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A COMMENT ON CLUSTERS FREE-ENERGY MODELS

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We discuss the concept of the clusters free-energy in nucleation phenomena, and we analyse and compare recent explicit expressions for this quantity.

The onset of condensation phenomena in supercooled vapors and the formation of the first nuclei of a solid in metastable fluids are familiar subjects in applied physics (atmospheric sciences, metallurgy, etc.) whose understanding has also a great interest to the foundations of nonequilibrium thermodynamics; as a matter of fact, one is faced here with a general and fundamental problem, the dynamics of metastable and unstable states [1,2].

The corresponding theory still uses nowadays many phenomenological ideas so that it seems very important to relate the most fundamental concepts to simple objects in well-defined models. A convenient reference for this purpose is the lattice gas model [3] defined through the hamiltonian  $H = -4J\sum_i n_i n_j$ ,  $J > 0$ , where the sum runs over all pairs  $(i, j)$  of nearest-neighbor sites in a simple cubic lattice ( $i = 1, 2, \dots, N$ ), for instance, and  $n_i = 1$  (particle) or 0 (hole). Any given state of the system can then be described in terms of *clusters* defined as sets of particles connected by nearest-neighbor bonds; the *size*  $k$  of a given cluster is defined as the number of particles which belong to it. The probability for the occurrence of a cluster of size  $k$  in the system,  $c_k$ , is thus expected to be related in some cases to the droplet or grain distributions observed directly by microscopy or indirectly by other means. Consequently, a basic problem is to describe theoretically the system equilibrium state at temperature  $T$  and density  $\rho$ , and also to study other questions such as metastability, etc., via explicit expressions for  $c_k$  [1,2].

This problem was addressed by us in a previous paper [4] where we proposed a simple modification of Fisher's droplet model [5], namely

$$c_k = c_0 k^{-\tau} \exp(-ak^{2/3}) [1 - \alpha \exp(-ak^{2/3})], \quad (1)$$

where  $a = a(T)$ ,  $\tau$  and  $\alpha$  are temperature (and density) independent, and  $c_0$  is determined by the sum rule

$$\rho = \sum_k k c_k. \quad (2)$$

The last factor in eq. (1) aims at representing approximately the probability of unoccupied sites surrounding the "average cluster". In addition, it seems interesting to make the extra assumption that eq. (1) is consistent near the critical temperature  $T_c$  with the scaling behavior

$$c_k = k^{-(2+y/\delta)} f(\epsilon k^{y/\beta\delta}), \quad (3)$$

where  $\epsilon \equiv 1 - T/T_c$  and  $y$  is Binder's critical exponent defining a cluster effective size  $k^y$  [6]. By combining eqs. (1)–(3) one is forced to write  $\tau = 2 + y/\delta$ ,  $a(t) = a_0 \epsilon^t$  and  $t = 2\beta\delta/3y$  so that the cluster distribution is determined by the usual critical exponents  $\beta$  and  $\delta$ , by the constants  $a_0$ , and  $\alpha$ , and by the parameter  $c_0(T)$  (the data independently evidence  $y \approx 0.45$ ) which are to be determined consistently with the sum rule (2); that is, no temperature dependent parameters are left in eq. (1). At points in the one phase region, on the other hand, we found (let  $h \equiv \mu H/k_B T$  with the usual notation) the scaling behavior  $\approx h k^y$  with the same exponent as before and  $c_k(h)/c_k(h=0) = \exp(-\eta k)$ , (4)

where  $\eta = bh^{1/y}$  for small "fields", say  $h < 0.1$ ; on the contrary, it follows the classical prediction, eq. (4) with  $\eta\alpha h$  for  $h > 0.2$  [7].

The above description was shown to reproduce very convincingly some Monte Carlo equilibrium cluster distributions for the lattice gas model over a wide range of temperatures and to contain other interesting theoretical features [4]. We shall discuss in the following some related concepts and compare our description to a different one for the clusters free-energy [8,9]; we hope the results in this letter will clarify some questions and help to use previous approaches in the analysis of experimental results in nucleation phenomena.

