On the behaviour of small clusters near the spinodal decomposition†

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Abstract. The canonical average of the Boltzmann factor of the interaction potential, as measured by a test particle, is shown to be equal to the inverse of the fraction of the average number \( m_1 \) of 1-particle Mayer clusters. The potential distribution theory is used to derive an analytic expression for a mean number of small clusters \( m_n \), \( 1 \leq n < N \), in an \( N \)-particle system in the mean-field expression. Near the spinodal density, the average number of small clusters undergo a sharp change. Computation of pressure shows that only the first four clusters produce surprisingly good agreement with known pressure even beyond the spinodal density.

Keywords. Behaviour of small clusters; spinodal decomposition; interaction potential; Mayer clusters; spinodal density; mean-field theory.

1. Introduction

The mean number, \( m_1 \), of 1-particle clusters plays a very important role in the theories of nucleation and metastability (Becker and Doring 1935; Abraham 1971; Kalos et al 1978; Penrose and Lebowitz 1979; Shing and Gubbins 1981 & Garcia and Soler Torraja 1981). In the statistical mechanical theories of nucleation, the mean numbers \( m_n \) of the larger clusters are usually written in the following form (Abraham 1971)

\[
\hat{m}_n = \hat{m}_1 \exp \left[ -\Delta F(n,p,T)/k_B T \right], \quad n \geq 2,
\]

where \( \Delta F(n,p,T) \) is the difference between the free energy of a cluster of \( n \) particles and that of a vapour of \( n \) monomers at temperature \( T \) and pressure \( p \). Equilibrium solutions of the Becker-Doring type of kinetic equation theories of nucleation also give \( \hat{m}_n \) in terms of \( \hat{m}_1 \) (Becker and Döring 1935; Penrose and Lebowitz 1979),

\[
\hat{m}_n = C_n(\hat{m}_1)^n,
\]

where \( C_n \) is a function of the size \( n \) of the cluster. Recent computer simulations (Penrose and Lebowitz 1979) of cluster size distribution on lattices have also re-emphasized the importance of \( \hat{m}_1 \) in the nucleation process.

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It is well-known that there is no unique way to define a cluster for continuous systems, although there exist several different prescriptions for doing so. These prescriptions differ from each other in some fundamental aspects, but it is believed that well below the critical temperature, when the attractive forces are important, these different prescriptions give qualitatively the same result. Recently it has been shown that the mean cluster size distribution (Bagchi 1980; Donoghue and Gibbs 1981; Gibbs et al 1981), defined by a reformulation of Mayer's theory of condensation (Mayer and Mayer 1980), can successfully describe the condensation process. Below the critical temperature, the cluster integrals are positive and a mean number of Mayer clusters of certain size can be defined rigorously. However, the clusters arising in the Mayer theory may not always be interpreted as an aggregate of molecules, the members of which remain within the sphere of influence of each other for a time appreciably larger than the duration of a bimolecular collision time. This is especially true at high temperatures. The formulation of a satisfactory definition of physical cluster concept has drawn considerable attention in recent years (Lee et al 1973; Gillis et al 1977; Powless 1980; Lockett 1980). In this paper, however, we consider only the Mayer clusters and show that an expression like (2) can also be derived for Mayer clusters in the mean-field approximation. It is interesting to find that the Mayer clusters, which are usually called mathematical clusters because of their apparent lack of physical reality, can so easily be substituted for physical clusters. We have already seen that near the condensation density the size distribution of these mathematical clusters suddenly becomes bimodal, signalling the appearance of large clusters in the system. Thus, these "mathematical" clusters seem to parallel the real physical clusters in more than one respect.

In this paper, we present the following results. We demonstrate that the canonical average of the Boltzmann factor of the interaction potential (Widom 1963; Hansen and McDonald 1976), \( \langle \text{BFT} \rangle \), as measured by a test particle, is equal to the inverse of the fraction of the mean number \( \bar{m}_1 \) of 1-particle Mayer clusters. Since recent advances in computer simulations have made it possible to calculate \( \langle \text{BFT} \rangle \) directly (Adams 1974; Romano and Singer 1979), our result could be of use in computing \( \bar{m}_1 \). Mean-field approximations to \( \langle \text{BFT} \rangle \), as developed by Widom (1963), is then used to derive an analytic expression for \( \bar{m}_1 \). In the limit of infinite system at fixed density, an accurate expression for the mean number of clusters \( \bar{m}_n (n \geq 2) \) can be derived for clusters whose sizes are much smaller than the total number of particles in the system. We find that the \( \bar{m}_n \) undergo a sharp change near the spinodal density. We have also computed the pressure from the mean number of these clusters and found that even by including only the first four clusters, good agreement with the exact pressure can be obtained even beyond the spinodal density.

