# ON EXACT BOUNDS FOR THE CLUSTER FREE ENERGY
# IN THE THREE-DIMENSIONAL LATTICE-GAS MODEL*

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The exact bounds by Lebowitz and Penrose for the cluster distribution of the simple cubic lattice-gas model with attractive interactions lead here to exact upper and lower bounds for the limiting cluster free energy or free energy per particle of a cluster of macroscopic size and, consequently, for the renormalized fugacity relating cluster distribution and partition functions. We also give practical realizations of the bounds for the cluster distribution. Our upper and lower bound expressions are always close enough to each other for $4J/k_B T > 1.5$. The nature of the bounds at higher temperatures is also analysed.

## 1. Introduction

A given configuration of the lattice-gas version of the Ising model can be described in terms of *clusters* defined, for instance, as maximal sets of connected occupied sites. For equilibrium states, the probabilities for the occurrence of these clusters are governed by the corresponding Gibbs distribution. Such a simple picture of the system as a collection of non-overlapping clusters is very convenient in the theory of nucleation[1]), e.g. to describe the decay of a metastable state. This is done in practice via the concept of the cluster free energy, $F_l$, which is defined as

$$F_l = -k_B T \ln Q_l . \tag{1}$$

Here $k_B$ is the Boltzmann constant, $T$ represents the temperature, and $Q_l$ is the partition function for the $l$-particle clusters[2]). The equilibrium cluster distribution, $c_l$, that is the number of $l$-particle clusters per lattice site as a function of the "size" $l$ in the equilibrium state, is in principle related to the partition function $Q_l$. A semiphenomenological relation of this kind is[3])

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$$c_l = \omega^l Q_l (1 - \rho)^{k_l} , \tag{2}$$

where $\rho$ is the system density (number of particles per lattice site), $\omega = \omega(\rho, T)$ is a renormalized fugacity and the parameter $k_l$ has a weak dependence on $l$ for very small $l$ (e.g. $k_1 = 3.25$, $k_2 = 4.5$, $k_l = 5$, $l \geqslant 3$ [4]).

Dickman and Schieve[5]) proved the existence of the limiting cluster free energy or free energy per particle for a cluster of macroscopic size, i.e. $q \equiv \lim_{l \to \infty} (\ln Q_l / l)$. The proof in ref. 5 uses ideas from the derivation by Penrose and Lebowitz[6]) of exact upper and lower bounds for the cluster free energy. These bounds, however, are often crude in practice and, consequently, this fact limits severely the utility of the resulting values for the limiting free energy $q$. In this paper we obtain upper and lower bounds for $q$ which are useful for temperatures below $0.6T_c$, $T_c$ being the corresponding critical temperature. We also deduce some interesting bounds for the renormalized fugacity in eq. (2) and give practical realizations of existing exact bounds for the cluster distribution.

## 2. Limiting free energy and renormalized fugacity

Our results apply to the familiar lattice-gas or Ising model in a simple cubic lattice with $N$ sites. At each site $i = 1, 2, \ldots, N$ of the lattice there is defined an occupation variable $n_i$ with two values, either 1 (particle) or 0 (unoccupied site), and there is an attractive interaction between particles; each configuration $C \equiv \{n_i\}$ has a configurational energy defined as

$$E\{C\} = -4J \sum_{i,j}{}' n_i n_j , \quad J > 0 , \tag{3}$$

where the sum runs over all the nearest-neighbor pairs of sites. One may introduce the grand partition function at temperature $T$ and fugacity $z$,

$$\Xi(z, T) = \sum_{\{C\}} z^{\rho N} \exp[-E\{C\} / k_B T] , \tag{4}$$

where the sum runs now over all the $2^N$ possible configurations. Here $\rho N = \sum_i n_i$ is the number of particles in configuration $C$. The probability for the occurrence at equilibrium of a given configuration $C$ is then given by $P(C) = \Xi^{-1} \exp[-E\{c\} / k_B T]$.

We shall need the following definitions concerning a given cluster $K$:
- $\Lambda$ is the set of lattice sites.
- $B(K)$ is the border of $K$, i.e. the set of sites which are nearest neighbors of any site in $K$ and do not belong to $K$.

