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Chi-Lun Lee[1] **and George Stell**[2]

[1] Department of Physics, State University of New York at Stony Brook, Stony Brook, NY 11794-3800, USA
[2] Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794-3400, USA

Abstract
We show the way in which the self-consistent Ornstein–Zernike approach to obtaining structure factors and thermodynamics for Hamiltonian models can best be applied to two-dimensional systems such as monolayer films. We use the nearest-neighbour lattice gas on a square lattice as an illustrative example.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The self-consistent Ornstein–Zernike approach (SCOZA) was introduced by Høye and Stell [1] as an approximation method specifically tailored to obtain structure factors and thermodynamics for Hamiltonian models in three or more spatial dimensions. It was subsequently found by Høye and Borge [2] that the SCOZA yields extremely accurate results for the two-dimensional lattice gas as well, when appropriately used, thus opening the way toward the use of SCOZA in treating thin-film problems. In this article we summarize the two-dimensional SCOZA results. We point out that these results for systems considered in the thermodynamic limit are strikingly similar to the results that would be found in an exact analysis of two-dimensional systems that are finite [3] or semi-infinite [4]. We note why this is to be expected, and using the behaviour of the specific heat as a criterion, we find the size of the finite and semi-infinite systems that yield the best match to the SCOZA results for the infinite square lattice.

2. Background

The SCOZA is based on an ansatz used by Ornstein and Zernike (OZ) [5], which is that the direct correlation function $c(r)$ introduced by those authors has the range of the pair potential. In the SCOZA, this ansatz is used along with a core condition that guarantees that the two-body distribution function $g(r)$ must be zero for values of r for which the pair potential is infinite.

In a lattice gas, the core condition implies the exclusion of multiple occupancy of a single lattice site or cell; for the equivalent Ising model in which the spin variable at site i is $+1$ or -1, the corresponding condition is that $\langle s_i s_j \rangle_{i=j} = 1$, which simply reflects the fact that the spin must be pointing either up or down with probability one.

An analysis of the OZ formalism made by one of the authors some time ago [6] showed that the core condition plus the assumption that $c(r)$ is proportional to the pair potential implies that for short-ranged potentials, a two-dimensional system cannot have a critical point at non-zero temperature. (In three or more dimensions there is no such restriction on criticality.) One knows, however, that in two dimensions, systems such as the nearest-neighbour lattice gas do in fact have a critical point at non-zero T_c. Hence the SCOZA did not initially appear to be a promising method for treating arbitrarily large two-dimensional systems. Its apparent unsuitability is also consistent with the observation [6, 7] that the assumption that $c(r)$ has the range of the potential implies that for short-ranged potentials, the critical exponent $\eta = 0$, with the result that at a critical point at $T_c \neq 0$, where one expects $g(r) - 1 \approx \text{const}/r^{d-2+\eta}$, the SCOZA would yield $g(r) - 1 \approx \text{const}/r^{d-2}$. In three dimensions, in which $\eta \approx 0.03$, and $d - 2 + \eta \approx 1.03$, this leads to negligible error. But for $d = 2$, for which $\eta = 1/4$, it represents the difference between $g(r) - 1 \approx \text{const}/r^{1/4}$ and a $g(r) - 1$ that does not appropriately decay with increasing r.

However, as we shall see below, in two dimensions, the SCOZA results for a square lattice of infinite extent are strikingly similar in some respects to exact results for either an $N \times N$ lattice or an $N \times \infty$ lattice, with $N \approx 22$.

It is not hard to understand why the assumption of a $c(r)$ for an infinite square lattice yields results that mimic exact results for a finite system. For a finite system, $c(r)$ is limited in range by the finite boundaries of the system. One also knows that in an exact analysis of an infinite one-dimensional system with short-ranged potential one finds no critical behaviour for non-zero temperature. From these qualitative statements, however, it is not clear what values of N in an $N \times N$ or $N \times \infty$ lattice will give rise to exact results that most closely match SCOZA results for an infinite square lattice. As we shall see in section 4, when one uses the behaviour of the specific heat as a criterion, N turns out to be around 22.

