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GRAND PARTITION FUNCTION FUNCTIONAL
FOR SIMPLE FLUIDS

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Функціонал великої статистичної суми для простих плиннів

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Анотація. В роботі послідовно представлено метод колективних змінних з системою відліку для класичної системи багатьох взаємодіючих частинок у великому канонічному ансамблі. Основна увага приділена деталям обчислень. Зокрема, використання повних кореляційних функцій означених для великого канонічного ансамблю дозволило детально дослідити кумулянти великої статистичної суми системи відліку. Показано, що будь-який кумулянт \mathfrak{M}_n можна представити як добуток трьох компонент: середнього числа частинок системи відліку, символ Кронекера n хвильових векторів, і n -частинкового структурного фактора. Отримано функціональний вираз для великої статистичної суми в якому всі величини представлені в явному вигляді. Розраховані координати критичної точки в наближенні середнього поля.

Grand partition function functional for simple fluids

I.R. Yukhnovskii, R.V. Romanik

Abstract. In this paper, we will systematically present the method of collective variables with a reference system for a classical many-particle interacting system in the grand canonical ensemble. The emphasis will be placed on the details of calculations. In particular, the usage of total correlation functions defined for the grand canonical ensemble allows us to investigate very accurately the cumulants of the grand partition function for the reference system. It is shown that any cumulant \mathfrak{M}_n can be expressed as a product of three components: the average particle number within the reference system, a Kronecker's symbol for n wave vectors, and the n -particle structure factor.

The functional expression for the grand partition function is derived, with all coefficients explicitly defined. The coordinates of the critical point are computed in the mean field approximation.

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ФУНКЦІОНАЛ ВЕЛИКОЇ СТАТИСТИЧНОЇ СУМИ ДЛЯ ПРОСТИХ
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Contents

1. Introduction	2
2. Problem statement	3
2.1. Potential energy of interparticle interaction	4
2.2. The Grand Partition Function with a reference system singled out	6
3. The Jacobian of transformation	8
4. Cumulants	10
4.1. Calculation of cumulants	10
4.2. Cumulants $\mathfrak{M}_n(\mathbf{k}^n)$ expressed via Fourier components of the total correlation functions $\hat{h}^{(n)}(\mathbf{k}^n)$	11
4.3. Explicit expressions for cumulants as functions of wave- vector and packing fraction	14
4.4. Cumulants at $\mathbf{k}_i = 0$	17
4.5. Cumulants as functions of packing fraction for the hard- spheres system	17
5. Grand partition function in the representation of collec- tive variables	18
5.1. Integration over ω	23
5.2. Coefficients of the effective Hamiltonian	27
6. Effective Hamiltonian in the mean-field approximation	30
6.1. Naive approximation	31
6.2. Applying condition $\langle N \rangle_0 = \langle N \rangle$	33
7. Conclusion	36
A. Total correlation functions	36
A.1. Definitions	36
A.2. Expressed via $g^{(n)}$ and $h^{(m<n)}$	37
A.3. Expressed via $g^{(n)}$ through $g^{(1)}$	38
A.4. Fourier components of total correlation functions	39
A.5. Fourier transform of the radial correlation function for the hard-spheres system	40
A.6. Some recurrence relations for correlation functions	41

B. Cumulants calculation	42
B.1. $n = 1$	42
B.2. $n = 2$	43
C. A method of calculation for cumulants at $\mathbf{k}_i = 0$	45
D. Notation	47

1. Introduction

The method of collective variables (CV) was developed in [1, 2], and applied to description of classical equilibrium systems [3] and phase transitions of the second order [4]. A more thorough review of results achieved with the method is presented in [5]. The method was then extended to describe the system of interacting particles in the grand canonical ensemble. For simple fluids, the noticeable works are [6–8]. For many-component systems see [9, 10]. The concept of a reference system (RS) was used along with the CV method. The interaction between particles was arbitrary divided into short-range repulsive and long-range attractive parts. The short-range repulsive part was usually considered as the reference system. In the current work we systematically introduce the collective variables in the grand canonical ensemble. We would like to emphasize the following distinguishable points of this work.

- The factor of $1/\sqrt{N}$ is not used in the expressions for the Fourier components of the microscopic particle density, which somewhat simplifies the summation over N in the grand partition function (GPF).
- We use total correlation functions defined in the grand canonical ensemble which makes the expressions for cumulants of the reference system grand partition function much simpler compared to ones obtained in [7, 8]. This also helps avoid complications related to explicitly performing thermodynamic limit in those expressions.
- The theory is presented in such a way that the reference system is not specified in general but is chosen as a hard-sphere system only to obtain numerical results for some quantities.

We obtain an explicit functional expression for the GPF of the classical many-particle interacting system with all coefficients known. The obtained expression is analogous to the one obtained in [7] except the coefficients are revisited using more modern definitions for total correlation

functions. Some properties of these correlation functions are additionally investigated in Appendix A. We conclude the work with calculation of the critical point coordinates in the mean-field (MF) approximation. The obtained value for the packing fraction is the same as was obtained in [8], thus showing that for this quantity a higher approach still needs to be developed. The obtained value for the critical temperature is higher than the corresponding value reported in [8], since the latter was obtained in a non-MF approximation. Finally, the critical value calculated for the excess chemical potential is published for the first time.

2. Problem statement

Consider a classical system of identical particles interacting via a pairwise additive potential $U(|\mathbf{r}|)$, where \mathbf{r} is the distance in the three-dimensional space. There are two assumptions made regarding the interaction between particles. First, the interaction can be decomposed into two parts

$$U(r_{ij}) = \Psi(r_{ij}) + \Phi(r_{ij}), \quad (2.1)$$

where $\Psi(r_{ij})$ is responsible for the repulsion between particles - denoted by i and j - at short distances, and $\Phi(r_{ij})$ for the attraction at long distances, $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$. Second, that the attraction part of the potential possesses a well-behaved Fourier transform. For more details on the interaction potential, see Section 2.1.

A physical observable dependent on the particle coordinates is, in general, a functional of the microscopic particle density defined as

$$n(\mathbf{r}) = \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j), \quad (2.2)$$

where \mathbf{r}_j is the coordinate of the j -th particle, N is the number of particles in the system, $\delta(\dots)$ is the Dirac's δ -function. The quantity $n(\mathbf{r})$ can be represented in the form of a Fourier series:

$$n(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k}} \hat{\rho}_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}, \quad (2.3)$$

where $\sum_{\mathbf{k}} = \sum_{k_x} \sum_{k_y} \sum_{k_z}$, $k_i = \frac{2\pi}{\sqrt{V}^{1/3}} n_i$, $i = x, y, z$, $n_i = 0, \pm 1, \pm 2, \dots$. V is the system volume, so that

$$\int_V n(\mathbf{r}) d\mathbf{r} = N.$$

The Fourier component $\hat{\rho}_{\mathbf{k}}$ is of the form:

$$\hat{\rho}_{\mathbf{k}} = \sum_{j=1}^N \exp(-i\mathbf{k}\mathbf{r}_j), \quad \hat{\rho}_{\mathbf{k}=0} = N. \quad (2.4)$$

Alternatively,

$$\hat{\rho}_{\mathbf{k}} = \hat{\rho}_{\mathbf{k}}^c - i\hat{\rho}_{\mathbf{k}}^s, \quad \hat{\rho}_{\mathbf{k}}^c = \sum_{i=1}^N \cos(\mathbf{k}\mathbf{r}_i), \quad \hat{\rho}_{\mathbf{k}}^s = \sum_{i=1}^N \sin(\mathbf{k}\mathbf{r}_i) \quad (2.5)$$

Let the system be open. The probability that an open system contains exactly N particles is given by:

$$p(N) = \frac{1}{\Xi} \frac{z^N}{N!} Z_N. \quad (2.6)$$

Here Ξ is the grand partition function (GPF) of the system:

$$\Xi = \sum_{N=0}^{\infty} \frac{z^N}{N!} Z_N. \quad (2.7)$$

where z is the activity:

$$z = \frac{\exp(\beta\mu)}{\Lambda^3} \quad (2.8)$$

with β being the inverse temperature, and μ the chemical potential, $\Lambda = (2\pi\beta\hbar^2/m)^{1/2}$ the de Broglie thermal wavelength, \hbar the Planck's constant, m the mass of a particle.

Z_N is the configuration integral:

$$Z_N = \int \exp(-\beta U_N(\mathbf{r}_1, \dots, \mathbf{r}_N)) d\mathbf{r}^N \quad (2.9)$$

where U_N is the potential energy of interparticle interaction, and the following notation is understood $d\mathbf{r}^N \equiv d\mathbf{r}_1 \dots d\mathbf{r}_N$.

Given the GPF, all the thermodynamic properties of the system can be obtained.

2.1. Potential energy of interparticle interaction

Based on the assumption made in (2.1), the potential energy of the interparticle interaction can be written in the form:

$$\begin{aligned} U_N(\mathbf{r}^N) &= \Psi_N(\mathbf{r}^N) + \Phi_N(\mathbf{r}^N) \\ &= \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \Psi(r_{ij}) + \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \Phi(r_{ij}) \end{aligned} \quad (2.10)$$

where the following notation is introduced $\mathbf{r}^N \equiv \mathbf{r}_1, \dots, \mathbf{r}_N$. Here

$$\Psi_N = \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \Psi(r_{ij}) \quad (2.11)$$

is the potential energy of the short-range repulsive interaction, and

$$\Phi_N = \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \Phi(r_{ij}) \quad (2.12)$$

is the long-range attractive counterpart.

One approach to separation the long- and short-range interaction is to choose $\Psi(r)$ as the hard-sphere (HS) potential

$$\Psi(r) = \begin{cases} \infty, & r \leq \sigma, \\ 0, & r > \sigma \end{cases} \quad (2.13)$$

where σ denotes the hard-sphere diameter.

Then $\Phi(r)$ can be chosen so that it possesses a potential well at $r > \sigma$, e.g.

$$\Phi(r) = \begin{cases} 0, & r \leq \sigma \\ U_{Morse}(r), & r > \sigma, \end{cases} \quad (2.14)$$

using the Morse potential

$$U_{Morse}(r) = \varepsilon \{ \exp\{-2(r - R_0)/\alpha\} - 2 \exp\{-(r - R_0)/\alpha\} \} \quad (2.15)$$

with ε being the characteristic energy of the potential, R_0 the coordinate of the minimum, and α the effective range of action. In what follows, we develop a general approach to deal with the system of interacting particles. Particular forms of the reference system and attractive part of the potential are chosen to obtain some numerical and graphical results.