- $\bar{K} = K \cup B(K)$.
- $N(K)$, $N(B(K))$ and $N(\bar{K})$ are, respectively, the number of particles in $K$, $B(K)$ and $\bar{K}$; $N(\bar{K}) = N(K) + N(B(K))$.
- $b(l) = \min\limits_{K:N(K)=l} N(B(K))$, i.e. the minimum value of the number of sites in the border of any $l$-particle cluster.
- $E(K) = -4J \sum\limits_{i,j \in K}' n_i n_j$ is the energy of the cluster.
- $\theta(K) = z^{N(K)} \exp[-E(k)/k_B T]$ .
- $Q_l = \sum\limits_{K:N(K)=l} \exp[-E(K)/k_B T] = z^{-N(K)} \sum\limits_{K:N(K)=l} \theta(k)$; $Q_l$ only depends on the temperature and it can be written as a polynomial in $y \equiv e^{\gamma} (\gamma \equiv 4J/k_B T)$: $Q_l = \sum\limits_{m} Q_l(m) y^{x_m}$.
- $\Xi(K)$ is the grand partition function for a lattice-gas confined to the sites of $K$.

The bounds we shall obtain for $q$ follow from the ones for $c_l$ by Lebowitz and Penrose [2]. These bounds for $c_l$ will be analyzed later on; for the moment it suffices to consider their crudest form, i.e.

$$Q_l z^l (1 - \rho)^{2+5l} \leqslant c_l \leqslant Q_l z^l (1 + z)^{-l-b(l)} . \tag{5}$$

This expression was the base for eq. (2) [3]); it can also be written as

$$\ln z - \left(\frac{2}{l} + 5\right) \ln(1 - \rho) \geqslant \frac{\ln Q_l}{l} - \frac{\ln c_l}{l}$$
$$\geqslant \left(1 + \frac{b(l)}{l}\right) \ln(1 + z) - \ln z . \tag{6}$$

Let us consider a phase point at "zero field", i.e. on the coexistence curve above or below $T_c$, and denote by $\omega_0, \rho_0, z_0, c_l^0, \ldots$ the corresponding values of $w, \rho, z, c_l, \ldots$, respectively. We then introduce the limit $l \to \infty$ in eq. (6) and use the following two lemmas:

*Lemma 1.* $\lim_{l \to \infty} (\ln c_l^0/l) = 0$. This follows from a rigorous result by Kunz and Souillard[7]) stating that $\ln c_l^0 \sim l^{2/3}$ as $l \to \infty$.

*Lemma 2.* $\lim_{l \to \infty} [b(l)/l] = 0$. The proof is as follows: Let $K$ be a cluster, $N(K) = l$, and $L \equiv [l^{1/3}] + 1$ ($[a]$ is largest integer contained in $a$).

For some very compact cluster, $\bar{K}$ will be contained in a box of side $L + 2$, and $N(\bar{K}) \leqslant (L + 2)^3$. Then, $N(B(K)) = N(\bar{K}) - N(K) \leqslant (L + 2)^3 - l < 9l^{2/3}$. As $b(l)$ is the minimum value of $N(B(K))$, one has $b(l) \leqslant N(BK) < 9l^{2/3}$, $b(l)/l < 9l^{-1/3}$, and the lemma follows.

By taking the limit $l \to \infty$ in eq. (6) and using the above two lemmas we finally have

$$-5 \ln(1 - \rho_0) \geq q - 3\gamma \geq \ln(1 + e^{-3\gamma}) , \tag{7}$$

where $z_0 = e^{-3\gamma}$ for a simple cubic lattice. These limits are in fact useful at low temperatures, say $T \leq 0.6 T_c$; for example, they give $4.573 \geq q \geq 4.511$ at $\gamma = 1.5$ and become even better for higher values of $\gamma$. This agrees with the value $q = 4.513$ given by Perini et al.[8]). See fig. 1.

We now need the following lemma:

*Lemma 3.* ("Soltz criterium" [9])). If $(q_l)$ is a succession in $l$, then $\lim_{l\to\infty}(q_l/l) = \lim_{l\to\infty}(q_l - q_{l-1})$. The proof is as follows: let $\alpha_l \equiv q_l - q_{l-1}$ ($q_0 \equiv 0$) and $\alpha \equiv \lim_{l\to\infty} \alpha_l$. This means that for any $\varepsilon > 0$, there exists an $N_0$ such that if $l > N_0$ then $\alpha_l = \alpha + \delta_l$ with $|\delta_l| < \varepsilon$. Let $N_1 = \max(N_0, \ \varepsilon^{-1}|\delta_1 + \cdots + \delta_{N_0}|)$. Now, if $l > N_1$ then $q_l/l = (\alpha_1 + \alpha_2 + \cdots + \alpha_l)/l = \alpha + (\delta_1 + \cdots + \delta_{N_0})/l + (\delta_{N_0+1} + \cdots + \delta_l)/l$. The last two terms here are respectively less than $|\delta_1 + \cdots + \delta_{N_0}|/N_1 < |\delta_1 + \cdots + \delta_{N_0}|/\varepsilon^{-1}|\delta_1 + \cdots + \delta_{N_0}| = \varepsilon$ and less than $\varepsilon(l - N_0^{-1})/l < \varepsilon$, so that it finally follows that $|q_l/l - \alpha| < 2\varepsilon$ and $\lim_{l\to\infty}(q_l/l) = \alpha$. Q.E.D.