3. Theory

In the following we consider the two-dimensional square lattice gas, which is isomorphic to the two-dimensional Ising model. The potential between particles is

$$v(r_i - r_j) = \begin{cases} +\infty & r_i = r_j \\ -w & i, j \text{ nearest neighbours} \\ 0 & \text{otherwise.} \end{cases} \tag{1}$$

For convenience w is scaled to be 1 in our calculations. In this convention the internal energy per spin for the Ising model U is related to the internal energy per particle for the lattice gas u via the following relation:

$$U = \rho u + \tfrac{1}{2} q \rho - \tfrac{1}{8} q \tag{2}$$

where q is the number of nearest neighbours ($q = 4$ for the square lattice), and ρ is the density for the lattice gas.

The SCOZA is based on the enforcement of thermodynamic consistency between different routes to thermodynamics. This imposes the following relation:

$$\frac{\partial (\beta \chi^{-1})}{\partial \beta} = \frac{\partial^2 (\rho u)}{\partial \rho^2} \tag{3}$$

where $\beta = 1/T$, the inverse temperature, $\rho^{-2}\chi$ is the isothermal compressibility, and u is the internal energy per particle for the lattice gas. These quantities can be given in terms of correlation functions through fluctuation theory, which yields

$$\beta\chi^{-1} = \frac{1}{\rho(1 + \rho\tilde{h}(0))} \tag{4}$$

and through the ensemble average of the Hamiltonian, which yields

$$u = -\tfrac{1}{2}q\rho g_1 = -\tfrac{1}{2}q\rho(1 + h_1) \tag{5}$$

where $h(r) \equiv g(r) - 1$, and $g(r)$ is the two-body distribution function. Here g_1 and h_1 represent the functional values of $g(r)$ and $h(r)$ at nearest-neighbour positions, and $\tilde{h}(k)$ is the Fourier transform of $h(r)$, which is related to the direct correlation function $c(r)$ by the OZ equation:

$$h(r_i) = c(r_i) + \rho \sum_j c(r_j)h(r_i - r_j) \tag{6}$$

or in the Fourier-transformed space:

$$1 + \rho\tilde{h}(k) = \frac{1}{1 - \rho\tilde{c}(k)}. \tag{7}$$

The above relations are exact. In order to proceed we shall approximate the form of the direct correlation function $c(r)$ by using the ansatz introduced by OZ that $c(r)$ has the range of the pair potential. In the SCOZA this can be done by generalizing somewhat the mean-spherical approximation (MSA), in which

$$\tilde{c}(k) = c_0 + qc_1\Phi(k) \tag{8}$$

where $\Phi(k)$ is the nearest-neighbour sum:

$$\Phi(k) = \frac{\cos k_x + \cos k_y}{2} \qquad \text{for a square lattice} \tag{9}$$

and c_0 and c_1 are functions of (ρ, β). Equation (8) is the OZ ansatz applied to the lattice gas. The MSA is the special case obtained by setting $c_1 = \beta$ and adjusting c_0 to be compatible with the core condition that assigns zero probability to multiple occupancy of a single site. In the SCOZA, one instead adjusts c_1 to ensure self-consistency between equations (4) and (5).

The core condition $h(0) = -1$ implies a relation between c_0 and c_1 through the OZ equation:

$$1 - \rho = \int \frac{\mathrm{d}^2 k}{(2\pi)^2} \frac{1}{1 - \rho\tilde{c}(k)} = \frac{1}{1 - \rho c_0} \int \frac{\mathrm{d}^2 k}{(2\pi)^2} \frac{1}{1 - z\Phi(k)} \equiv \frac{P(z)}{1 - \rho c_0} \tag{10}$$

where $z \equiv q\rho c_1/(1 - \rho c_0)$. $P(z)$ is the value for the lattice Green function $P(z, r)$ at $r = 0$. For a two-dimensional square lattice we have