In general we assume that the attractive part of the interaction potential possesses a well behaved Fourier component $\hat{\Phi}_{\mathbf{k}}$ such that:

$$\Phi(r) = \frac{1}{V} \sum_{\mathbf{k}} \hat{\Phi}_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} = \frac{1}{(2\pi)^3} \int d\mathbf{k} \hat{\Phi}_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}, \quad (2.16)$$

and

$$\hat{\Phi}_{\mathbf{k}} = \int \Phi(r) e^{-i\mathbf{k}\mathbf{r}} d\mathbf{r}. \quad (2.17)$$

In such a case, the potential energy of the attractive interaction can be written in terms of $\hat{\rho}_{\mathbf{k}}$:

$$\begin{aligned}\Phi_N(\mathbf{r}^N) &= \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \Phi(r_{ij}) \\ &= \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \frac{1}{V} \sum_{\mathbf{k}} \hat{\Phi}_{\mathbf{k}} e^{i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)} \\ &= \frac{1}{2V} \sum_{\mathbf{k}} \hat{\Phi}_{\mathbf{k}} \hat{\rho}_{\mathbf{k}} \hat{\rho}_{-\mathbf{k}} - \frac{N}{2V} \sum_{\mathbf{k}} \hat{\Phi}_{\mathbf{k}}.\end{aligned}\quad (2.18)$$

Note, that in our approach we put $\Phi(0) = 0$, see (2.14), thus

$$\frac{1}{V} \sum_{\mathbf{k}} \hat{\Phi}_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}|_{\mathbf{r}=0} = \frac{1}{V} \sum_{\mathbf{k}} \hat{\Phi}_{\mathbf{k}} \equiv \Phi(0) = 0$$

and the second term for Φ_N vanishes

$$\Phi_N(\mathbf{r}^N) = \frac{1}{2V} \sum_{\mathbf{k}} \hat{\Phi}_{\mathbf{k}} \hat{\rho}_{\mathbf{k}} \hat{\rho}_{-\mathbf{k}}.\quad (2.19)$$

2.2. The Grand Partition Function with a reference system singled out

The GPF is now written as

$$\Xi = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{N! \Lambda^{3N}} \int \exp(-\beta\Psi_N(\mathbf{r}^N) - \beta\Phi_N(\mathbf{r}^N)) d\mathbf{r}^N.\quad (2.20)$$

Let's consider a system characterized only by the repulsive part of the interaction potential as a reference system (RS). The GPF for the RS system is

$$\Xi_0 = \sum_{N=0}^{\infty} \frac{1}{N!} \frac{\exp(\beta\mu_0 N)}{\Lambda^{3N}} \int \exp(-\beta\Psi_N(\mathbf{r}^N)) d\mathbf{r}^N\quad (2.21)$$

where μ_0 is the RS chemical potential. Now, the GPF is expressed as

$$\begin{aligned}\Xi &= \Xi_0 \sum_{N=0}^{\infty} \frac{\exp(\beta\mu_0 N)}{N! \Lambda^{3N}} \times \\ &\times \int \frac{\exp(-\beta\Phi_N(\mathbf{r}^N))}{\Xi_0} \exp(\beta(\mu - \mu_0)N - \beta\Phi_N(\mathbf{r}^N)) d\mathbf{r}^N.\end{aligned}$$

Taking into account (2.19) and (2.4), the second exponent under the integral can be expressed in terms of $\hat{\rho}_{\mathbf{k}}$:

$$\exp(\beta(\mu - \mu_0)N - \beta\Phi_N(\mathbf{r}^N)) = \exp\left(h\hat{\rho}_0 - \frac{1}{2} \sum_{\mathbf{k}} \alpha(k) \hat{\rho}_{\mathbf{k}} \hat{\rho}_{-\mathbf{k}}\right).\quad (2.22)$$

Here the following notations were introduced:

$$h = \beta(\mu - \mu_0); \quad \alpha(k) = \frac{\beta\hat{\Phi}_{\mathbf{k}}}{V}.\quad (2.23)$$

Let's define the set of collective variables $\rho_{\mathbf{k}} = \rho_{\mathbf{k}}^c - i\rho_{\mathbf{k}}^s$ via the following expressions:

$$\begin{aligned}\hat{\rho}_{\mathbf{k}}^c &= \int \rho_{\mathbf{k}}^c J(\rho - \hat{\rho})(d\rho), \\ \hat{\rho}_{\mathbf{k}}^s &= \int \rho_{\mathbf{k}}^s J(\rho - \hat{\rho})(d\rho), \\ \hat{\rho}_0 &= \int \rho_0 J(\rho - \hat{\rho})(d\rho) = N.\end{aligned}\quad (2.24)$$

Here

$$J(\rho - \hat{\rho}) = \delta(\rho_0 - \hat{\rho}_0) \prod'_{\mathbf{k}} \delta(\rho_{\mathbf{k}}^c - \hat{\rho}_{\mathbf{k}}^c) \delta(\rho_{\mathbf{k}}^s - \hat{\rho}_{\mathbf{k}}^s),\quad (2.25)$$

$$(d\rho) = d\rho_0 \prod'_{\mathbf{k}} d\rho_{\mathbf{k}}^c d\rho_{\mathbf{k}}^s.\quad (2.26)$$

The 'prime' sign over the product means that the wave-vector takes on values only from the upper semi-space of the reciprocal space, i.e. $k_z > 0$, and $\mathbf{k} \neq 0$.

The collective variables $\rho_{\mathbf{k}}$ possess the following properties:

$$\rho_{-\mathbf{k}} = \rho_{\mathbf{k}}^*; \quad \rho_{\mathbf{k}}^c = \rho_{-\mathbf{k}}^c; \quad \rho_{\mathbf{k}}^s = -\rho_{-\mathbf{k}}^s.\quad (2.27)$$

Equations (2.24) can be written in a more concise form

$$\hat{\rho}_{\mathbf{k}} = \int \rho_{\mathbf{k}} J(\rho - \hat{\rho})(d\rho).\quad (2.28)$$

Valid is also a more general equality

$$f(\hat{\rho}_{\mathbf{k}}) = \int f(\rho_{\mathbf{k}}) J(\rho - \hat{\rho})(d\rho),\quad (2.29)$$

where f is some function of $\hat{\rho}_{\mathbf{k}}$. Applied to (2.22), it leads

$$\begin{aligned} \exp(\beta(\mu - \mu_0)N - \beta\Phi_N(\mathbf{r}^N)) &= \exp\left(h\hat{\rho}_0 - \frac{1}{2} \sum_{\mathbf{k}} \alpha(k)\hat{\rho}_{\mathbf{k}}\hat{\rho}_{-\mathbf{k}}\right) \\ &= \int \exp\left(h\rho_0 - \frac{1}{2} \sum_{\mathbf{k}} \alpha(k)\rho_{\mathbf{k}}\rho_{-\mathbf{k}}\right) J(\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}})(d\rho). \end{aligned} \quad (2.30)$$

And for the GPF one has:

$$\Xi = \Xi_0 \int \exp\left(h\rho_0 - \frac{1}{2} \sum_{\mathbf{k}} \alpha(k)\rho_{\mathbf{k}}\rho_{-\mathbf{k}}\right) \tilde{\mathfrak{J}}(\rho)(d\rho) \quad (2.31)$$

where the Jacobian function is defined as

$$\begin{aligned} \tilde{\mathfrak{J}}(\rho) &= \frac{1}{\Xi_0} \sum_{N=0}^{\infty} \frac{z_0^N}{N!} \int \exp(-\beta\Psi_N(\mathbf{r}^N)) J(\rho - \hat{\rho}) d\mathbf{r}^N \\ &= \langle J(\rho - \hat{\rho}) \rangle_{RS}. \end{aligned} \quad (2.32)$$

Here $z_0 = \exp(\beta\mu_0/\Lambda^3)$ is the activity of the reference system, and the average value over the reference system is defined as

$$\langle \dots \rangle_{RS} = \Xi_0^{-1} \sum_{N=0}^{\infty} \frac{z_0^N}{N!} \int \exp(-\beta\Psi_N(\mathbf{r}^N)) \dots d\mathbf{r}^N. \quad (2.33)$$

3. The Jacobian of transformation

Let's rewrite the expression for the Jacobian (2.32) using the integral representation for δ -functions:

$$\delta(\rho_0 - \hat{\rho}_0) \prod_{\mathbf{k}} \delta(\rho_{\mathbf{k}}^c - \hat{\rho}_{\mathbf{k}}^c) \delta(\rho_{\mathbf{k}}^s - \hat{\rho}_{\mathbf{k}}^s) = \int \exp\left(2\pi i \sum_{\mathbf{k}} (\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}})\omega_{\mathbf{k}}\right) (d\omega),$$

where $\omega_{\mathbf{k}}$ is a variable conjugate to $\rho_{\mathbf{k}}$

$$\omega_{\mathbf{k}} = \frac{1}{2}(\omega_{\mathbf{k}}^c + i\omega_{\mathbf{k}}^s), \quad (3.1)$$

$$(d\omega) = d\omega_0 \prod_{\mathbf{k}} d\omega_{\mathbf{k}}^c d\omega_{\mathbf{k}}^s. \quad (3.2)$$

The Jacobian can now be expressed as

$$\begin{aligned} \mathfrak{J}(\rho) &= \frac{1}{\Xi_0} \sum_{N=0}^{\infty} \frac{z_0^N}{N!} \times \\ &\quad \times \int \exp\left(-\beta\Psi_N(\mathbf{r}^N) + i2\pi \sum_{\mathbf{k}} (\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}})\omega_{\mathbf{k}}\right) (d\omega) d\mathbf{r}^N \\ &= \int \exp\left(i2\pi \sum_{\mathbf{k}} \rho_{\mathbf{k}}\omega_{\mathbf{k}}\right) \tilde{\mathfrak{J}}(\omega)(d\omega) \end{aligned} \quad (3.3)$$

where the following notation is introduced

$$\tilde{\mathfrak{J}}(\omega) = \frac{1}{\Xi_0} \sum_{N=0}^{\infty} \frac{z_0^N}{N!} \int \exp\left(-\beta\Psi_N(\mathbf{r}^N) - i2\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}}\hat{\rho}_{\mathbf{k}}\right) d\mathbf{r}^N. \quad (3.4)$$

The expression for $\tilde{\mathfrak{J}}(\omega)$ can be expanded into a cumulant series to give

$$\tilde{\mathfrak{J}}(\omega) = \exp\left(\sum_{n \geq 1} D_n(\omega)\right) \quad (3.5)$$

where

$$D_n(\omega) = \frac{(-i2\pi)^n}{n!} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_n}. \quad (3.6)$$

The cumulants \mathfrak{M}_n are calculated by the following formula:

$$\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) = \frac{1}{(-i2\pi)^n} \left(\frac{\partial^n \ln \tilde{\mathfrak{J}}(\omega)}{\partial \omega_{\mathbf{k}_1} \dots \partial \omega_{\mathbf{k}_n}} \right)_{\omega_{\mathbf{k}_i}=0} \quad (3.7)$$

The calculation of the cumulants \mathfrak{M}_n is the objective of the next Section 4.

The Jacobian $\mathfrak{J}(\rho)$ is now expressed as

$$\begin{aligned} \mathfrak{J}(\rho) &= \int \exp\left(i2\pi \sum_{\mathbf{k}} \rho_{\mathbf{k}}\omega_{\mathbf{k}} + \sum_{n \geq 1} D_n(\omega)\right) (d\omega) \\ &= \int \exp\left(i2\pi \sum_{\mathbf{k}} \rho_{\mathbf{k}}\omega_{\mathbf{k}} + \sum_{n \geq 1} \frac{(-i2\pi)^n}{n!} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_n}\right) (d\omega) \end{aligned}$$

The partition function is now written as

$$\begin{aligned} \Xi &= \Xi_0 \int \exp \left[h\rho_0 - \frac{1}{2} \sum_{\mathbf{k}} \alpha(\mathbf{k}) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right] \\ &\times \exp \left(i2\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} + \right. \\ &\left. + \sum_{n \geq 1} \frac{(-i2\pi)^n}{n!} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_n} \right) (d\omega)(d\rho) \end{aligned} \quad (3.8)$$

4. Cumulants

4.1. Calculation of cumulants

Let's calculate $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$ based on Eqs. (3.7), (3.4). To simplify notation for the average value defined in (2.33), the subscript 0 will be used to indicate RS

$$\langle \dots \rangle_0 \equiv \langle \dots \rangle_{RS}$$

For the first cumulant one gets:

$$\mathfrak{M}_1(\mathbf{k}) = \frac{1}{(-i2\pi)} \frac{\partial \ln \tilde{\mathfrak{J}}(\omega)}{\partial \omega_{\mathbf{k}_1}} \Big|_{\omega_{\mathbf{k}_i}=0} = \langle \hat{\rho}_{\mathbf{k}} \rangle_0 \quad (4.1)$$

For the second cumulant:

$$\mathfrak{M}_2(\mathbf{k}_1, \mathbf{k}_2) = \frac{1}{(-i2\pi)^2} \frac{\partial^2 \ln \tilde{\mathfrak{J}}(\omega)}{\partial \omega_{\mathbf{k}_1} \partial \omega_{\mathbf{k}_2}} \Big|_{\omega_{\mathbf{k}_i}=0} = \langle \hat{\rho}_{\mathbf{k}_1} \hat{\rho}_{\mathbf{k}_2} \rangle_0 - \langle \hat{\rho}_{\mathbf{k}_1} \rangle_0 \langle \hat{\rho}_{\mathbf{k}_2} \rangle_0$$

