (3.7) provides values for the remaining densities. As  $a \rightarrow 0$  ( $\bar{\rho} \rightarrow \infty$ ), Eq. (3.7) leads to the following asymptotic behavior:

$$I_2(a) \sim \frac{2\pi}{3^{1/2}a^2} \left[ 1 + 6 \exp\left(\frac{-4\pi^2}{a^2}\right) + \dots \right], \quad (3.9)$$

where once again the leading term represents the uniform density estimate of the interaction

$$\int \bar{\rho} \exp(-s^2) d\bar{s} = 2\pi/(3^{1/2}a^2). \quad (3.10)$$

The general family of functions which satisfies duality relation (3.7) for real positive  $a$  is

$$I_2(a) = \left( \frac{2\pi}{3^{1/2}a^2} \right)^{1/2} \exp\left( F_e \left( \ln \left[ \left( \frac{3^{1/2}a^2}{2\pi} \right)^{1/2} \right] \right) \right),$$

where as before  $F_e$  is an arbitrary even function.

#### IV. THREE DIMENSIONS

Numerical evaluation of lattice sums for  $D=3$  shows that at zero temperature the Gaussian core model exhibits two different crystal forms.<sup>1</sup> When the density  $\bar{\rho}$  is low the stable structure is face-centered cubic, while at high density the body-centered structure prevails. The transformation between these forms is thermodynamically first order, with discontinuities in volume and in energy. In the zero-temperature limit, the density region of phase coexistence was previously found to be<sup>1</sup>

$$0.17941 \leq \bar{\rho} \leq 0.17977, \quad (4.1)$$

by use of the Maxwell double-tangent construction on plots of  $\Phi/N$  vs  $1/\bar{\rho}$ . The density at which homogeneous face-centered-cubic and body-centered-cubic crystals have the same lattice energy was found to occur near the middle of the coexistence range.

The relation between  $\bar{\rho}$  and the nearest-neighbor distance  $a$  is not the same for the two lattices. Specifically one has

$$\begin{aligned} (\text{fcc}) \quad \bar{\rho} &= 2^{1/2}/a^3, \\ (\text{bcc}) \quad \bar{\rho} &= 3^{3/2}/(4a^3). \end{aligned} \quad (4.2)$$

In the one- and two-dimensional cases, the direct lattice and the reciprocal lattice were the same species (though with different spacings). However, this is not so in three dimensions. The face-centered-cubic direct lattice has a reciprocal lattice that is body-centered cubic, and *vice versa*.<sup>6</sup> As a consequence the duality relation for  $D=3$  will link values of lattice energy for one crystal structure to those of the other,

rather than values for the same crystal structure at different densities.

We shall start with the body-centered-cubic direct lattice for which

$$I_{\text{bcc}}(a) = \lim_{\alpha \rightarrow \infty} \int d\bar{s} \rho_{\text{bcc}}(\bar{s}, \alpha) \exp(-s^2), \quad (4.3)$$

$$\rho_{\text{bcc}}(\bar{s}, \alpha) = \left( \frac{\alpha}{\pi} \right)^{3/2} \sum_j \exp[-\alpha(\bar{s} - \bar{s}_j)^2].$$

The  $\bar{s}_j$  are the particle positions in this lattice. The Fourier series for the periodic function  $\rho_{\text{bcc}}(\bar{s}, \alpha)$  is analogous to the previous case in Eq. (3.4)

$$\rho_{\text{bcc}}(\bar{s}, \alpha) = \sum_{\bar{k}} f_{\text{bcc}}(\bar{k}) \exp(i\bar{k} \cdot \bar{s}), \quad (4.4)$$

$$f_{\text{bcc}}(\bar{k}) = \bar{\rho} \exp(-k^2/4).$$

where the set of  $\bar{k}$ 's forms a face-centered-cubic lattice with nearest-neighbor spacing  $6^{1/2}\pi/a$ .

By substituting Eqs. (4.4) into the first of Eq. (4.3) we find

$$I_{\text{bcc}}(a) = \pi^{3/2} \bar{\rho} \sum_{\bar{k}} \exp(-k^2/4). \quad (4.5)$$

Upon identifying the sum in terms of  $I_{\text{fcc}}$  we finally have

$$I_{\text{bcc}}(a) = [(3\pi)^{3/2}/4a^3] I_{\text{fcc}}(3^{1/2}\pi/2^{1/2}a). \quad (4.6)$$

This is the only duality relation that can be obtained for  $D=3$ ; by starting alternatively with the face-centered-cubic direct lattice and following the analogous procedure the same result (4.6) emerges.