The renormalized fugacity at coexistence, $\omega_0$, can be obtained in practice[3]) as the radius of convergence of the series

$$\rho = \sum_{l=1}^{\infty} l\omega^l Q_l (1 - \rho)^{k_l} . \tag{8}$$

That is, $\omega_0 = \lim_{l\to\infty}(Q_l/Q_{l+1})$ and the lemma 3 implies $-\ln \omega_0 = \lim_{l\to\infty}(\ln Q_l/l)q$. From eq. (7) we then get

$$z_0(1 - \rho_0)^5 \leq \omega_0 \leq z_0/(1 + z_0). \tag{9}$$

This gives $0.0103 \leq \omega_0 \leq 0.0110$ at $\gamma = 1.5$, thus including the value $\omega_0 = 0.01056$ obtained previously as an empirical fit to eqs. (8) and (2) [4]).

## 3. Cluster distribution bounds

Lebowitz and Penrose[2]) have established more accurate bounds than those in eq. (5) for the probability $c(K)$ of occurrence of a given cluster $K$. These bounds are based on the inequalities by Fortuin, Kasteleyn and Ginibre[9]] which apply (among others) to systems with attractive two-body interactions. The bounds

read as follows:

*Lower bounds*:

$$c(K) \geqslant \theta(K) \prod_{i \in \bar{K}} (1 - \rho) , \tag{10a}$$

$$c(K) \geqslant \frac{\theta(K)}{\Xi(K)} \prod_{i \in B(K)} (1 - \rho) . \tag{10b}$$

*Upper bounds*:

$$c(K) \leqslant \frac{\theta(K)}{\Xi(K)} \prod_{i \in B(K)} (1 + z)^{-1} , \tag{11a}$$

$$c(K) \leqslant \theta(K) \prod_{i \in K} (1 + z)^{-1} , \tag{11b}$$

$$c(K) \leqslant \theta(K) \left\{ \Xi(K) \left[ 1 + \sum_{i \in \bar{K}} \sum_{j \in \Lambda - \bar{K}} \left( \frac{z}{1 + z} \right)^2 (e^{-\beta V_{ij}} - 1) \right] \right\} . \tag{11c}$$

$V_{ij}$ is the interaction energy between sites $i$ and $j$; it is equal to $-4J$ when $(i, j)$ are nearest neighbors and 0 otherwise. By realizing that $c_l = \Sigma_{K:N(K)=l} c(K)$, a detailed study of all the clusters $K$ up to a size $N(K) = 5$ gives the following realizations of eqs. (10) and (11):

From eq. (10a) ($y \equiv e^\gamma$):

$$c_1 \geqslant z(1 - \rho)^7 ,$$
$$c_2 \geqslant 3z^2 y(1 - \rho)^{12} ,$$
$$c_3 \geqslant 3z^3 y^2 (1 - \rho)^{16}(5 - \rho) ,$$
$$c_4 \geqslant z^4 y^3 (1 - \rho)^{19}[83 - 105\rho + 33\rho^2 - 3\rho^3 + 3y(1 - \rho)] , \tag{12}$$
$$c_5 \geqslant 3z^5 y^4 (1 - \rho)^{22}[8(2 - 3\rho + \rho^2)y + 162 - 346\rho + 278\rho^2$$
$$- 102\rho^3 + 17\rho^4 - \rho^5] .$$