Continuing this procedure, for the next cumulants one gets:

$$\begin{aligned} \mathfrak{M}_3(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) &= \langle \hat{\rho}_{\mathbf{k}_1} \hat{\rho}_{\mathbf{k}_2} \hat{\rho}_{\mathbf{k}_3} \rangle_0 \\ &- \sum_{\mathbf{l}=\left\{ \begin{smallmatrix} 1,2,3 \\ 1,3,2 \\ 2,3,1 \end{smallmatrix} \right\}} \langle \hat{\rho}_{\mathbf{k}_{l_1}} \hat{\rho}_{\mathbf{k}_{l_2}} \rangle_0 \langle \hat{\rho}_{\mathbf{k}_{l_3}} \rangle_0 \\ &+ 2 \langle \hat{\rho}_{\mathbf{k}_1} \rangle_0 \langle \hat{\rho}_{\mathbf{k}_2} \rangle_0 \langle \hat{\rho}_{\mathbf{k}_3} \rangle_0 \end{aligned} \quad (4.2)$$

$$\begin{aligned} \mathfrak{M}_4(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4) &= \langle \hat{\rho}_{\mathbf{k}_1} \hat{\rho}_{\mathbf{k}_2} \hat{\rho}_{\mathbf{k}_3} \hat{\rho}_{\mathbf{k}_4} \rangle_0 \\ &- \sum_{\mathbf{l}=\left\{ \begin{smallmatrix} 1,2,3,4 \\ 1,2,4,3 \\ 1,3,4,2 \\ 2,3,4,1 \end{smallmatrix} \right\}} \langle \hat{\rho}_{\mathbf{k}_{l_1}} \hat{\rho}_{\mathbf{k}_{l_2}} \hat{\rho}_{\mathbf{k}_{l_3}} \rangle_0 \langle \hat{\rho}_{\mathbf{k}_{l_4}} \rangle_0 \\ &- \sum_{\mathbf{l}=\left\{ \begin{smallmatrix} 1,2,3,4 \\ 1,3,2,4 \\ 1,4,2,3 \end{smallmatrix} \right\}} \langle \hat{\rho}_{\mathbf{k}_{l_1}} \hat{\rho}_{\mathbf{k}_{l_2}} \rangle_0 \langle \hat{\rho}_{\mathbf{k}_{l_3}} \hat{\rho}_{\mathbf{k}_{l_4}} \rangle_0 \\ &+ 2 \sum_{\mathbf{l}=\left\{ \begin{smallmatrix} 1,2,3,4 \\ 1,3,2,4 \\ 1,4,2,3 \\ 2,3,1,4 \\ 2,4,1,3 \\ 3,4,1,2 \end{smallmatrix} \right\}} \langle \hat{\rho}_{\mathbf{k}_{l_1}} \hat{\rho}_{\mathbf{k}_{l_2}} \rangle_0 \langle \hat{\rho}_{\mathbf{k}_3} \rangle_0 \langle \hat{\rho}_{\mathbf{k}_4} \rangle_0 \\ &- 6 \langle \hat{\rho}_{\mathbf{k}_1} \rangle_0 \langle \hat{\rho}_{\mathbf{k}_2} \rangle_0 \langle \hat{\rho}_{\mathbf{k}_3} \rangle_0 \langle \hat{\rho}_{\mathbf{k}_4} \rangle_0 \end{aligned} \quad (4.3)$$

The expressions in the right-hand sides of (4.1)-(4.3) can be called cumulant averages of $\hat{\rho}_{\mathbf{k}}$, since they remind formulae for cumulants expressed via non-central moments. In other words, if $\langle \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_n} \rangle$ are considered non-central moments (of a probability distribution), then $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$ can be considered as cumulants (semi-invariants) and the relationships between them are known [11].

As per our knowledge, the generic expression for cumulant average is not found so far, however, \mathfrak{M}_n can be derived for any n based on generating functional $\ln \tilde{\mathfrak{J}}(\omega)$ by virtue of (3.7).

4.2. Cumulants $\mathfrak{M}_n(\mathbf{k}^n)$ expressed via Fourier components of the total correlation functions $\hat{h}^{(n)}(\mathbf{k}^n)$

In this subsection, explicit expressions for cumulants \mathfrak{M}_n are presented in terms of the Fourier components of total correlation functions $\hat{h}^{(n)}$. See Appendix A for the definition and some properties of total correlation functions. The calculation of the first two cumulants is presented in details in Appendix B.

$$\mathfrak{M}_1(\mathbf{k}) = \rho \hat{h}^{(1)}(\mathbf{k}) = \langle N \rangle_0 \delta_{\mathbf{k}} \quad (4.4)$$

$$\begin{aligned} \mathfrak{M}_2(\mathbf{k}_1, \mathbf{k}_2) &= \rho \hat{h}^{(1)}(\mathbf{k}_1 + \mathbf{k}_2) + \rho^2 \hat{h}^{(2)}(\mathbf{k}_1, \mathbf{k}_2) \\ &= \langle N \rangle_0 \delta_{\mathbf{k}_1 + \mathbf{k}_2} (1 + \rho \hat{h}^{(2)}(\mathbf{k}_1)). \end{aligned} \quad (4.5)$$

$$\begin{aligned}
\mathfrak{M}_3(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) &= \rho \hat{h}^{(1)}(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3) \\
&+ \rho^2 \sum_{\mathbf{l}=\left\{\begin{smallmatrix} 1,2,3 \\ 1,3,2 \\ 2,3,1 \end{smallmatrix}\right\}} \hat{h}^{(2)}(\mathbf{k}_{l_1} + \mathbf{k}_{l_2}, \mathbf{k}_{l_3}) \\
&+ \rho^3 \hat{h}^{(3)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) \\
&= \langle N \rangle_0 \delta_{\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3} \left[1 + \rho (\hat{h}^{(2)}(\mathbf{k}_1) + \hat{h}^{(2)}(\mathbf{k}_2) + \hat{h}^{(2)}(\mathbf{k}_1 + \mathbf{k}_2)) \right. \\
&\quad \left. + \rho^2 \hat{h}^{(3)}(\mathbf{k}_1, \mathbf{k}_2) \right]. \tag{4.6}
\end{aligned}$$

$$\begin{aligned}
\mathfrak{M}_4(\mathbf{k}_1, \dots, \mathbf{k}_4) &= \rho \hat{h}^{(1)}(\mathbf{k}_1 + \dots + \mathbf{k}_4) \\
&+ \rho^2 \sum_{\mathbf{l}=\left\{\begin{smallmatrix} 1,2,3,4 \\ 1,2,4,3 \\ 1,3,4,2 \\ 2,3,4,1 \end{smallmatrix}\right\}} \hat{h}^{(2)}(\mathbf{k}_{l_1} + \mathbf{k}_{l_2} + \mathbf{k}_{l_3}, \mathbf{k}_{l_4}) \\
&+ \rho^2 \sum_{\mathbf{l}=\left\{\begin{smallmatrix} 1,2,3,4 \\ 1,3,2,4 \\ 1,4,2,3 \end{smallmatrix}\right\}} \hat{h}^{(2)}(\mathbf{k}_{l_1} + \mathbf{k}_{l_2}, \mathbf{k}_{l_3} + \mathbf{k}_{l_4}) \\
&+ \rho^3 \sum_{\mathbf{l}=\left\{\begin{smallmatrix} 1,2,3,4 \\ 1,3,2,4 \\ 1,4,2,3 \\ 2,3,1,4 \\ 2,4,1,3 \\ 3,4,1,2 \end{smallmatrix}\right\}} \hat{h}^{(3)}(\mathbf{k}_{l_1} + \mathbf{k}_{l_2}, \mathbf{k}_{l_3}, \mathbf{k}_{l_4}) \\
&+ \rho^4 \hat{h}^{(4)}(\mathbf{k}_1, \dots, \mathbf{k}_4); \tag{4.7}
\end{aligned}$$

$$\begin{aligned}
\mathfrak{M}_4(\mathbf{k}_1, \dots, \mathbf{k}_4) &= \langle N \rangle_0 \delta_{\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4} \\
&\times \left[1 + \rho \sum_{l=1}^4 \hat{h}^{(2)}(\mathbf{k}_l) + \rho \sum_{\mathbf{l}=\left\{\begin{smallmatrix} 1,2 \\ 1,3 \\ 1,4 \end{smallmatrix}\right\}} \hat{h}^{(2)}(\mathbf{k}_{l_1} + \mathbf{k}_{l_2}) \right. \\
&\quad \left. + \rho^2 \sum_{\mathbf{l}=\left\{\begin{smallmatrix} 3,4 \\ 2,4 \\ 2,3 \\ 1,4 \\ 1,3 \\ 1,2 \end{smallmatrix}\right\}} \hat{h}^{(3)}(\mathbf{k}_{l_1}, \mathbf{k}_{l_2}) + \rho^3 \hat{h}^{(4)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) \right].
\end{aligned}$$

The expression in the square brackets next to the δ -function for $\mathfrak{M}_4(\mathbf{k}^n)$ can be also written in a form where it depends only on $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3$, but does not depend on \mathbf{k}_4 . Let's write for \mathfrak{M}_4 :

$$\mathfrak{M}_4(\mathbf{k}, \dots, \mathbf{k}_4) = \langle N \rangle_0 \delta_{\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4} \mathbf{m}_4(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) \tag{4.8}$$

Then

$$\begin{aligned}
\mathbf{m}_4(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) &= 1 \\
&+ \rho \left(\sum_{l=1}^3 \hat{h}^{(2)}(\mathbf{k}_l) + \sum_{\mathbf{l}=\left\{\begin{smallmatrix} 1,2 \\ 1,3 \\ 2,3 \end{smallmatrix}\right\}} \hat{h}^{(2)}(\mathbf{k}_{l_1} + \mathbf{k}_{l_2}) + \hat{h}^{(2)}(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3) \right) \\
&+ \rho^2 \left(\sum_{\mathbf{l}=\left\{\begin{smallmatrix} 1,2 \\ 1,3 \\ 2,3 \end{smallmatrix}\right\}} \hat{h}^{(3)}(\mathbf{k}_{l_1}, \mathbf{k}_{l_2}) + \sum_{\mathbf{l}=\left\{\begin{smallmatrix} 1,2,3 \\ 1,3,2 \\ 2,3,1 \end{smallmatrix}\right\}} \hat{h}^{(3)}(\mathbf{k}_{l_1} + \mathbf{k}_{l_2}, \mathbf{k}_{l_3}) \right) \\
&+ \rho^3 \hat{h}^{(4)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) \tag{4.9}
\end{aligned}$$

This should be true for any n : a cumulant \mathfrak{M}_n can be written in such a way, that dependence on \mathbf{k}_n will be present only in $\delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n}$, and other part, let's denote it by \mathbf{m}_n , will depend only on $\mathbf{k}_1, \dots, \mathbf{k}_{n-1}$, or $\mathbf{m}_n = \mathbf{m}_n(\mathbf{k}^{n-1})$

$$\mathfrak{M}_n(\mathbf{k}^n) = \langle N \rangle_0 \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n} \mathbf{m}_n(\mathbf{k}^{n-1}). \tag{4.10}$$

A few first \mathbf{m}_n are expressed via total correlation functions $\hat{h}^{(n)}$ as follows:

$$\mathbf{m}_1 = 1. \quad (4.11)$$

$$\mathbf{m}_2(\mathbf{k}) = 1 + \rho \hat{h}^{(2)}(\mathbf{k}). \quad (4.12)$$

$$\begin{aligned} \mathbf{m}_3(\mathbf{k}_1, \mathbf{k}_2) = & 1 + \rho(\hat{h}^{(2)}(\mathbf{k}_1) + \hat{h}^{(2)}(\mathbf{k}_2) + \hat{h}^{(2)}(\mathbf{k}_1 + \mathbf{k}_2)) \\ & + \rho^2 \hat{h}^{(3)}(\mathbf{k}_1, \mathbf{k}_2) \end{aligned} \quad (4.13)$$

and the expression for \mathbf{m}_4 is given by (4.9). It is seen from (4.12) that $\mathbf{m}_2(\mathbf{k})$ is the structure factor (see e.g Eq. (3.6.10) in [12]). By analogy, \mathbf{m}_n can be considered as the n -particle structure factor.