In the next section, we derive the expressions necessary to evaluate \( \bar{m}_n \). In §3, we present the results. Section 4 concludes with a brief discussion.

2. Theory

In the potential distribution theory (Hansen and McDonald 1976; Widom 1963), an expression for the canonical average of the Boltzmann factor of the interaction
energy of a test particle with all other particles of the system is derived. The configurational partition function $Z_N$ for a system of $N$-particles is given by

$$Z_N = \frac{1}{N!} \int \ldots \int \exp \left[ -\beta U_N \right] d\tau_1 \ldots d\tau_N,$$

where $U_N$ is the energy of interaction of $N$-particles, $\tau_i$ is the element of volume $i$-th particle and $\beta = (k_B T)^{-1}$, $T$ being the temperature and $k_B$ the Boltzmann constant.

Equation (3) can also be written in the following form

$$Z_N = \frac{V}{N!} \int \ldots \int \exp \left[ -\beta (U_{N-1} + \psi) \right] d\tau_1 \ldots d\tau_{N-1},$$

where one of the particles is labelled as a test particle and $\psi$ is the energy of interaction between this test particle and the rest of the system. Equation (4) can be written in the form (Hansen and McDonald 1976).

$$Z_N = \frac{V}{N!} (N-1)! Z_{N-1} \langle e^{-\beta \psi} \rangle,$$

where $\langle \ldots \rangle$ indicates a canonical average in the $(N-1)$ particle system.

An interesting relation, which is inverse of (5), has recently been derived

$$Z_{N-1} = \frac{N!}{V(N-1)!} Z_N \langle e^{\beta \psi} \rangle,$$

where $\langle \ldots \rangle$ is a canonical average in the $N$-particle system and the particle that experiences the potential $\psi$ is one of the $N$-particles and not a test particle.

We will discuss Widom’s mean-field approximation to (BFT) later. First, let us show how (5) can be used to relate BFT to the mean number $\bar{m}_1$ of one particle clusters.

We start with the Mayer-Ursell cluster expansion (Mayer and Mayer 1980) for the function $Z_N$, given by

$$Z_N = \sum_{(m_i)} \prod_{l=1}^{N} \frac{[V b_l(T,V)]^{m_l}}{m_l!},$$

with $\sum_{l=1}^{N} l m_l = N.$ (7a)

The $b_l(T,V)$ is the $l$th connected cluster integral and $m_l$'s are positive integers or zero. Recently it has been shown that the cluster expansion (7) is related to a general class of polynomials known as the Bell-polynomials (Gibbs et al 1981). These polynomials arise in the task of simplifying the $n$th derivative of a composite function.

As long as the $b_l$'s are positive, a mean number $\bar{m}_k$ for the population of the clusters of size $k$ can be defined as (Donoghue and Gibbs 1981; Gibbs et al 1981; Hill 1956);
We note that as long as $b_i$'s are positive, the statistical weight factor \[ N \prod_{i=1}^{N} (Vb_i)^{m_i}/m_i! \] is well defined.

There is considerable amount of controversy in the literature (Hill 1956) over the nature of the clusters as defined through (8). Above the critical temperature, $b_i(T, V)$ may become negative and $m_i$ may not represent the occupation number of a real cluster. As explained in the introduction, Mayer clusters are considered to be mathematical rather than physical, but these clusters have many properties which parallel the properties expected of real physical clusters.

By exploiting the properties of the Bell-polynomials (Bell 1934; Riordan 1978), we can express (8) in the following simple and elegant form (Gibbs et al 1981),

\[ m_k(T, V, N) = \sum_{m_i} m_k \prod_{i=1}^{N} \frac{(Vb_i)^{m_i}}{m_i!} / Z_N(T, V), \]

where we have used the fact that $b_1 = 1$.

Equation (10) expresses the mean number in terms of the canonical average, $\langle BFT \rangle$. We shall now use (10) to derive an expression for $\bar{m}_1/N$. We now show that one can easily derive a mean-field approximation to $\langle BFT \rangle$. In this approximation, one starts by separating the potential into the hard core repulsive and the attractive parts, and one replaces the attractions by a mean-field. If $W$ is the probability that the hard spherical core of the test particle will fit at an arbitrary point without overlapping with the hard cores of any other molecules that are already there, and if $\psi_{\text{attr}}$ is the attractive part of the potential felt by the test particle, then we can write

\[ \langle e^{-\psi/kT} \rangle = W(e^{-\psi_{\text{attr}}/kT}). \]

The probability $W$ is identified as $\rho/z_{HS}$, where $z_{HS}$ is the fugacity of the hard sphere fluid at density $\rho$. We replace the average of the exponential on the right hand side of (11) by the exponential of the average which we denote by $\psi_{m_f}$,
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\[ \psi_{m_f} = \rho \int_r \phi_{\text{attr}}(r) \, dr = 2a. \]  