Equation (4.6) can be used to locate precisely the density at which the two crystal structures have identical lattice energies. Note that the factor in square brackets in Eq. (4.6) reduces to unity when the bcc lattice distance has the value

$$a_{\text{bcc}} = 3^{1/2}\pi^{1/2}/2^{2/3}. \quad (4.7)$$

The fcc lattice distance serving as the argument of  $I_{\text{fcc}}$  in Eq. (4.6), implied by Eq. (4.7), is

$$a_{\text{fcc}} = 3^{1/2}\pi/(2^{1/2}a_{\text{bcc}}) = 2^{1/6}\pi^{1/2}. \quad (4.8)$$

Reference to expressions (4.2) establishes that both of these lattice spacings correspond to the same density

$$\bar{\rho} = \pi^{-3/2} = 0.1795871221\dots, \quad (4.9)$$

which thus must be the density of equal lattice energies, and which indeed falls in the middle of the previously identified coexistence range (4.1).

#### V. DISCUSSION

The three-dimensional duality relation (4.6) can be used to establish separate high-density asymptotes for

$I_{\text{bcc}}$  and  $I_{\text{fcc}}$ . The results are the following ( $a \rightarrow 0, \bar{\rho} \rightarrow \infty$ ):

$$I_{\text{bcc}}(a) \sim \frac{(3\pi)^{3/2}}{4a^3} \left[ 1 + 12 \exp\left(\frac{-3\pi^2}{2a^2}\right) + \dots \right] \\ \equiv \pi^{3/2} \bar{\rho} [1 + 12 \exp(-2^{1/3} \pi^2 \bar{\rho}^{2/3}) + \dots] \quad (5.1)$$

$$I_{\text{fcc}}(a) \sim \left( \frac{2^{1/2} \pi^{3/2}}{a^3} \right) \left[ 1 + 8 \exp\left(\frac{-3\pi^2}{2a^2}\right) + \dots \right] \\ \equiv \pi^{3/2} \bar{\rho} \left[ 1 + 8 \exp\left(\frac{-3\pi^2 \bar{\rho}^{2/3}}{2^{4/3}}\right) + \dots \right] \quad (5.2)$$

As was the case with the analogous results (2.13) and (3.9) for  $D=1$  and  $D=2$ , only exponentially vanishing corrections appear to the uniform density estimate for lattice energy

$$\int \bar{\rho} \exp(-s^2) d\vec{s} = \pi^{3/2} \bar{\rho} \quad (5.3)$$

These results strongly support the contention<sup>1</sup> that in the high-density limit  $\Phi$  becomes insensitive to details of particle arrangement.

This last concept can be supported by considering the simple-cubic arrangement of particles in the Gaussian core model. Although this is not a stable crystal structure it does have the advantage of being self-dual, i.e., the dual lattice is also simple cubic. By

using the same method as before one easily establishes that

$$I_{\text{sc}}(a) = (\pi^{3/2}/a^3) I_{\text{sc}}(\pi/a) \quad (5.4)$$

From this the high-density limiting behavior readily follows:

$$I_{\text{sc}}(a) \sim \left( \frac{\pi^{3/2}}{a^3} \right) \left[ 1 + 6 \exp\left(\frac{-\pi^2}{a^2}\right) + \dots \right] \\ \equiv \pi^{3/2} \bar{\rho} [1 + 6 \exp(-\pi^2 \bar{\rho}^{2/3}) + \dots] \quad (5.5)$$

exhibiting once more an exponential approach to the random distribution form.

This common behavior is suggestive of how the melting and freezing temperatures for the Gaussian core model may behave in the high-density limit. If indeed all relevant configurations for both crystal and fluid phases differed in energy only by an amount proportional to  $\exp(-K \bar{\rho}^{2/3})$  in the high-density regime, where  $K$  is an appropriate constant, then we would expect this to control the behavior of the melting and freezing temperatures as  $\bar{\rho} \rightarrow \infty$ ,

$$T_m, T_f \propto \exp(-K \bar{\rho}^{2/3}) \quad (5.6)$$

The corresponding result in two dimensions would be

$$T_m, T_f \propto \exp(-K' \bar{\rho}) \quad (5.7)$$

Evaluation of this simplistic hypothesis must await more powerful analysis.

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<sup>3</sup>F. H. Stillinger and T. A. Weber, *J. Chem. Phys.* **68**, 3837 (1978).

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<sup>5</sup>L. Onsager, *Phys. Rev.* **65**, 117 (1944).

<sup>6</sup>L. Brillouin, *Wave Propagation in Periodic Structures* (Dover, New York, 1953).