$$P(z) = \frac{2}{\pi} \int_0^{\pi/2} \frac{\mathrm{d}\varphi}{\sqrt{1 - z^2\sin^2\varphi}} = \frac{2}{\pi}K(z) \tag{11}$$

where $K(z)$ is the complete elliptic integral of the first kind. From equation (10) we have

$$c_0 = \frac{1}{\rho}\left[1 - \frac{P(z)}{1 - \rho}\right] \tag{12}$$

and

$$c_1 = \frac{zP(z)}{q\rho(1 - \rho)}. \tag{13}$$

By taking $r_i = 0$ in equation (6), we get

$$-1 = h(0) = c_0 - \rho c_0 + q\rho c_1 h_1 \tag{14}$$

so

$$h_1 = -\frac{1}{q\rho c_1}[1 + (1 - \rho)c_0] = -\frac{1 - \rho}{\rho}\frac{1 - P(z)}{zP(z)}. \tag{15}$$

After substitutions, equations (4) and (5) become

$$\beta\chi^{-1} = \frac{(1 - z)P(z)}{\rho(1 - \rho)} \tag{16}$$

and

$$u = -\frac{1}{2}q\left(\rho - (1 - \rho)\frac{1 - P(z)}{zP(z)}\right). \tag{17}$$

From equation (16) we conclude that in the SCOZA the criticality, if any, occurs at $z = 1$, since at the critical point one has $\chi^{-1} = 0$, and we have $P(z) > 0$ for all z.

Finally, by applying the thermodynamic consistency via equation (3), we get the SCOZA partial differential equation:

$$\frac{1}{\rho(1 - \rho)}\frac{\partial}{\partial\beta}[(1 - z)P(z)] = -\frac{q}{2}\frac{\partial^2}{\partial\rho^2}\left[\rho(1 - \rho)\frac{P(z) - 1}{zP(z)}\right] - q. \tag{18}$$

The boundary conditions are $z = 0$, i.e., $P(z) = 1$, at $\beta = 0$ and $\rho = 0, 1$.

4. Specific results and discussion

Since for the two-dimensional square lattice $P(z)$ diverges when $z \to 1$, the renormalized inverse-temperature parameter c_1 also diverges. As a result, the SCOZA fails to predict a true critical point above zero temperature in this case. Nevertheless, the SCOZA results for u match the exact Onsager expression [4] for u remarkably well over the whole temperature range. Instead of having an infinite slope at the exact critical temperature, the SCOZA slope achieves its maximum at a temperature within a fraction of a percent of the exact value. The non-singular but near-singular behaviour near the ideal transition temperature makes our results strikingly similar to the exact results for a finite-size Ising model on a square lattice, $N \times N$ [3], or a finite-width strip, $N \times \infty$ [4], for an N a bit greater than 20.

In figure 1 we plot the negative internal energy $-U$ versus the inverse temperature β along the critical isochore $\rho = \rho_c = 1/2$, i.e., magnetization being equal to 0, for the comparison between SCOZA and both infinite- and finite-size Ising exact results. The comparison is made even clearer by plotting their residuals in figure 2. We find that the deviations between the SCOZA and the other results are very small over the whole temperature range. The deviations get larger near the critical point $\beta = \beta_c$, although the largest deviation is still within 3%. Comparing with finite-size and finite-width exact results, we find that this deviation gets minimized when we choose $N = 22$ for an $N \times N$ Ising model or $N = 21$ for an $N \times \infty$ Ising model.