(12)

\( \phi_{\text{attr}}(r) \) is the attractive component of the inter-molecular potential, \( \sigma \) is the diameter of the hard core, and

\[ a = -\frac{1}{2} \int_r \phi_{\text{attr}}(r) \, dr \]  

(13)

is van der Waals' parameter \( a \). Combining (11)–(13), we get

\[ \langle e^{-\psi/kT} \rangle = \rho/z_{HS} e^{2\alpha kT}. \]  

(14)

For hard sphere fluid, the density expansion provides a very good approximation to \( z_{HS} \) even at fairly high densities. Formally this is obtained by inverting the well-known (Hill 1956; Mayer and Mayer 1980) fugacity expansion of density

\[ \rho(z) = \sum_{l=1} lb_l(T) z^l, \]  

(15)

which can be inverted to give

\[ z_{HS}(\rho) = \rho e^{-F(\rho)}, \]  

(16)

At very low densities, \( z \) and \( \rho \) are practically identical, so the function \( F(\rho) \) must tend to zero as \( \rho \to 0 \). Therefore, it can be expressed as a power series in

\[ F(\rho) = \sum_{k=1} \beta_k^H \rho^k. \]  

(17)

The \( \beta_k^H \)'s can be identified as star (or irreducible cluster) integrals (Hill 1956; Mayer and Mayer 1980).

By combining (10), (14), (16) and (17) we obtain

\[ \frac{\bar{m}_1}{N} = e^{-2\alpha kT} \sum_{k=1} \beta_k^{HS} \rho^k. \]  

(18)

For temperatures below the critical temperature, (18) predicts an exponential fall with increasing density at lower densities. This behaviour has been observed in recent numerical calculations (Donoghue and Gibbs 1981).

We can also calculate the occupation number \( \bar{m}_k \) for cluster sizes larger than single particle if we make the following approximation

\[ \frac{Z_{N-k}}{Z_N} = \frac{Z_{N-1}}{Z_N} \times \frac{Z_{N-2}}{Z_{N-1}} \times \ldots \times \frac{Z_{N-k}}{Z_{N-k+1}} \]

\[ \approx \left( \frac{Z_{N-1}}{Z_N} \right)^k ; \quad k \ll N, \]  

(19)

The approximate relation (19) is reasonable for large systems so long as cluster size \( k \) is much smaller than total number of particles in the system. In this paper we shall
use (19) to compute \( \tilde{n}_k \) only for very small values of \( k \). Now, \( \tilde{n}_k \)'s are given by the following expression

\[
\frac{\tilde{n}_k}{N} = b_k p^{k-1} \left( \frac{\tilde{m}_1}{N} \right)^k.
\]

Equation (20) is very much similar to (2) which is the equilibrium solution of the kinetic equation of Becker and Doring (1935) for the time evolution of cluster sizes in nucleation. A closed form expression for the cluster integrals are given by (Mayer and Mayer 1980).

\[
b_k = \frac{1}{k^2} \sum_{m_1} \prod_{l} \left( k \beta_l \right)^{m_l} / m_l!; \sum m_l = k - 1.
\]

Pressure can be expressed as the sum of the mean cluster sizes

\[
p/kT = \rho \sum_{k=1}^{\tilde{n}_k} \left( \frac{\tilde{n}_k}{N} \right).
\]

Next, we present a calculation of the mean number of these cluster sizes for van der Waals' fluid. The reason for choosing van der Waals’ fluid is three-fold. First, all of the irreducible cluster integrals are available. Second, an extensive numerical calculation of the mean cluster size distribution for this system has recently been carried out by Donoghue and Gibbs (1981) who used the exact relation (9) to evaluate all the \( \tilde{m}_k \)'s. Their calculation was done numerically and was limited to small system sizes. Third, the mean-field argument is exact for this system.

The star integrals, \( \beta_k \)'s, can be found by expanding the van der Waals’ equation of state,

\[
\left( p + \frac{N^2 a}{V^2} \right) \left( \frac{V}{N} - b \right) = k_B T.
\]

For convenience, dimensional variables are introduced,

\[
p^* = \frac{b^2 p}{a}, \quad \rho^* = \frac{N b}{V}, \quad T^* = \frac{b k_B T}{a}.
\]

In this reduced unit

\[
\beta_{1,HS} = -2,
\]

\[
\beta_{k,HS} = \left( \frac{k+1}{k} \right).
\]

One can easily sum the series (17) to obtain

\[
F(\rho^*) = -\rho^*/1 - \rho^* + \ln(1 - \rho^*),
\]

so that (18) becomes,

\[
\frac{\tilde{m}_1}{N} (T^*, \rho^*) = (1/1 - \rho^*) \exp(-2\rho^*/T^* + \rho^*/1 - \rho^*).
\]
Other $m_k$'s are given by (20).

