Statistical mechanics of hard spheres: validity of the basic relations of the scaled particle theory for frozen structures

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Abstract. In a previous article (J. Math. Phys. 36(201), 1995), an equation of state for a hard sphere system was derived from the basic relations of the scaled particle theory without making use of some specific properties of the fluid state; they were only involved in the calculation of the two parameters which appear in that equation. In a later article (Z. Phys. B 102(255), 1997) it was therefore used to describe the glassy states, assuming tacitly that the basic relations of the scaled particle theory not only hold for the fluid state, but also for frozen structures. That assumption shall now be discussed in more detail and it will be shown that the basic relations are valid for all possible states of the system.

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1. Introduction

In the scaled particle theory [1, 2] the so-called contact correlation function $G(y, \lambda)$ plays a central role. It fulfills a number of relations which form the basis of that theory; the aim of this paper is to show that they are not only valid for the fluid state, but also for frozen structures. That assumption shall now be discussed in more detail and it will be shown that the basic relations are valid for all possible states of the system.

The contact correlation function is closely related to the contact correlation function $G(y, \lambda)$, which we denote by $g(\lambda, \lambda)$.

In the next section we introduce singlet correlation functions which are related to the solute particle. They will allow us to generalize not only the definition of $G(y, \lambda)$, but also the derivations of the basic relations.

2. Fundamental concepts

In this paper, the following functions are of importance:

1. the singlet correlation function $g_1(r, \lambda)$ of the solute particle
2. the conditional singlet correlation function $g_2(r_1, r_2, \lambda)$ for the solvent particles around the solute
3. the pair correlation function $g_2(r_2 | r_1, \lambda)$ for the solvent particles around the solute

The particle diameter $\sigma$ is used as a unit of length. The above functions are defined as follows:

1. $V^{-1} g_1(r, \lambda) dr = \text{the probability of finding the center of the solute particle in } dr \text{ at } r$
2. $V^{-1} g_1(r_1 | r_2, \lambda) dr_2 = \text{the conditional probability of finding the center of a specific solvent particle in } dr_2 \text{ at } r_2 \text{ if the center of the solute is at } r_1$
3. $V^{-1} g_2(r_1, r_2, \lambda) dr_1 dr_2 = \text{the probability of finding the center of the solute particle in } dr_1 \text{ at } r_1 \text{ and the center of a specific solvent particle in } dr_2 \text{ at } r_2$

$g_1(r, \lambda)$ has the normalization

$$\int_V g_1(r, \lambda) dr = V$$

(2)

If $\lambda = \sigma$ (or $\sigma = \sigma'$) the above defined functions are identical with the usual correlation functions which we denote by $g_1(r)$, $g_1(r_2 | r_1)$ and $g_2(r_1, r_2)$ respectively. The local macroscopic density $\rho(r)$ is then given by

$$\rho(r) = \rho g_1(r)$$

(3)

where $\rho = N/V$. Only if the system is in the fluid state we have that $\rho(r) = \text{constant} = \rho$. In a one-phase system the function $g_1(r_2 | r_1, \lambda)$ depends only on the difference $r_1 - r_2$, which we denote by

$$g_1(r_2 | r_1, \lambda) = g(r_{12}, \lambda)$$

(4)
From the product rule of probabilities follows that
\[ g_2(r_1, r_2, \lambda) = g_1(r_1, \lambda)g(r_1, \lambda) \]
and that
\[ g_2(r_1, r_2) = g_1(r_1)g(r_1, \lambda) \]  
(6)
In the case of a fluid or an amorphous solid \( g(r, \lambda) \) depends only on \( r = |r| \) (and \( \lambda \)) whereas in the crystalline state it depends also on the direction of \( r \) which we denote by \( g(r, \lambda) = g(r, \theta, \phi, \lambda) \). Generally the radial distribution function for the solvent molecules around the solute is defined by
\[ g(r, \lambda) = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi g(r, \theta, \phi, \lambda) \sin \theta d\theta \]
so that for \( \lambda = \sigma \):
\[ g(r) = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi g(r, \theta, \phi) \sin \theta d\theta \]
(8)
Setting \( r = \lambda \) we obtain the contact value of \( g(\lambda, \lambda) \) which corresponds to the contact correlation function. Thus we have that
\[ G(y, \lambda) = g(\lambda, \lambda) \]
(9)
A consequence of the definition of \( g_1(r_2|r_1, \lambda) \) and of the fact that the presence of the solute particle is equivalent to the existence of an empty spherical region \( \Sigma \) with radius \( \lambda \) is the following assertion
\[ 4\pi \lambda^2 \rho G(y, \lambda) d\lambda = \text{the conditional probability of finding a particle center in the spherical shell with radii} \lambda \text{and} \lambda + d\lambda, \]
if the concentric sphere \( \Sigma \) with radius \( \lambda \) is empty.