In figure 3 we plot the specific heat versus β along the critical isochore. The SCOZA result has a specific heat that stays finite at its maximum, as all the finite-size and finite-width specific heats do in an exact theory. In this comparison we again find that the SCOZA infinite-lattice result has a great resemblance to the 22×22 or $21 \times \infty$ Ising model. The SCOZA curve matches well with the $21 \times \infty$ Ising model for $\beta < \beta_c$. But for $\beta > \beta_c$ the SCOZA result has somewhat less difference from the 22×22 solution. The maximum of the SCOZA curve occurs at $\beta_{SCOZA} = 1.758$, whereas the exact critical point for the infinite Ising model is $\beta_c = 1.763$. The maxima for the 22×22 and $21 \times \infty$ Ising models occur at $\beta_{22\times22} = 1.735$ and $\beta_{21\times\infty} = 1.764$,
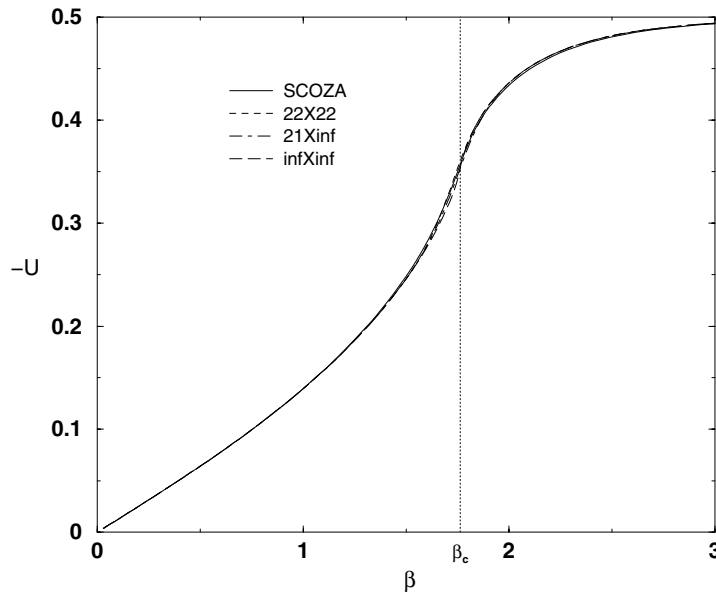
Figure 1. Negative internal energy for the two-dimensional Ising model $-U$, versus the inverse temperature β. The solid curve is the SCOZA result. Other curves are exact solutions for 22×22, $21 \times \infty$, and $\infty \times \infty$ Ising models, respectively. β_c is the exact critical point for the $\infty \times \infty$ model.
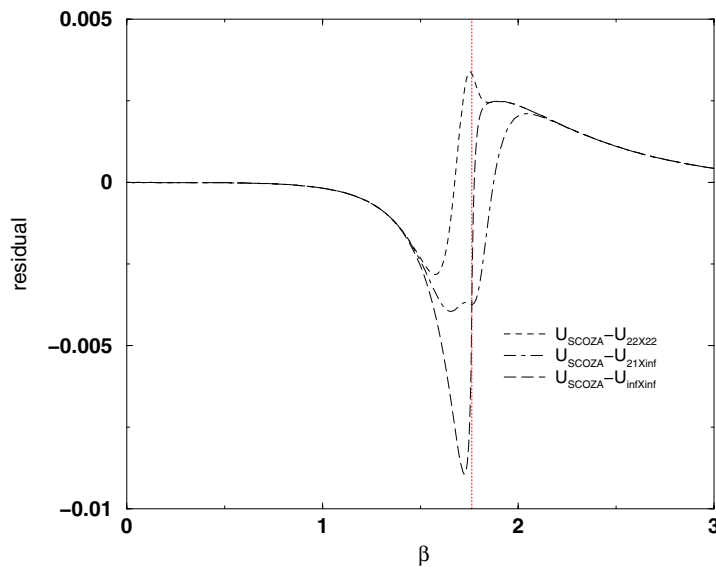

Figure 2. Residuals between the SCOZA and exact results. For optimal finite-size results, the deviations are smaller than the $\infty \times \infty$ exact results.