Expressions (4.4)-(4.7) for cumulants obtained in this work can be compared with corresponding expressions presented in other works. In [8] (see Appendix B therein), and in [13] (see Eq. (3.7) therein), the expressions for \mathfrak{M}_2 through \mathfrak{M}_4 were presented in a similar form, but different permutations of wave-vector values were not accounted for. For example, it was considered that $\hat{h}^{(2)}(\mathbf{k}_1) + \hat{h}^{(2)}(\mathbf{k}_2) + \hat{h}^{(2)}(\mathbf{k}_1 + \mathbf{k}_2) = 3\hat{h}^{(2)}(\mathbf{k}_1)$. In [6] (see Eqs. (2.6), (2.10), and (2.11) therein), the expressions for $\mathfrak{M}_n(\mathbf{k}^n)$ were presented in a more complicated form, possibly due to the fact that correlation functions were defined in the canonical ensemble.

In [9] the expressions analogous to (4.4)-(4.7) were written for cumulants of multicomponent system.

There are a few interesting properties to note about general expression for \mathbf{m}_n . First, that the number of all terms contributing to \mathbf{m}_n is equal to the Bell number B_n [14, 15]. Second, if the terms are grouped by the powers in ρ then the number of terms at the k -th power in ρ is the Stirling number of the second kind $S(n, k)$ [14, 16].

4.3. Explicit expressions for cumulants as functions of wave-vector and packing fraction

To start with, one can use an explicit equation for the structure factor of hard-spheres system. For example, let's use Eq. (3) from [17] for the structure factor as a function of wave-vector and packing fraction η in the Percus-Yevick approximation

$$\mathfrak{M}_2(\mathbf{k}, -\mathbf{k}) / \langle N \rangle_0 = \mathbf{m}_2(\mathbf{k}), \quad (4.14)$$

$$\mathbf{m}_2(k) = (1 - \rho c(k))^{-1}, \quad (4.15)$$

where $c(k)$ is the Fourier component of the direct correlation function:

$$c(k) = -4\pi\sigma^3 \int_0^1 ds s^2 \frac{\sin(sk\sigma)}{sk\sigma} (A + Bs + Cs^3) \quad (4.16)$$

The parameters A , B , and C are functions of η :

$$\begin{aligned} A &= (1 + 2\eta)^2 / (1 - \eta)^4 \\ B &= -6\eta(1 + \eta/2)^2 / (1 - \eta)^4 \\ C &= (1/2)\eta(1 + 2\eta)^2 / (1 - \eta)^4. \end{aligned} \quad (4.17)$$

In Figure 1 \mathbf{m}_2 is shown as a function of $k \cdot \sigma$ at different values of η . In Figure 2 \mathbf{m}_2 is shown as a function of η at $k = 0$.

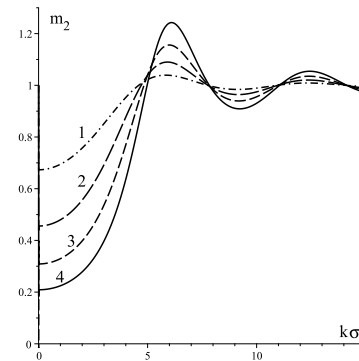


Figure 1. Cumulant \mathbf{m}_2 as a function of $k\sigma$ at different values of packing fraction η . 1 - $\eta = 0.05$, 2 - $\eta = 0.1$, 3 - $\eta = 0.15$, and 4 - $\eta = 0.2$.

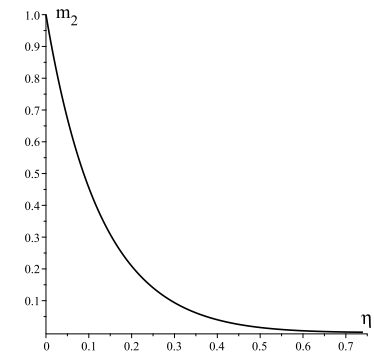


Figure 2. Cumulant \mathbf{m}_2 as a function of packing fraction η at $\mathbf{k} = 0$

The formulas for $\mathfrak{M}_3(\mathbf{k}, -\mathbf{k}, 0)$ and $\mathfrak{M}_4(\mathbf{k}, -\mathbf{k}, 0, 0)$ can be obtained from $\mathfrak{M}_2(\mathbf{k}, -\mathbf{k})$ based on the recurrence relations for n -particle distribution functions g_n found in [18] (see Eq. (A8) therein). Such formulas were obtained in [8] (see Appendix B therein) and in our notation they read:

$$\mathbf{m}_3(\mathbf{k}, -\mathbf{k}) = \mathbf{m}_2(0) \left[\mathbf{m}_2(\mathbf{k}) + \eta \frac{\partial \mathbf{m}_2(\mathbf{k})}{\partial \eta} \right], \quad (4.18)$$

$$\begin{aligned} \mathbf{m}_4(k, -k, 0) = & \mathbf{m}_2(0) \left[\mathbf{m}_2(k) \mathbf{m}_2(0) + 3\eta \mathbf{m}_2(0) \frac{\partial \mathbf{m}_2(k)}{\partial \eta} \right. \\ & + \eta \mathbf{m}_2(k) \frac{\partial \mathbf{m}_2(0)}{\partial \eta} + \eta^2 \frac{\partial \mathbf{m}_2(0)}{\partial \eta} \frac{\partial \mathbf{m}_2(k)}{\partial \eta} \\ & \left. + \eta^2 \mathbf{m}_2(0) \frac{\partial^2 \mathbf{m}_2(k)}{\partial \eta^2} \right] \end{aligned} \quad (4.19)$$

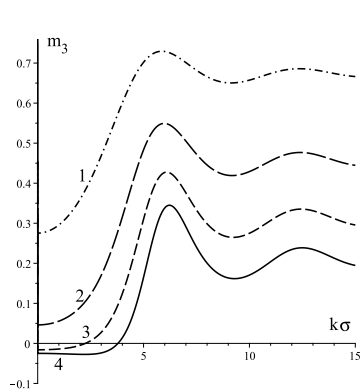


Figure 3. Cumulant m_3 as a function of $k\sigma$ at different values of packing fraction η . 1 - $\eta = 0.05$, 2 - $\eta = 0.1$, 3 - $\eta = 0.15$, and 4 - $\eta = 0.2$.

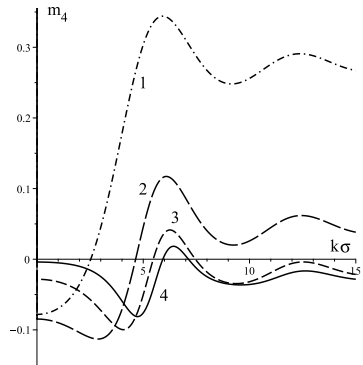


Figure 5. Cumulant m_4 as a function of $k\sigma$ at different values of packing fraction η . 1 - $\eta = 0.05$, 2 - $\eta = 0.1$, 3 - $\eta = 0.15$, and 4 - $\eta = 0.2$.

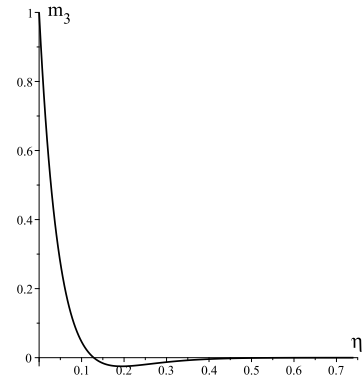


Figure 4. Cumulant m_3 as a function of packing fraction η at $\mathbf{k} = 0$

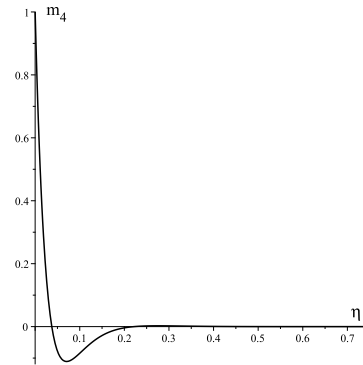


Figure 6. Cumulant m_4 as a function of packing fraction η at $\mathbf{k} = 0$

In Figure 3 m_3 is shown as a function of $k \cdot \sigma$ at different values of η . In Figure 4 m_3 is shown as a function of η at $k = 0$. In Figure 5 m_4 is shown as a function of $k \cdot \sigma$ at different values of η . In Figure 6 m_4 is shown as a function of η at $k = 0$.

4.4. Cumulants at $\mathbf{k}_i = 0$

At $\mathbf{k}_i = 0$ cumulants are expressed via the average number of particles in the reference system. Here the final expressions are presented. They are obtained directly from (4.1)–(4.3) by substituting $\mathbf{k}_i = 0$ and using $\hat{\rho}_0 = N$. Some alternative methods to calculate them are presented in Appendix C.

$$\mathfrak{M}_1(0) = \langle N \rangle_0; \quad (4.20)$$

$$\mathfrak{M}_2(0, 0) = \langle N^2 \rangle_0 - \langle N \rangle_0^2 = \langle (N - \langle N \rangle_0)^2 \rangle_0; \quad (4.21)$$

$$\begin{aligned} \mathfrak{M}_3(0, 0, 0) &= \langle N^3 \rangle_0 - 3\langle N^2 \rangle_0 \langle N \rangle_0 + 2\langle N \rangle_0^3 \\ &= \langle (N - \langle N \rangle_0)^3 \rangle_0; \end{aligned} \quad (4.22)$$

$$\begin{aligned} \mathfrak{M}_4(0, 0, 0, 0) &= \langle N^4 \rangle_0 - 4\langle N^3 \rangle_0 \langle N \rangle_0 + 12\langle N^2 \rangle_0 \langle N \rangle_0^2 \\ &\quad - 3\langle N^2 \rangle_0^2 - 6\langle N \rangle_0^4 \\ &= \langle (N - \langle N \rangle_0)^4 \rangle_0 - 3\langle (N - \langle N \rangle_0)^2 \rangle_0^2. \end{aligned} \quad (4.23)$$

4.5. Cumulants as functions of packing fraction for the hard-spheres system

For the system of hard spheres the cumulants m_n can be found explicitly as functions of the packing fraction η based on a given equation of state

$$\frac{PV}{NkT} = f(\eta) \quad (4.24)$$

where $f(\eta)$ is a function of the packing fraction only. The structure factor at zero wave-vector value is found via

$$m_2 = S(0) = kT \left(\frac{\partial \rho}{\partial P} \right)_T. \quad (4.25)$$

From here one has

$$\frac{1}{m_2} = f(\eta) + \eta \frac{\partial f(\eta)}{\partial \eta}. \quad (4.26)$$

For example, in [13], the following expressions were obtained based on the equation of state by Carnahan and Starling [19] for HS:

$$\mathbf{m}_2 = \frac{(1-\eta)^4}{(1+2\eta)^2 - 4\eta^3 + \eta^4},$$

$$\mathbf{m}_3 = \frac{(1-\eta)^7(1-5\eta-20\eta^2-4\eta^3+5\eta^4-\eta^5)}{((1+2\eta)^2-4\eta^3+\eta^4)^3},$$

$$\mathbf{m}_4 = (1-\eta)^{10}(1-26\eta-35\eta^2+408\eta^3+758\eta^4+28\eta^5-114\eta^6-40\eta^7+37\eta^8-10\eta^9+\eta^{10})((1+2\eta)^2-4\eta^3+\eta^4)^{-5}.$$

Note that here the signs for the term $4\eta^3$ in \mathbf{m}_3 and for $408\eta^3$ in \mathbf{m}_4 were corrected.