It is important to note that \( G(y, \lambda) \) does not depend on the position vector \( r_1 \) of the sphere center, since \( g_1(r_2|r_1, \lambda) = g(r_2, \lambda) \) only depends on the difference \( r_1 - r_2 \). Furthermore, we will see in the next section that \( G(y, \lambda) \) is closely related to the following concepts:
1. the probability \( \pi_0(y, \lambda, r_1) \) that the sphere \( \Sigma \) with radius \( \lambda \) and with its center at \( r_1 \) is empty
2. the probability \( p_0(y, \lambda) \) of finding an empty sphere with radius \( \lambda \) anywhere in the system.

Generally, \( \pi_0 \) depends on the position of the sphere center. It is also clear that \( \pi_0 \) and \( p_0 \) are related by
\[ p_0(y, \lambda) = \frac{1}{V} \int_{V'} \pi_0(y, \lambda, r_1) dr_1 \]
(10)
If the system is in the fluid state, we have that \( \pi_0(y, \lambda, r_1) = p_0(y, \lambda) \) since in this case \( \pi_0(y, \lambda, r_1) \) does not depend on the position of the sphere.

Let us now consider the potential energy function \( U_N(\lambda, r_1, r_2, \ldots, r_N) \) of the system. The potential of the interaction between two solvent particles is of the form \( u(r_{ij}) = \phi(r_{ij}/\sigma) \) where \( i, j > 1 \) if we assign the label 1 to the solute particle. For hard spheres we have that \( \phi(x) = 0 \) if \( x > 1 \) and \( \phi(x) = \infty \) if \( x \leq 1 \). The potential of the interaction between the solute particle and one of the others is then given by \( u(r_{1j}/\lambda) \) (\( j > 1 \)) if \( \lambda = 1 \) is set. It is clear that
\[ U_N(\lambda, r_1, r_2, \ldots, r_N) = U_{N-1}(r_2, \ldots, r_N) + \sum_{j=2}^N u \left( \frac{r_{1j}}{\lambda} \right) \]
(11)
where \( U_{N-1}(r_2, \ldots, r_N) \) denotes the potential energy function of the system without the solute particle. The configuration integral takes the form
\[ Q_N(\lambda, V) = \int_V e^{-U_N(\lambda, r_1, r_2, \ldots, r_N)/kT} dr_1 dr_2 \ldots dr_N \]
(12)
and the pair correlation function of the solvent particles around the solute is given by
\[ g_2(r_1, r_2, \lambda) = \frac{V^2}{Q_N(\lambda, V)} \int_V e^{-U_N(\lambda, r_1, r_2, \ldots, r_N)/kT} dr_3 \ldots dr_N \]
(13)

3. The basic relations of the scaled particle theory

In [1] it was shown that the contact correlation function of a hard sphere fluid fulfills the following relations (\( Q = \) compression factor = \( pV/NkT \) and \( y = N\sigma^3/6V = \) packing fraction)
\[ G(y, \infty) = Q(y) \]
(14)
\[ Q(y) = 1 + 4yG(y, 1) \]
(15)
\[ \frac{d}{dy} (yG(y)) = \frac{1}{1 - y} + 24y \int_{1/2}^1 \frac{d}{dy} (G(y, \lambda)) \lambda^2 d\lambda \]
(16)
\[ G \left( y, \frac{1}{2} \right) = \frac{1}{1 - y} \]
(17)
\[ G' \left( y, \frac{1}{2} \right) = \frac{6y}{(1 - y)^2} \]
(18)
and
\[ G'' \left( y, \frac{1}{2} \right) = 12 \frac{1 + 5y^2}{(1 - y)^3} - \frac{12Q(y)}{1 - y} \]
(19)

Here
\[ G' \left( y, \frac{1}{2} \right) = \lim_{\lambda \to 1/2} \frac{dG(y, \lambda)}{d\lambda}, \text{ etc.} \]

4. Validity of the basic relations for the fluid state

In the proof of the relation (14) no restrictions with regard to the phase of the system appear [1–3]. On the other hand, in the derivations of (15) and (16) which can be found in the literature it is – as far as we know – always supposed that the pair correlation function \( g_2(r_1, r_2, \lambda) \) may be replaced by the radial distribution function \( g(r_{12}, \lambda) \), which is only allowed if the system is in the fluid state [1, 3, 4]. The same holds for the relations (17)–(19); in this section, their derivation [1] will be discussed in more detail, since some of its elements will be used in Sect. 5.

We consider a spherical region \( \Sigma \) with radius \( \lambda \) and with its center at \( r_1 \). From the above interpretation of \( G(y, \lambda) \) then follows that
\[ 1 - 4\pi \lambda^2 \rho G(y, \lambda) d\lambda = \text{the conditional probability that the spherical shell with radii} \lambda \text{and} \lambda + d\lambda \]
(20)