(This figure is in colour only in the electronic version)

respectively. The deviations between these maximum temperatures and the exact critical temperature is of the same order for the SCOZA and $21 \times \infty$ results, whereas it is a bit larger for the 22×22 case. In this regard the SCOZA is a bit more similar to the $21 \times \infty$ model.
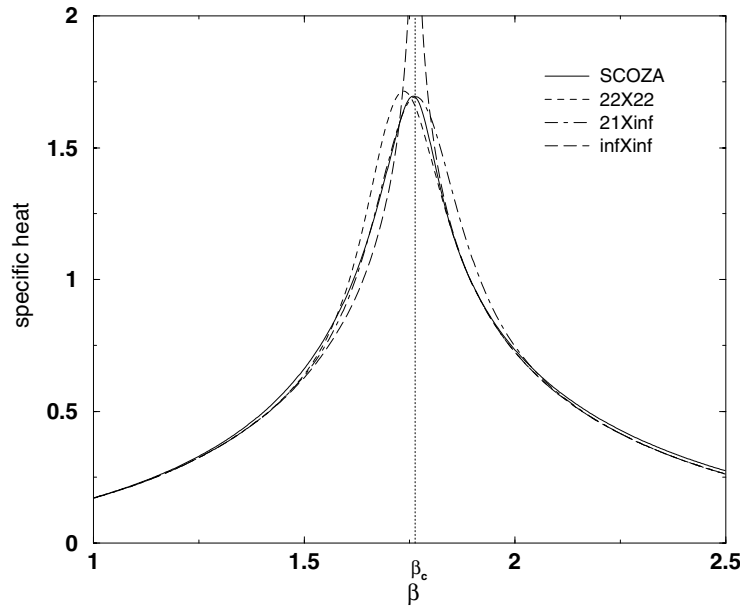
Figure 3. Constant-volume specific heat C_V for SCOZA compared with exact results. Note that the specific heat for SCOZA does not diverge at its maximum, showing a resemblance to finite-size models.

For each fixed value of ρ, we define the temperature where the specific heat is at its maximum as the pseudo-singular temperature. Here we try to determine a 'pseudo'-spinodal curve by collecting the set of (ρ, T) points that correspond to those pseudo-singularities. This 'pseudo'-spinodal curve is shown in figure 4. Note that the points on the curve do not mark real singularities, and both the specific heat and the compressibility remain finite, but very large, at these points. Furthermore, near the pseudo-critical point $\rho = \rho_c = 1/2$, by defining $\Delta\rho = \rho - \rho_c$, $\Delta T = T_c - T$, we find

$$\Delta\rho \sim (\Delta T)^{\beta_{\text{spinodal}}} \tag{19}$$

with a classical exponent $\beta_{\text{spinodal}} = 1/2$ when $T < T_c$.

From equations (7) and (8) we find that in the SCOZA the function $1 + \rho\tilde{h}(\boldsymbol{k})$ has a form proportional to the Fourier transform of the lattice Green function $P(z, \boldsymbol{k})$. Hence we have $\delta(\boldsymbol{r}) + \rho h(\boldsymbol{r}) \propto P(z, \boldsymbol{r})$. From the fact that

$$h(\boldsymbol{r}) \sim P(z, \boldsymbol{r}) \sim \exp\left(-2r\sqrt{\frac{1-z}{z}}\right) \tag{20}$$