5. Grand partition function in the representation of collective variables

The grand partition function is now written as

$$\Xi = \Xi_0 \int \exp \left[h\rho_0 - \frac{1}{2} \sum_{\mathbf{k}} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right] \quad (5.1)$$

$$\times \exp \left(i2\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} \right)$$

$$+ \sum_{n \geq 1} \frac{(-i2\pi)^n}{n!} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \tilde{\mathfrak{M}}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_n}$$

$$\times (d\omega)(d\rho)$$

This expression was obtained in [7] (see Eq.(2.16) therein).

The next step in calculation is to integrate over $\omega_{\mathbf{k}}$ with $\mathbf{k} > B$. This integration can be performed with Gaussian measure, i.e. the expressions in the exponent is restricted to the powers of ω not higher than 2. Let us denote the result of this integration by Ξ_G . Then the grand partition function takes the form:

$$\Xi = \Xi_0 \Xi_G \Xi_L \quad (5.2)$$

Here Ξ_L denotes long-wave contributions to the GPF and is the object of our further investigation in this paper. The expression for Ξ_L is following

(see also Eq.(3.5) in [7]):

$$\Xi_L = \int \exp \left[h\rho_0 - \frac{1}{2} \sum_{\substack{\mathbf{k} \\ k \leq B}} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right] \quad (5.3)$$

$$\times \exp \left(i2\pi \sum_{\substack{\mathbf{k} \\ k \leq B}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} \right)$$

$$+ \sum_{n \geq 1} \frac{(-i2\pi)^n}{n!} \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_n \\ k_i \leq B}} \tilde{\mathfrak{M}}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_n}$$

$$\times (d\omega)^{N_B} (d\rho)^{N_B}$$

Here $\tilde{\mathfrak{M}}_n$ denote renormalized cumulants \mathfrak{M}_n due to integration over $k > B$, and

$$(d\omega)^{N_B} (d\rho)^{N_B} = \left(\prod_{\substack{\mathbf{k} \\ k \leq B}} d\omega_{\mathbf{k}}^c d\rho_{\mathbf{k}}^c d\omega_{\mathbf{k}}^s d\rho_{\mathbf{k}}^s \right) d\omega_0 d\rho_0 \quad (5.4)$$

In the approximation of the 4th basic measure density, Ξ_L is expressed as:

$$\Xi_L = \int \left(1 + D_4 + \frac{1}{2} D_4^2 + \dots \right) W_4(\rho; \omega) (d\rho)^{N_B} (d\omega)^{N_B}, \quad (5.5)$$

where the measure density $W_4(\rho; \omega)$ is

$$W_4(\rho; \omega) = \exp \left\{ h\rho_0 - \frac{1}{2} \sum_{\substack{\mathbf{k} \\ k \leq B}} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + i2\pi \sum_{\substack{\mathbf{k} \\ k \leq B}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} + \sum_{n=1}^4 \frac{(-i2\pi)^n}{n!} \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_n \\ k_i \leq B}} \tilde{\mathfrak{M}}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_n} \right\}. \quad (5.6)$$

and the following notation is introduced:

$$D_4 = \sum_{m > 4} \frac{(-i2\pi)^m}{m!} \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_m \\ k_i \leq B}} \tilde{\mathfrak{M}}_m(\mathbf{k}_1, \dots, \mathbf{k}_m) \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_m} \quad (5.7)$$

The quantity N_B is the number of variables to be integrated over. It is equal to the number of values that the wave vector takes on in the sphere of radius B in reciprocal space. Let's assume that the wave-vector values are distributed uniformly, then

$$N_B = \frac{B^3}{6\pi^2} V. \quad (5.8)$$

To derive this equation, consider the following arguments. If we had a simple cubic lattice of spacing c in real space, the first Brillouin zone of it would be a simple cubic lattice in the reciprocal space with spacing $2B'$, where $B' = \pi/c$. The number of values taken by wave vector in this zone would be $N_B = V/c^3 = V(B'/\pi)^3$. Under our assumption, the wave vector values are distributed uniformly. Hence, the sphere of volume Ω in reciprocal space must contain the same number of wave vector values as a cube of the same volume Ω . Since $\Omega = (2B')^3 = \frac{4}{3}\pi B^3$, one finds that $B'^3 = \frac{\pi}{6}B^3$ and, therefore, arrives at Eq. (5.8).

In the current investigation the following approximations are to be applied.

Approximation 1. D_4 is neglected in the expression (5.5) for Ξ_L ;

Approximation 2. The difference between renormalized values of cumulants $\tilde{\mathfrak{M}}_n$ and original cumulants \mathfrak{M}_n is ignored, so that:

$$\tilde{\mathfrak{M}}_n(\mathbf{k}^n) \approx \mathfrak{M}_n(\mathbf{k}^n) \quad (5.9)$$

Approximation 3. The dependence of cumulants \mathfrak{M}_n on the wave vectors \mathbf{k}_i is neglected, except for the dependence via δ -functions

$$\mathfrak{M}_n(\mathbf{k}^n) \approx \mathfrak{M}_n(0^n) \delta_{\mathbf{k}_1+\dots+\mathbf{k}_n} \quad (5.10)$$

where the following notation is used for simplicity: $\mathbf{k}^n \equiv \mathbf{k}_1, \dots, \mathbf{k}_n$.

With these approximations applied, one arrives at the following expressions:

$$\Xi_L = \int W_4(\rho; \omega) (d\rho)^{N_B} (d\omega)^{N_B}, \quad (5.11)$$

and

$$W_4(\rho; \omega) = \exp \left\{ h\rho_0 - \frac{1}{2} \sum_{\mathbf{k} \leq B} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + i2\pi \sum_{\mathbf{k} \leq B} \omega_{\mathbf{k}} \rho_{\mathbf{k}} \right. \quad (5.12)$$

$$\left. + \sum_{n=1}^4 \frac{(-i2\pi)^n}{n!} \mathfrak{M}_n(0^n) \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_n \\ \mathbf{k}_i \leq B}} \delta_{\mathbf{k}_1+\dots+\mathbf{k}_n} \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_n} \right\}.$$

See also Eqs. (3.12), (3.13) in [7].

The expression 5.12 for the 4-th measure density contains non-zero terms in all powers of ω up to 4. Let's eliminate the coefficient next to the 3-rd power in ω . For this, the following change of variables is performed:

$$\omega_0 = \omega'_0 + \frac{\mathfrak{M}_3}{(i2\pi)\mathfrak{M}_4} \quad (5.13)$$

From now on, we will understand \mathfrak{M}_n as $\mathfrak{M}_n(0^n)$ where it is not ambiguous. One should remember that \mathfrak{M}_n are still dependent on the packing fraction η . The 4-th measure density $W_4(\rho; \omega)$ takes the form:

$$W_4(\rho; \omega) = \exp \left\{ \mathfrak{M}_0 + (h + \mathfrak{M}_3/\mathfrak{M}_4)\rho_0 \right. \\ \left. - \frac{1}{2} \sum_{\substack{\mathbf{k} \\ k \leq B}} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} - i2\pi \tilde{\mathfrak{M}}_1 \omega_0 + \right. \\ \left. + i2\pi \sum_{\substack{\mathbf{k} \\ k \leq B}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} + \frac{(-i2\pi)^2}{2!} \tilde{\mathfrak{M}}_2 \sum_{\substack{\mathbf{k} \\ k \leq B}} \omega_{\mathbf{k}} \omega_{-\mathbf{k}} \right. \\ \left. + \frac{(-i2\pi)^4}{4!} \mathfrak{M}_4 \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_4 \\ \mathbf{k}_i \leq B}} \delta_{\mathbf{k}_1+\dots+\mathbf{k}_4} \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_4} \right\} \quad (5.14)$$

with

$$\mathfrak{M}_0 = -\frac{\mathfrak{M}_1 \mathfrak{M}_3}{\mathfrak{M}_4} + \frac{\mathfrak{M}_2 \mathfrak{M}_3^2}{2\mathfrak{M}_4^2} - \frac{\mathfrak{M}_3^4}{8\mathfrak{M}_4^3}, \quad (5.15)$$

$$\tilde{\mathfrak{M}}_1 = \mathfrak{M}_1 - \frac{\mathfrak{M}_2 \mathfrak{M}_3}{\mathfrak{M}_4} + \frac{\mathfrak{M}_3^3}{3\mathfrak{M}_4^2}, \quad (5.16)$$

$$\tilde{\mathfrak{M}}_2 = \mathfrak{M}_2 - \frac{\mathfrak{M}_3^2}{2\mathfrak{M}_4}. \quad (5.17)$$

In (5.14) the prime at ω_0 is omitted.

We also want to eliminate the term at ω_0 . This is achieved by the change of variables

$$\rho_0 = \rho'_0 + \tilde{\mathfrak{M}}_1. \quad (5.18)$$

The expression for $W_4(\rho; \omega)$ becomes

$$W_4(\rho; \omega) = \exp \left\{ \begin{aligned} &\tilde{\mathfrak{M}}_0 + \mu^* \rho_0 - \frac{1}{2} \sum_{\mathbf{k}}_{k \leq B} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \\ &+ i2\pi \sum_{\mathbf{k}}_{k \leq B} \omega_{\mathbf{k}} \rho_{\mathbf{k}} + \frac{(-i2\pi)^2}{2!} \tilde{\mathfrak{M}}_2 \sum_{\mathbf{k}}_{k \leq B} \omega_{\mathbf{k}} \omega_{-\mathbf{k}} \\ &+ \frac{(-i2\pi)^4}{4!} \mathfrak{M}_4 \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_4 \\ k_i \leq B}} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_4} \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_4} \end{aligned} \right\} \quad (5.19)$$

with

$$\tilde{\mathfrak{M}}_0 = \mathfrak{M}_0 + (h + \mathfrak{M}_3/\mathfrak{M}_4) \tilde{\mathfrak{M}}_1 - \frac{\alpha(0)}{2} \tilde{\mathfrak{M}}_1^2 \quad (5.20)$$

$$\mu^* = h + \mathfrak{M}_3/\mathfrak{M}_4 + \alpha(0) \tilde{\mathfrak{M}}_1 \quad (5.21)$$

In (5.19) the prime at ρ_0 is omitted.

We can compare the expression (5.19) with Eq. (3.14) from [7], Eq. (12) from [8], and Eq. (3.5) from [20].

Table 1. The zero values of the cumulant \mathfrak{M}_4 . $\mathfrak{M}_4 < 0$ for $\eta_{min} < \eta < \eta_{max}$.

Approximation	η_{min}	η_{max}
Percus-Yevick, compressibility equation [21]	0.037346	0.221675
Percus-Yevick, virial equation [22]	0.037673	0.233899
Carnahan-Starling [19]	0.037455	0.225572
Ree-Hoover [23]	0.037423	0.224260

The first thing to note in Eq. (5.19) is that the integral for Ξ_L in (5.11) converges only for $\mathfrak{M}_4 < 0$. The values of \mathfrak{M}_4 are negative only in some range of η . Table 1 summarizes numerical solutions for the equation $\mathfrak{M}_4 = 0$ in a few approximations. Thus one can conclude that the 4-th measure density $W_4(\rho; \omega)$ is applicable only in this range of packing fraction η . We are going to work in range $0.04 \leq \eta \leq 0.22$. The dependence of $\mathbf{m}_4 = \mathfrak{M}_4/\langle N \rangle_0$ on η is presented in Figure 7.