From eq. (10b):

$$c_1 \geqslant \frac{z}{1 + z} (1 - \rho)^6 ,$$

$$c_2 \geqslant \frac{3z^2 y(1 - \rho)^{10}}{1 + 2z + z^2 y} ,$$

$$c_3 \geqslant \frac{3z^3y^2(1-\rho)^{13}(5-\rho)}{1+3z+(1+2y)z^2+z^3y^2} \, ,$$

$$c_4 \geqslant z^4y^3(1-\rho)^{15}\left\{ \frac{3y(1-\rho)}{1+4z+2(1+2y)z^2+4z^3y^2+z^4y^4} \right.$$

$$+ \frac{3(21-31\rho+11\rho^2-\rho^3)}{1+4z+3(1+y)z^2+2y(1+y)z^3+z^4y^3}$$

$$\left. + \frac{4(5-3\rho)}{1+4z+3(1+y)z^2+(1+3y^2)z^3+z^4y^3} \right\} \, ,$$

$$c_l \geqslant \frac{(1-\rho)^{4l+2}Q_l z^l}{1+\binom{l}{1}z+\binom{l}{2}z^2y+\cdots+\binom{l}{m}z^my^{x_m}+\cdots} \, . \tag{13}$$

From eq. (11a) $(p \equiv (1+z)^{-1})$:

$$c_1 \leqslant zp^7 \, ,$$

$$c_2 \leqslant \frac{3z^2yp^{10}}{1+2z+z^2y} \, ,$$

$$c_3 \leqslant \frac{3z^3y^2p^{13}(p+4)}{1+3z+(1+2y)z^2+z^3y^2} \, ,$$

$$c_4 \leqslant z^4y^3\left\{ \frac{3p^{16}(p^2+8p+12)}{1+4z+3(1+y)z^2+2y(1+y)z^3+z^4y^3} \right. \tag{14}$$

$$\left. + \frac{4p^{15}(3p+2)}{1+4z+3(1+y)z^2+(1+3y^2)z^3+z^4y^3} \right\}$$

$$+ \frac{3z^4y^4p^{16}}{1+4z+(1+2y)2z^2+4z^3y^2+z^4y^4} \, .$$

From eq. (11b):

$$c_1 \leqslant zp^7 \, ,$$

$$c_2 \leqslant 3z^3yp^{12} \, ,$$

$$c_3 \leqslant 3z^3y^2p^{16}(p+4) \, , \tag{15}$$

$$c_4 \leqslant 3z^4y^4p^{20}+z^4y^3p^{19}[3p^3+24p^2+48p+8] \, ,$$

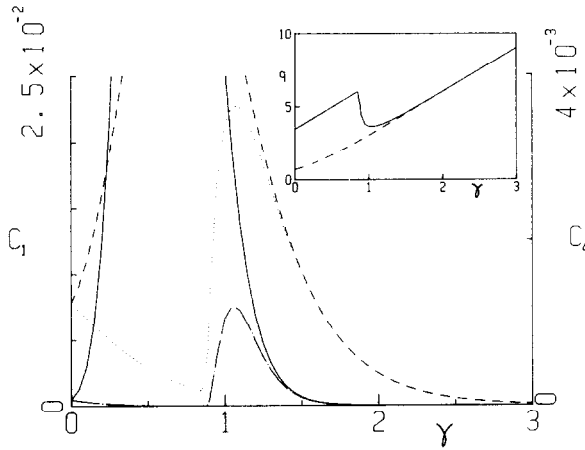$$c_5 \leqslant 24z^5y^5p^{23}(p+1)+3z^5y^4p^{22}(8+33p+64p^2+44p^3+12p^4+p^5) \, .$$

Fig. 1. Behavior with the inverse temperature $\gamma = 4J/k_B T$ of the bounds in this paper: the upper bound for $c_1$ (— — — — —) as given by eq. (16), the lower bound for $c_1$ (· · · · · · · · · ·) as given by eq. (15), the upper bound for $c_4$ (————) as given by eq. (14) and the lower bound for $c_4$ ( — · — · — ) as given by eq. (13). The curves for the upper bounds present rather broad peaks below $T_c$ which are not shown in the figure. $T_c$ corresponds to the minimum in the curves for the lower bounds. The inset shows the bounds in eq. (7) for the limiting cluster free energy $q$.

And, from eq. (11c):

$$c_1 \leq z[1 + 18(y - 1)z^2 p^2]^{-1}/[1 + 7z + (2y + 5)3z^2 + (3y + 4)5z^3$$
$$+ (4y + 3)5z^4 + (5y + 2)3z^5 + 7z^6 + z^7],\tag{16}$$

$$c_2 \leq 3yz^2[1 + 26(y - 1)z^2 p^2]^{-1}[1 + 12z + (15y + 51)z^2]^{-1}.$$

The above expressions are in fact useful realizations of the bounds in eqs. (10) and (11), i.e. they are close enough to each other at low temperatures, say $\gamma \gtrsim 1.5$. Fig. 1 depicts the typical behavior with temperature of the above bounds.

## References

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