The concept of clusters immediately leads one to introduce that of clusters free-energy. This plays in fact a fundamental role in most quantitative descriptions; for example, to compute the rate at which clusters are formed or the lifetime of a given metastable state [10,11]. There are in practice several ways to define a relevant clusters free-energy. A related quantity is the *partition function* for clusters of  $k$  particles [11] defined as

$$Q_k = \sum_i e^{-H_i/k_B T},$$

where the sum runs over all translationally invariant clusters of  $k$ -particles, and  $H_i$  denotes the clusters configurational energy. It then follows the *internal free energy* for clusters of  $k$  particles as

$$F_k = -k_B T \ln Q_k = -k_B T \ln \left( \sum_i e^{-H_i/k_B T} \right). \quad (5)$$

The concept of a clusters free-energy can however be approached from a different point of view. Lebowitz and Penrose [11,12] provided exact bounds for  $c_k$  which suggest one to look for relations

$$c \approx z^k Q_k, \tag{6}$$

where  $z$  represents the fugacity, at low temperatures and densities. As a matter of fact, the expression

$$c_k = w_s^k Q_k (1 - \rho_s)^{m_k}, \tag{7}$$

where  $\rho_s$  and  $w_s$  are respectively the density and a *renormalized fugacity* at the coexistence curve, and  $m_k$  is a parameter slightly dependent on  $k$  (say,  $m_1 = 3.25$ ,  $m_2 = 4.5$ ,  $m_k = 5$  for  $k \geq 3$ ), has been used successfully over a relatively broad range of temperatures and densities [13–15,4]. By combining eqs. (5) and (7) one has

$$c_k \approx \exp[-F_k/k_B T + k \ln z], \tag{8}$$

so that one of the usual definitions in nucleation theory [10] for the *formation free energy* associated to clusters of  $k$  particles, that is

$$c_k = c_1 \exp(-\tilde{F}_k/k_B T), \tag{9}$$

then implies ( $F_1 \equiv 0$ )

$$\tilde{F}_k \approx F_k - (l-1)k_B T \ln z \tag{10}$$

at the (low) temperatures and densities for which eq. (6) holds. Note that eq. (10) is an interesting expression which clarifies the approximate nature of  $\tilde{F}_k$  and its relation to the more rigorous concept  $F_k$ ; this difference is not always made clear in the literature. A similar relation holds in the case of other phenomenological definitions for the free-energy of clusters [11].

Perini et al. [9] have computed directly the differences  $F_{k+1} - F_k$  ( $k \leq 20$ ) for the simple cubic lattice gas by Monte Carlo methods to conclude that

$$F'_k/k_B T \cong a_p k + b_p k^{2/3} + c_p k^{1/3} + \tau_p \ln(k/\rho_s) + d_p, \tag{11}$$

where  $\gamma = 4J/k_B T$  and it is assumed  $\tau_p = -1/9$ . The first two terms here correspond to the classical "capillarity approximation" [10] and  $\ln k$  is an entropic correction [5]; the term  $k^{1/3}$  is a "line contribution" attributed by Perini et al. to the curvature dependence of the surface free energy. The free energy defined by these authors is related by

$$F'_k/k_B T = 3\gamma k + F_k/k_B T \tag{12}$$

to the internal free energy (5).

On the other hand, it follows from our previous work, namely eqs. (1) and (7) and the definition (5) that

$$F_k/k_B T = k \ln w_s + ak^{2/3} - \ln[1 - \alpha \exp(-ak^{2/3})] + \tau \ln k + [m_k \ln(1 - \rho_s) - \ln c_0], \tag{13}$$

where  $\tau = 2.09$ .

The expressions in the last two paragraphs reveal a close relation between the results by Perini et al. [8,9] and ours [4] which was unrecognized before: the "line contribution" of eq. (11) is replaced in eq. (13) by the probability in brackets depicted by eq. (1), the "point contribution" of eq. (11) is replaced in eq. (13) by a term with a weak dependence on  $k$  for very small  $k$ , and consequently the values of the constants affecting terms which are non-dominant in the limit  $k \rightarrow \infty$  change from one description to the other. That is, the actual differences are irrelevant for large  $k$  at low temperatures, and eq. (11) seems preferable for, say  $T < 0.5T_c$ .

The most interesting experimental region is however at high temperatures [16] and the two descriptions show then a very different behavior. For instance, a negative value of  $\tau$  (as in eq. (11)) only seems consistent with exact results for  $c_k$  at very low temperatures [17], that is at temperatures where eq. (6) is a good approximation. Otherwise it seems preferable eq. (13), which even has the proper structure, to extrapolate up to  $T_c$  and includes interesting scaling properties; in fact, it was previously shown that eqs. (13) and (7) provide a very good description of Monte Carlo data over a broad range of temperatures,  $0.6 \leq T/T_c \leq 0.9$ , and densities [4]. In conclusion, we have analysed the origin of some reported discrepancies between different expressions for the free energy of clusters (c.f. eqs. (10) and (12)) and a possible cause of ambiguity in nucleation theory. It then follows in particular a clear comparison between two recently proposed droplet models, [4] and [8,9]. The differences between these two models could be experimentally observable, either directly or indirectly. In particular, we hope our description eqs. (1), (4), (7) and (13) can be useful in the analysis of some practical problems in nucleation theory such as a nucleation rates, completion times, etc. A computation along those lines showing explicitly that fact will soon be published by us elsewhere [18].

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