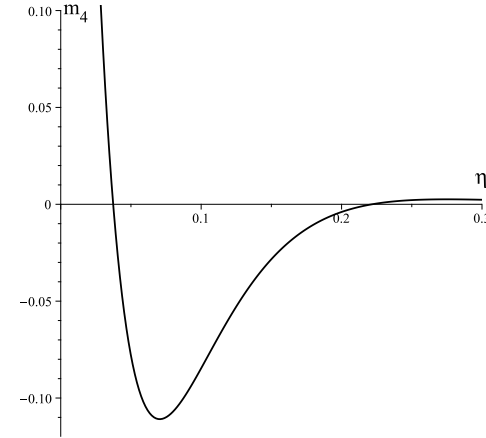


Figure 7. Cumulant $\mathbf{m}_4 = \mathfrak{M}_4/\langle N \rangle_0$ as a function of packing fraction η at $\mathbf{k}_i = 0$. In this Figure the range of negative values for \mathbf{m}_4 is emphasized.

5.1. Integration over ω .

Let's perform integration over ω in (5.11), using (5.19) for $W_4(\rho; \omega)$. First let's single out the integral over ω

$$J(\rho) = \int \exp \left(i2\pi \sum_{\mathbf{k}}_{k \leq B} \omega_{\mathbf{k}} \rho_{\mathbf{k}} + \frac{(-i2\pi)^2}{2!} \tilde{\mathfrak{M}}_2 \sum_{\mathbf{k}}_{k \leq B} \omega_{\mathbf{k}} \omega_{-\mathbf{k}} + \frac{(-i2\pi)^4}{4!} \mathfrak{M}_4 \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_4 \\ k_i \leq B}} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_4} \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_4} \right) (d\omega)^{N_B}$$

To factorize this integral, perform the following change of variables

$$\tilde{\omega}_1 = \frac{1}{\sqrt{N_B}} \sum_{\mathbf{k}}_{k \leq B} \omega_{\mathbf{k}} e^{-i\mathbf{k} \cdot \mathbf{l}}, \quad \tilde{\rho}_1 = \frac{1}{\sqrt{N_B}} \sum_{\mathbf{k}}_{k \leq B} \rho_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{l}}. \quad (5.22)$$

The following relations are valid:

$$\sum_1 \tilde{\omega}_1 \tilde{\rho}_1 = \frac{1}{N_B} \sum_1 \sum_{\mathbf{k}} \omega_{\mathbf{k}} \sum_{\mathbf{k}'} \rho_{\mathbf{k}'} e^{-i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{l}} = \sum_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}}, \quad (5.23)$$

$$\sum_{\mathbf{l}} \tilde{\omega}_1^2 = \sum_{\mathbf{k}} \omega_{\mathbf{k}} \omega_{-\mathbf{k}}, \quad (5.24)$$

$$N_B \sum_{\mathbf{l}} \tilde{\omega}_1^4 = \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_4 \\ k_i \leq B}} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_4} \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_4} \quad (5.25)$$

where the following expression for the Kronecker's δ -symbol is used:

$$\delta_{\mathbf{k}} = \frac{1}{N_B} \sum_{\mathbf{l}} e^{-i\mathbf{k}\mathbf{l}}. \quad (5.26)$$

The sum over \mathbf{l} should be understood as running over N_B values in real space corresponding to the wave-vector values \mathbf{k} , $k \leq B$.

The element of integration is changed as following:

$$d\omega_0 \prod_{\substack{\mathbf{k} \\ k \leq B}} d\omega_{\mathbf{k}}^c d\omega_{\mathbf{k}}^s = j \prod_{\mathbf{l}} d\tilde{\omega}_1 \quad (5.27)$$

where j is the Jacobian of transition from $\omega_{\mathbf{k}}$ to $\tilde{\omega}_1$.

Since the approximation of the 4-th measure density is applicable only when \mathfrak{M}_4 is negative, we will write the following expressions using the absolute value of this cumulant. Thus, the factorized expression for the integral over ω is

$$J(\rho) = j \prod_{\mathbf{l}} \int \exp\left(i2\pi\tilde{\omega}_1\tilde{\rho}_1 - \frac{(2\pi)^2}{2}\tilde{\mathfrak{M}}_2\tilde{\omega}_1^2 - \frac{(2\pi)^4}{4!}N_B|\mathfrak{M}_4|\tilde{\omega}_1^4\right) d\tilde{\omega}_1.$$

If we denote the integral as

$$J_1(\tilde{\rho}_1) = \int \exp\left(i2\pi\tilde{\omega}_1\tilde{\rho}_1 - \frac{(2\pi)^2}{2}\tilde{\mathfrak{M}}_2\tilde{\omega}_1^2 - \frac{(2\pi)^4}{4!}N_B|\mathfrak{M}_4|\tilde{\omega}_1^4\right) d\tilde{\omega}_1 \quad (5.28)$$

then the result of integration can be presented in the following form

$$J(\rho) = j \prod_{\mathbf{l}} e^{a_0} \exp\left(-\sum_{n \geq 1} \frac{a_n}{n!} \tilde{\rho}_1^n\right) \quad (5.29)$$

where coefficients a_n are found by the following formulae

$$a_n = -\left(\frac{\partial^n \ln J_1(\tilde{\rho}_1)}{\partial \tilde{\rho}_1^n}\right)_{\tilde{\rho}_1=0}. \quad (5.30)$$

First, let's calculate e^{a_0}

$$Q(\tilde{\mathfrak{M}}_2, \mathfrak{M}_4) \equiv e^{a_0} = \int_{-\infty}^{\infty} \exp\left(-\frac{(2\pi)^2}{2}\tilde{\mathfrak{M}}_2\tilde{\omega}_1^2 - \frac{(2\pi)^4}{4!}N_B|\mathfrak{M}_4|\tilde{\omega}_1^4\right) d\tilde{\omega}_1.$$

Using the following representation for the Weber parabolic cylinder function $U(a, x)$

$$U(a, x) = \frac{2}{\Gamma(a + \frac{1}{2})} e^{-\frac{x^2}{4}} \int_0^{\infty} t^{2a} \exp\left(-xt^2 - \frac{1}{2}t^4\right) dt \quad (5.31)$$

one obtains:

$$Q(\tilde{\mathfrak{M}}_2, \mathfrak{M}_4) = \frac{1}{2\sqrt{\pi}} \left(\frac{12}{N_B|\mathfrak{M}_4|}\right)^{1/4} e^{y^2/2} U(0, y) \quad (5.32)$$

where

$$y = \left(\frac{3\tilde{\mathfrak{M}}_2^2}{N_B|\mathfrak{M}_4|}\right)^{1/2}. \quad (5.33)$$

Now, let's calculate a_2 .

For a_2 the result is

$$a_2 = \left(\frac{3}{N_B|\mathfrak{M}_4|}\right)^{1/2} U(y), \quad (5.34)$$

where

$$U(y) = \frac{U(1, y)}{U(0, y)}. \quad (5.35)$$

For a_4 the result is

$$a_4 = \frac{3}{N_B|\mathfrak{M}_4|} \left(3U^2(y) - 3\frac{U(2, y)}{U(0, y)}\right) = \frac{3}{N_B|\mathfrak{M}_4|} \phi(y) \quad (5.36)$$

where

$$\phi(y) = 3U^2(y) + 2yU(y) - 2. \quad (5.37)$$

In the above equation we used the following recurrence relation for the parabolic cylinder function U :

$$3U(2, y) = -2yU(1, y) + 2U(0, y). \quad (5.38)$$

The quantity $J(\rho)$ takes the form

$$J(\rho) = jQ(\tilde{\mathfrak{M}}_2, \mathfrak{M}_4)^{N_B} \times \exp\left(-\frac{a_2}{2} \sum_{\mathbf{k} \leq B} \rho_{\mathbf{k}} \rho_{-\mathbf{k}} - \frac{a_4}{N_B 4!} \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_4 \\ k_i \leq B}} \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_4} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_4}\right) \quad (5.39)$$

where the following equations were taken into account

$$\sum_1 \tilde{\rho}_1^2 = \sum_{\mathbf{k}} \rho_{\mathbf{k}} \rho_{-\mathbf{k}}, \quad (5.40)$$

$$\sum_1 \tilde{\rho}_1^4 = \frac{1}{N_B} \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_4 \\ k_i \leq B}} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_4} \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_4} \quad (5.41)$$

Finally, the quantity Ξ_L takes the form

$$\Xi_L = jQ(\tilde{\mathfrak{M}}_2, \mathfrak{M}_4)^{N_B} \exp(\tilde{\mathfrak{M}}_0) \Xi_L^{(1)} \quad (5.42)$$

where $Q(\tilde{\mathfrak{M}}_2, \mathfrak{M}_4)$ is given by (5.32), N_B by (5.8), $\tilde{\mathfrak{M}}_0$ by (5.20), and $\Xi_L^{(1)}$ is defined as follows

$$\Xi_L^{(1)} = \int \exp\left(\mu^* \rho_0 - \frac{1}{2} \sum_{\mathbf{k} \leq B} d(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} - \frac{a_4}{4! N_B} \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_4 \\ k_i \leq B}} \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_4} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_4}\right) (d\rho)^{N_B} \quad (5.43)$$

where μ^* is given by (5.21), and

$$d(k) = a_2 + \alpha(k), \quad (5.44)$$

where $\alpha(k)$ is given by (2.23).

Expression (5.43) is the main result of this work. In future, this expression will be subject to renormalization group transformation near the liquid-gas critical point. In CV approach it is implemented via layer-by-layer integration of the integral (5.43) in k -space.

5.2. Coefficients of the effective Hamiltonian

The argument y of functions entering different expressions in the previous subsection is itself a function of η and $B\sigma$. Let's show this.

$$y = \left(\frac{3\tilde{\mathfrak{M}}_2^2}{N_B |\mathfrak{M}_4|}\right)^{1/2} = \left(\frac{\langle N \rangle_0}{N_B}\right)^{1/2} \left(\frac{3\tilde{\mathfrak{m}}_2^2}{|\mathfrak{m}_4|}\right)^{1/2}, \quad (5.45)$$

where the following notation is introduced

$$\tilde{\mathfrak{m}}_2 = \mathfrak{m}_2 - \frac{\mathfrak{m}_3^2}{2\mathfrak{m}_4}. \quad (5.46)$$

In the expression for y the second multiplier depends only on η . Let's take a look at the first multiplier. Taking into account (5.8), one has

$$\frac{\langle N \rangle_0}{N_B} = \frac{\langle N \rangle_0}{V} \frac{6\pi^2}{B^3} = \frac{\langle N \rangle_0}{V} \sigma^3 \frac{6\pi^2}{(B\sigma)^3} = \frac{\pi}{6} \frac{\langle N \rangle_0}{V} \sigma^3 \frac{36\pi}{(B\sigma)^3} = \eta \frac{36\pi}{(B\sigma)^3}.$$

The quantity $B\sigma$ is dimensionless but its value depends on how B is selected. Based on the previous works, the condition for selecting B is $\hat{\Phi}_{k=B} = 0$. This condition imposes some restrictions on the attractive part of the interaction potential, in particular that $\hat{\Phi}_0 < 0$. However, section of the potential in the form of Eq. (2.14) obeys this condition very well.