Equation (26) gives the explicit dependence of the fraction of monomers on the temperature and density of the system. This equation should prove useful in the study of nucleation phenomena, especially where the van der Waals' equation provides a good description for the gas phase.

We note that the above mean-field approximation can further be improved if we do a judicious separation of the total potential, e.g. the separation of potential introduced by Weeks, Anderson and Chandler (WCA) (Weeks et al 1971). This will lead to an augmented van der Waals' type description (Hansen and McDonald 1976) of the cluster sizes.

3. Results

Figure 1 describes the dependence of $m_1/N$ on the density at three temperatures below the critical point ($T^*_c = 0.296$). At low densities, $m_1/N$ decreases rapidly with increasing density. In the intermediate region, which is bounded by the two spinodal densities, the dependence of $m_1/N$ on $\rho^*$ is almost linear. This is in agreement with the numerical calculations of Donoghue and Gibbs (1981) who observed that large clusters appear in the system near the spinodal density. The larger clusters grow in the system as the population of the single particle clusters get depleted.

$m_1/N$ shows an increase at still higher densities. We have found that the density at which $m_1/N$ again starts to rise is very close to the density at which $\rho^*$ also starts to rise. However, Mayer's theory with volume independent clusters cannot be trusted near the pure liquid density where very large clusters appear in the system, and Mayer's theory breaks down.

![Figure 1](image.png)

Figure 1. The variation of the number-fraction of monomers ($m_1/N$) with the reduced density ($\rho^*$) at three different temperatures, all below the critical point.
Figure 2 describes the variation of the average occupation numbers $m_2/N$, $m_3/N$ and $m_4/N$ with density at a temperature below the critical point. As expected, all of them increase rapidly with density when the density of the system is small. Then they all reach maximum at densities which are little lower than the spinodal density. Beyond the spinodal density, there is a sharp drop in the population of these clusters and they pass through a linear region before they start rising again at a density close to the liquid density.

The sharp decrease in the population of these small clusters near the spinodal density indicates that the population is being shifted to the larger cluster sizes. The sudden appearance of these larger clusters indicates the onset of condensation.

Figure 3 depicts the variation of pressure with density; the pressure is computed from the mean numbers of the first four clusters with the help of (22). We see that the agreement of this pressure with the van der Waals' pressure is very good, even beyond the spinodal density. There is a small loop present in this pressure which is, of course, expected due to the mean-field approximation used in deriving (14) for $\langle BFT \rangle$. It is rather surprising that so few cluster sizes can give such a good description of the pressure of the system, even beyond the spinodal density.

From figure 1 and from (10), we can learn about the density dependence of $\langle BFT \rangle$. As density is increased past the spinodal density, $\langle BFT \rangle$ undergoes a sharp increase indicating the rapid increase of the attractive interactions in the system.

4. Discussion

There are two main results that have come out of the present work. First, we have shown that simple analytic expressions for the average number of small Mayer
clusters can be obtained in the mean-field limit. Thus, in order to obtain the population of these small clusters, we do not need to evaluate the full partition function as was done by Gibbs et al (1981) and by Donoghue and Gibbs (1981). Second, the main contribution to pressure at densities near the spinodal density arises only from the very small clusters.

The pressure computed from (22) becomes very large at a density \( \rho_1^* \) which is given by the solution of the following equation

\[
\ln \left( 1 - \rho_1^* \right) + \frac{\rho_1^*}{1 - \rho_1^*} = \frac{2\rho_1^*}{T^*}.
\]

The solution of this equation in fact coincides with the density at which \( (\partial p / \partial v)_T \) becomes zero for the second time i.e. at the spinodal point of the superheated van der Waals' liquid. The large liquid like clusters comparable in size to the volume of the system become important at this density and this gives rise to an explosive rise in the value of the pressure.

In conclusion, we want to re-emphasize that the clusters considered in this work are mathematical clusters. However, we have found that these clusters in many respects mimic the behaviour of real physical clusters. We have recently shown (Bagchi 1987) that Mayer's theory breaks down when large mathematical clusters appear in the system which happens near the condensation density. There are, however, some systems for which Mayer clusters do represent the physical reality, Bose-Einstein condensation in ideal Bose gas (Bagchi and Mohanty 1982; Mohanty et al 1982). In these cases, the symmetry properties of the wave function of Bose particles give rise to an effective attraction among the particles and large clusters appear precisely at the condensation density (Bagchi and Mohanty 1982; Mohanty et al 1982). In these cases, volume dependent cluster integrals are always positive.
and since there is no hard-core repulsion, the difference between mathematical and physical clusters do not exist. In the presence of hard core interactions in realistic systems, mathematical and physical clusters may have similar properties at low temperatures \( T \left( \frac{1}{T_c} \right) \) where the attractive part of the potential plays important role.

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