when $r \to \infty$ [8], we find in the SCOZA the correlation length

$$\xi = \frac{1}{2}\sqrt{\frac{z}{1-z}}. \tag{21}$$

In figure 5 we plot the correlation length ξ versus temperature at the critical isochore. Since for the two-dimensional SCOZA scheme $z \to 1$ only when $T \to 0$, the correlation length keeps finite at the exact critical temperature T_c and only diverges when $T \to 0$. However, when $T = T_c$ we have $\xi \simeq 44$ according to the SCOZA scheme, which already indicates strong correlations. Furthermore, the correlation length increases sharply immediately below $T = T_c$.
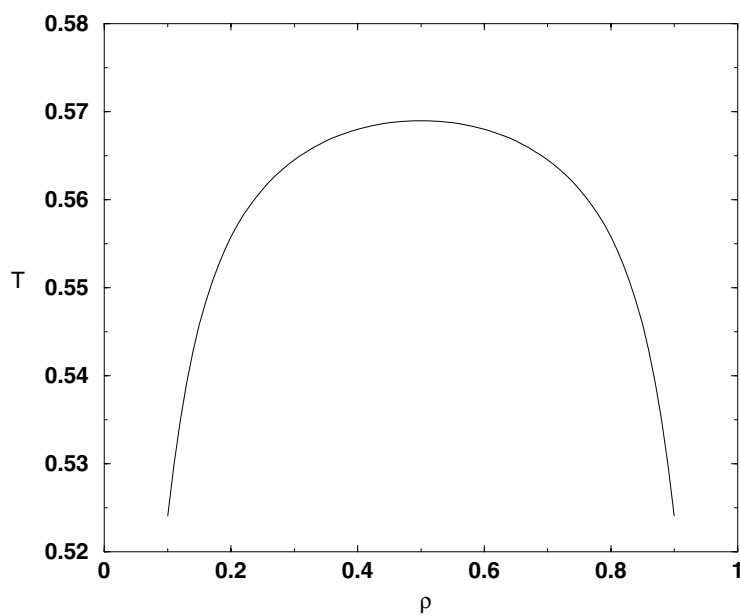
Figure 4. The pseudo-spinodal curve in the (T, ρ) plane, derived from the SCOZA. Near the pseudo-critical point $\rho = 1/2$, there is the relation $\Delta\rho \sim (\Delta T)^{\beta_{\text{spinodal}}}$ with $\beta_{\text{spinodal}} = 1/2$.
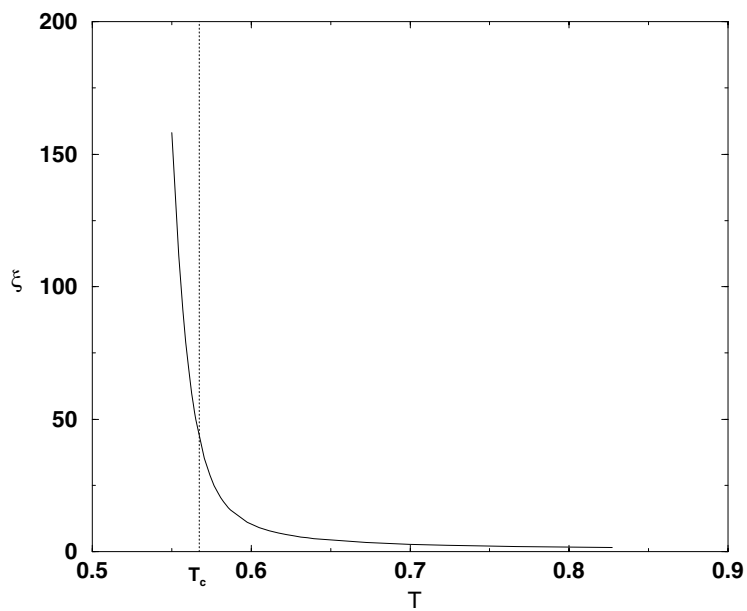

Figure 5. Correlation length ξ versus temperature from the SCOZA results. Note that ξ starts to increase sharply for $T \simeq T_c$.

Acknowledgment

References

[1] Høye J S and Stell G 1977 *J. Chem. Phys.* **67** 439
    Høye J S and Stell G 1977 *Mol. Phys.* **52** 1071
[2] Høye J S and Borge A 1998 *J. Chem. Phys.* **108** 8830
[3] McCoy B M and Wu T T 1973 *The Two-Dimensional Ising Model* (Cambridge, MA: Harvard University Press)
[4] Onsager L 1944 *Phys. Rev.* **65** 117
[5] Ornstein L S and Zernike F 1914 *Proc. Akad. Sci. (Amsterdam)* **17** 793
[6] Stell G 1969 *Phys. Rev.* **184** 135
[7] Dickman R and Stell G 1996 *Phys. Rev. Lett.* **77** 996