The explicit expression for the Fourier component of such potential is the following

$$\hat{\Phi}_k = -16\pi\epsilon\alpha^3 \left\{ \frac{1}{1+k^2\alpha^2} \left(\frac{\sigma}{\alpha} + \frac{2}{1+k^2\alpha^2} \right) \cos(k\sigma) - \frac{1}{4+k^2\alpha^2} \left(\frac{\sigma}{\alpha} + \frac{4}{4+k^2\alpha^2} \right) \cos(k\sigma) + \frac{\sigma/\alpha}{1+k^2\alpha^2} \left(\frac{\sigma}{\alpha} + \frac{1-k^2\alpha^2}{1+k^2\alpha^2} \right) \frac{\sin(k\sigma)}{k\sigma} - \frac{\sigma/\alpha}{4+k^2\alpha^2} \left(\frac{2\sigma}{\alpha} + \frac{4-k^2\alpha^2}{4+k^2\alpha^2} \right) \frac{\sin(k\sigma)}{k\sigma} \right\}. \quad (5.47)$$

In this expression it is already taken into account that

$$\sigma = R_0 - \alpha \ln(2). \quad (5.48)$$

In Figure 8 the dependence of $\hat{\Phi}_k/(\epsilon\sigma^3)$ on $k\sigma$ is shown for a few values of parameter R_0/α . Values of $B\sigma$ for different R_0/α are presented in Table 2

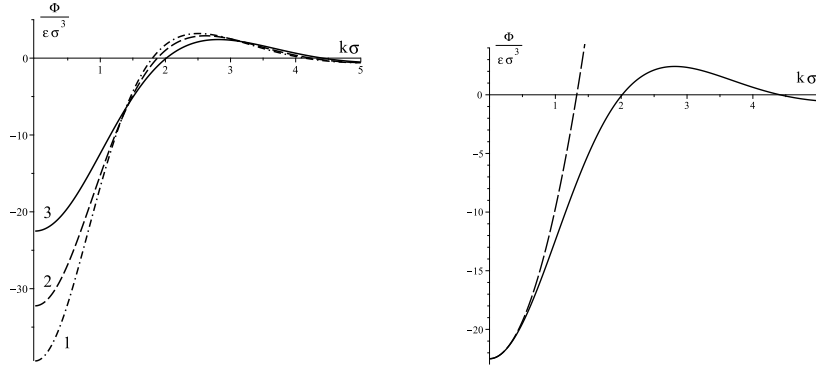


Figure 8. Fourier component of the attractive part of interaction potential, Eq. (5.47), for different values of R_0/α . 1 - 2.77, 2 - 3.0, 3 - 3.5.

Figure 9. Fourier component of the attractive part of interaction potential for $R_0/\alpha = 3.5$ (solid line) and corresponding parabolic approximation, Eq. (5.49) (dashed line).

In some particular calculations further on, the following approximation will be used for the Fourier transform at $k < B$

$$\hat{\Phi}_k = \hat{\Phi}_0(1 - 2b^2k^2) \quad (5.49)$$

where

$$2b^2 = -\frac{1}{2\hat{\Phi}_0} \left. \frac{\partial^2 \hat{\Phi}_k}{\partial k^2} \right|_{k=0}. \quad (5.50)$$

Values of $2b^2$ along with $1/(\sqrt{2}b)$ (the point at which the parabolic approximation is equal to zero) are also presented in Table 2. Figure 9 shows $\hat{\Phi}_k$ together with its parabolic approximation in one picture.

At this point we can build some graphics for coefficients a_2 and a_4 as functions of η . First, for a_2 one has

$$a_2 = \left(\frac{3}{N_B \langle N \rangle_0 |\mathbf{m}_4|} \right)^{1/2} U(y) = \frac{1}{\langle N \rangle_0} \left(\frac{\langle N \rangle_0}{N_B} \right)^{1/2} \left(\frac{3}{|\mathbf{m}_4|} \right)^{1/2} U(y) \quad (5.51)$$

and from here it is seen that the quantity $\langle N \rangle_0 a_2$ depends only on η and the parameter $B\sigma$ of the interaction potential, see Figure 10

For a_4 one has

$$a_4 = \frac{3}{N_B \langle N \rangle_0 |\mathbf{m}_4|} \phi(y) = \frac{1}{\langle N \rangle_0^2} \frac{\langle N \rangle_0}{N_B} \frac{3}{|\mathbf{m}_4|} \phi(y) \quad (5.52)$$

Table 2. The zero values $B\sigma$ and parameters of the parabolic approximation of the Fourier component $\hat{\Phi}_k$ for different values of R_0/α .

R_0/α	$B\sigma$	$2b^2$	$\frac{1}{\sqrt{2}b}$
2.0	1.47	1.68	0.77
2.5	1.70	1.02	0.99
3.0	1.88	0.72	1.18
3.5	2.01	0.57	1.33
4.0	2.13	0.48	1.45
4.5	2.22	0.42	1.55
5.0	2.29	0.37	1.64

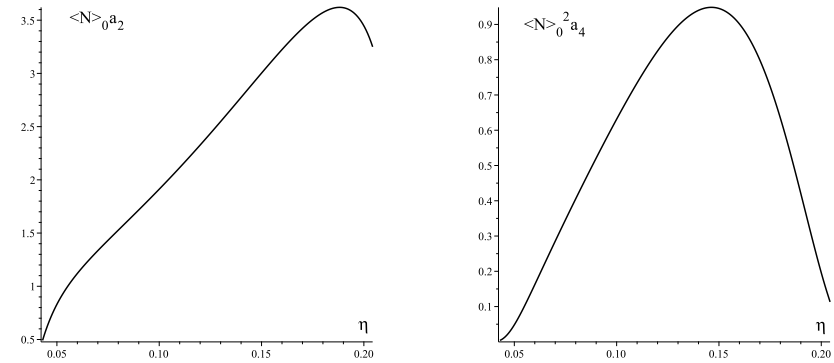


Figure 10. Quantity $\langle N \rangle_0 a_2$ as a function of η for $R_0/\alpha = 3.5$.

Figure 11. Quantity $\langle N \rangle_0^2 a_4$ as a function of η for $R_0/\alpha = 3.5$.

and from here it is seen that the quantity $\langle N \rangle_0^2 a_4$ depends only on η and the parameter $B\sigma$ of the interaction potential, see Figure 11

To rewrite $d(k)$ in a useful form, let's first consider the quantity $\alpha(k)$

$$\alpha(k) = \frac{\beta \hat{\Phi}_k}{V} = \frac{1}{\langle N \rangle_0} \frac{6}{\pi} \eta \frac{\varepsilon}{k_B T} \frac{\hat{\Phi}_k}{\varepsilon \sigma^3}. \quad (5.53)$$

It is seen now that the quantity $\langle N \rangle_0 d(k)$ is a function of η , but also depends on the parameter of the interaction potential Φ , as well as on the temperature T .

6. Effective Hamiltonian in the mean-field approximation

Consider the long-wave contribution Ξ_L to the GPF, Eq. (5.42). Let's calculate Ξ_L in the approximation when all $\mathbf{k}_i = 0$

$$\Xi_L^{(1)} = \int \exp\left(\mu^* \rho_0 - \frac{d(0)}{2} \rho_0^2 - \frac{a_4}{4! N_B} \rho_0^4\right) d\rho_0. \quad (6.1)$$

Since, as previously learned, $d(0) \propto \langle N \rangle_0$ and $a_4 \propto \langle N \rangle_0^2$, it is convenient to perform the following substitution of variables $\rho = \langle N \rangle_0 \rho'_0$ in the the above expression and obtain

$$\Xi_L^{(1)} = \langle N \rangle_0 \int \exp[\langle N \rangle_0 E(\rho'_0)] d\rho'_0 \quad (6.2)$$

where the following notations were introduced

$$E(\rho'_0) = \mu^* \rho'_0 - \frac{d'(0)}{2} \rho'^2_0 - \frac{a'_4}{4!} \rho'^4_0, \quad (6.3)$$

$$d'(0) = \langle N \rangle_0 d(0) = a'_2 + \frac{6}{\pi} \eta \frac{\varepsilon}{k_B T} \frac{\hat{\Phi}_0}{\varepsilon \sigma^3}. \quad (6.4)$$

$$a'_2 = \langle N \rangle_0 a_2, \quad a'_4 = \frac{\langle N \rangle_0}{N_B} \langle N \rangle_0^2 a_4 \quad (6.5)$$

The presence of $\langle N \rangle_0$ in the exponent justifies the application of the steepest-descent method for integration. The result is the following

$$\Xi_L^{(1)} = \langle N \rangle_0 \exp(\langle N \rangle_0 E(\rho_{0,\max})) \quad (6.6)$$

where $\rho_{0,\max}$ maximizes the quantity $E(\rho'_0)$ and is found from the following conditions

$$\frac{\partial E}{\partial \rho'_0} = 0; \quad \frac{\partial^2 E}{\partial \rho'^2_0} < 0. \quad (6.7)$$

In explicit form these conditions become

$$\mu^* - d'(0) \rho_0 - \frac{a'_4}{3!} \rho'^3_0 = 0, \quad (6.8)$$

$$-d'(0) - \frac{a'_4}{2} \rho'^2_0 < 0. \quad (6.9)$$

6.1. Naive approximation

In the most simple approximation, the quantity μ^* plays the same role as an external magnetic field in the Ising model. For Ising model it is known that the critical point appears at the absence of the external field, thus to find the critical point in our approximation, one condition is

$$\mu^* = 0.$$

The quantity μ^* depends on the chemical potential, through the term $\beta(\mu - \mu_0)$, on the temperature, through the term proportional to $\alpha(0)$, and on the packing fraction η . If we assume that $\mu = \mu_0$, then the condition $\mu^* = 0$ will relate the temperature and η

$$\mathfrak{M}_3 / \mathfrak{M}_4 + \alpha(0) \tilde{\mathfrak{M}}_1 = 0.$$

This is the first condition that relates these two quantities. The second condition is obtained from the requirement that non-zero solution exists for ρ'_0 :

$$\rho'^3_0 + \frac{3!d'(0)}{a'_4} \rho'_0 = 0$$

$$\rho_{01} = 0;$$

$$\rho_{02,03} = \pm \sqrt{-\frac{3!d'(0)}{a'_4}}$$

Since a'_4 is always positive in the region $0.04 \leq \eta \leq 0.22$, the solutions ρ_{02} and ρ_{03} are real when $d'(0) \leq 0$. Thus the second condition for the critical point is

$$d'(0) = 0$$

Thus in explicit form the system of two equations relating the temperature and packing fraction is as follows

$$\begin{aligned} \frac{\mathfrak{m}_3}{\mathfrak{m}_4} + \frac{6\eta}{\pi} \frac{1}{T^*} \frac{\hat{\Phi}_0}{\varepsilon \sigma^3} \left(1 - \frac{\mathfrak{m}_2 \mathfrak{m}_3}{\mathfrak{m}_4} + \frac{\mathfrak{m}_3^3}{3\mathfrak{m}_4^2}\right) &= 0; \\ a'_2 + \frac{6\eta}{\pi} \frac{1}{T^*} \frac{\hat{\Phi}_0}{\varepsilon \sigma^3} &= 0, \end{aligned} \quad (6.10)$$

where $T^* = k_B T / \varepsilon$ is the reduced temperature. The equation for finding the critical value of η is

$$\frac{\mathfrak{m}_3}{\mathfrak{m}_4} - a'_2 \left(1 - \frac{\mathfrak{m}_2 \mathfrak{m}_3}{\mathfrak{m}_4} + \frac{\mathfrak{m}_3^3}{3\mathfrak{m}_4^2}\right) = 0. \quad (6.11)$$

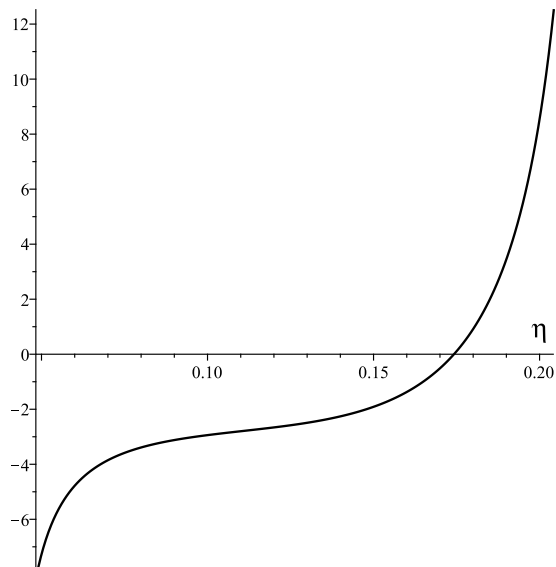


Figure 12. Equation (6.11) for the critical packing fraction η_c .

Figure 12 shows this equation graphically. The numerical solution to the equation gives the following value in the Percus-Yevick approximation

$$\eta_c = 0.1742,$$

or the critical value for the reduced density $\rho^* = \sigma^3 \langle N \rangle / V$

$$\rho_c^* = 0.3327.$$

In the Carnahan-Starling approximation the corresponding values are

$$\eta_c = 0.1766, \quad \rho_c^* = 0.3374. \quad (6.12)$$

The critical temperature is now found

$$T_c^* = -\frac{6\eta_c}{\pi a'_2} \frac{\hat{\Phi}_0}{\varepsilon \sigma^3}$$

which for the parameters value $R_0/\alpha = 3.5$ is $T_c^* = 2.14$ in Percus-Yevick approximation, and $T_c^* = 2.15$ in the Carnahan-Starling one. It is very important to note that both critical density and critical temperature depend on the parameters of the attractive part of potential. In particular,

the critical temperature T_c approaches zero as the interaction potential becomes more and more narrow ($\alpha \rightarrow \infty$, $\hat{\Phi}_0 \rightarrow 0$).

The solutions to the equation (6.8) for ρ'_0 can be written in general form via the discriminant of this cubic equation (via the Cardano's formulas). We are not going to do so for this simple approximation, but are going to integrate expression (5.42) over non-zero values of k , obtain similar equation for ρ_0 but with re-normalized coefficients, and investigate the obtained equation more closely.

6.2. Applying condition $\langle N \rangle_0 = \langle N \rangle$

Another way to address the problem of finding the critical point coordinates is to impose the condition of equality between particle numbers averages for the reference system and the whole system

$$\langle N \rangle_0 = \langle N \rangle. \quad (6.13)$$

This condition was, for example, applied in [8].

The general equation to find the average (equilibrium) number of particles is

$$\left(\frac{\partial \ln \Xi}{\partial (\beta \mu)} \right)_{T,V} = \langle N \rangle. \quad (6.14)$$

In the expression 5.2 for the grand partition function Ξ only Ξ_L depends on the chemical potential. Taking into account its expression 5.42, as well as the expression 6.6 for $\Xi_L^{(1)}$, we arrive at the equation

$$\langle N \rangle_0 \left(\mathbf{m}_1 + \frac{\mathbf{m}_2 \mathbf{m}_3}{|\mathbf{m}_4|} + \frac{\mathbf{m}_3^3}{3\mathbf{m}_4^2} + \rho_0^{\max} \right) = \langle N \rangle. \quad (6.15)$$

Applying the conditions $\langle N \rangle_0 = \langle N \rangle$ and $\mathbf{m}_1 = 1$, we get

$$\rho_0^{\max} = - \left(\frac{\mathbf{m}_2 \mathbf{m}_3}{|\mathbf{m}_4|} + \frac{\mathbf{m}_3^3}{3\mathbf{m}_4^2} \right). \quad (6.16)$$

In a number of works, see e.g. [8, 20, 24], the right-hand side expression is considered as a distinct quantity and is denoted as Δ

$$\Delta \equiv - \left(\frac{\mathbf{m}_2 \mathbf{m}_3}{|\mathbf{m}_4|} + \frac{\mathbf{m}_3^3}{3\mathbf{m}_4^2} \right). \quad (6.17)$$

Thus there are three conditions to be met at the critical point. The first one, which follows from the requirements of Ising model symmetry, is

$$\mu^* = 0. \quad (6.18)$$

The second one is

$$d'(0) = 0, \quad (6.19)$$

and the third one, which follows from the requirement that $\rho_0^{\max} = 0$ at the critical point, is

$$\Delta = 0. \quad (6.20)$$

From the last condition we can immediately find the value of the critical density. Solving the equation $\Delta = 0$ numerically gives us

$$\eta_c = 0.12867, \quad \rho_c^* = 0.24574 \quad (6.21)$$

in the Percus-Yevick approximation, and

$$\eta_c = 0.13044, \quad \rho_c^* = 0.24913 \quad (6.22)$$

in the Carnahan-Starling approximation. It worth noting that the condition $\Delta = 0$ is equivalent to $\mathfrak{M}_3 = 0$, and consequently to $\mathfrak{m}_3 = 0$.

The equation for the critical temperature follows from the second condition

$$T_c^* = -\frac{6\eta_c}{\pi a_2'} \frac{\hat{\Phi}_0}{\varepsilon\sigma^3} = -\frac{\rho_c^*}{a_2'} \frac{\hat{\Phi}_0}{\varepsilon\sigma^3}. \quad (6.23)$$

Its numerical values for the potential parameter $R_0/\alpha = 3.5$ are $T_c^* = 2.197$ and $T_c^* = 2.202$ in the Percus-Yevick and Carnahan-Starling approximations, respectively.

There are a few important conclusions regarding results based on the condition $\langle N \rangle_0 = \langle N \rangle$. First, the value of the critical density does not depend on the parameters of the attractive part of the potential. This consequence is very contradictory since the critical density is the same for any form of $\Phi(r)$ at $r \geq \sigma$, including very weak interactions. The value of η_c does not depend on the approximation used for the grand partition function calculation, and its mean-field value obtained in this work is the same as the one obtained in [8].

Second, the critical temperature does depend on the parameters of interaction, and approaches zero as the range of interaction becomes shorter and shorter ($\alpha \rightarrow \infty$, $\hat{\Phi}_0 \rightarrow 0$).

In this approach we can also find the value of the chemical potential at the critical point. From the condition $\mu^* = 0$ and Eq. (5.21) we get

$$\beta(\mu_c - \mu_0) = -\mathfrak{M}_3/\mathfrak{M}_4 - \alpha(0)\tilde{\mathfrak{M}}_1 = -\mathfrak{m}_3/\mathfrak{m}_4 - \frac{6\eta}{\pi} \frac{\varepsilon}{k_B T} \frac{\hat{\Phi}_0}{\varepsilon\sigma^3} \tilde{\mathfrak{m}}_1$$

Table 3. Critical values of chemical potential for different parameters R_0/α .

R_0/α	$\beta(\mu_c - \mu_0)$	$\beta\mu_c^{\text{ex}}$
2.0	2.6699	4.0342
2.5	2.6228	3.9872
3.0	2.5812	3.9456
3.5	2.5453	3.9097
4.0	2.5143	3.8787
4.5	2.4877	3.8520
5.0	2.4645	3.8289
5.5	2.4444	3.8088
6.0	2.4268	3.7911

where the following notation was introduced by the analogy with Eq. (5.16)

$$\tilde{\mathfrak{m}}_1 = \mathfrak{m}_1 - \frac{\mathfrak{m}_2\mathfrak{m}_3}{\mathfrak{m}_4} + \frac{\mathfrak{m}_3^3}{3\mathfrak{m}_4^2}, \quad (6.24)$$

Since $\mathfrak{m}_3 = 0$ at the critical point, and $\mathfrak{m}_1 = 1$, we get

$$\beta(\mu_c - \mu_0) = -\frac{\rho_c^*}{T_c^*} \frac{\hat{\Phi}_0}{\varepsilon\sigma^3} = a_2'. \quad (6.25)$$

The numerical values of the chemical potential difference at the critical point are summarized in Table 3 for different interaction parameters.

The chemical potential of a system can be represented as a sum of ideal and excess parts

$$\mu = \mu^{\text{id}} + \mu^{\text{ex}}.$$

Thus the difference $\beta(\mu - \mu_0)$ is essentially the difference between excess chemical potentials. The excess chemical potential of a hard-sphere system in the Carnahan-Starling approximation is

$$\beta\mu_0^{\text{ex}} = \frac{8\eta - 9\eta^2 + 3\eta^3}{(1 - \eta)^3}. \quad (6.26)$$

At the critical density $(\beta\mu_0^{\text{ex}})_c = 1.3644$. Thus, we can calculate the excess chemical potential of the whole system at the critical point. The results are presented in Table 3.

7. Conclusion

We have obtained the functional-integral representation for the grand partition function for the classical many-particle interacting system. The main result is presented with Eq. (5.43). This expression will be subject to applying the renormalization group transformation near the liquid-gas critical point in future works. In this paper, the mean-field approximation was applied to calculate the coordinates of critical point, using a system of hard-spheres with the Morse potential as an example.

A. Total correlation functions

A.1. Definitions

The definition of the n-particle distribution function is taken from [25] (see Eq. (2.6.7) therein)

$$g^{(n)}(\mathbf{r}^n) = \frac{\rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)}{\prod_{i=1}^n \rho^{(1)}(\mathbf{r}_i)} \quad (\text{A.1})$$

where $\rho^{(n)}$ is the n-particle density (see Eq. (2.6.1) in [25]), which is defined as:

$$\rho^{(n)}(\mathbf{r}^n) = \frac{1}{\Xi} \sum_{N=n}^{\infty} \frac{z^N}{(N-n)!} \int \exp(-\beta U_N) d\mathbf{r}^{(N-n)} \quad (\text{A.2})$$

Here $\mathbf{r}^n \equiv \mathbf{r}_1, \dots, \mathbf{r}_n$, and $d\mathbf{r}^{(N-n)} = d\mathbf{r}_{n+1} \dots d\mathbf{r}_N$.

Let's introduce an hierarchy of total correlation functions. The most widely known element of this hierarchy is the pair correlation function

$$h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - 1 \quad (\text{A.3})$$

(e.g., see Eq. (2.6.8) in [25]).

Let's express the total correlation functions in terms of the n-particle distribution functions. Formally, one can introduce the hierarchy of total correlation functions starting from $n = 1$ and on. By definition

$$g^{(1)}(\mathbf{r}) \equiv 1. \quad (\text{A.4})$$

Thus, for $n = 1$ one has:

$$h^{(1)}(\mathbf{r}) = g^{(1)}(\mathbf{r}) = 1. \quad (\text{A.5})$$

For $n = 2$:

$$h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - 1 \quad (\text{A.6})$$

For $n = 3$:

$$h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - g^{(2)}(\mathbf{r}_1, \mathbf{r}_3) - g^{(2)}(\mathbf{r}_2, \mathbf{r}_3) + 2. \quad (\text{A.7})$$

For $n = 4$:

$$\begin{aligned} h^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) &= g^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) - g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ &\quad - g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_4) - g^{(3)}(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_4) - g^{(3)}(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \\ &\quad - g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)g^{(2)}(\mathbf{r}_3, \mathbf{r}_4) - g^{(2)}(\mathbf{r}_1, \mathbf{r}_3)g^{(2)}(\mathbf{r}_2, \mathbf{r}_4) \\ &\quad - g^{(2)}(\mathbf{r}_1, \mathbf{r}_4)g^{(2)}(\mathbf{r}_2, \mathbf{r}_3) \\ &\quad + 2(g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + g^{(2)}(\mathbf{r}_1, \mathbf{r}_3) + g^{(2)}(\mathbf{r}_1, \mathbf{r}_4) \\ &\quad + g^{(2)}(\mathbf{r}_2, \mathbf{r}_3) + g^{(2)}(\mathbf{r}_2, \mathbf{r}_4) + g^{(2)}(\mathbf{r}_3, \mathbf{r}_4)) \\ &\quad - 6. \end{aligned} \quad (\text{A.8})$$

A.2. Expressed via $g^{(n)}$ and $h^{(m < n)}$

The total correlation functions $h^{(n)}$ can be expressed via $g^{(n)}$ and $h^{(m < n)}$. Such representation for total correlation functions $h^{(3)}$ and $h^{(4)}$ was used in [26].

For $n = 3$:

$$h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - h^{(2)}(\mathbf{r}_1, \mathbf{r}_3) - h^{(2)}(\mathbf{r}_2, \mathbf{r}_3) - 1. \quad (\text{A.9})$$

For $n = 4$:

$$\begin{aligned} h^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) &= g^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) - h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ &\quad - h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_4) - h^{(3)}(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_4) - h^{(3)}(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \\ &\quad - h^{(2)}(\mathbf{r}_1, \mathbf{r}_2)h^{(2)}(\mathbf{r}_3, \mathbf{r}_4) - h^{(2)}(\mathbf{r}_1, \mathbf{r}_3)h^{(2)}(\mathbf{r}_2, \mathbf{r}_4) \\ &\quad - h^{(2)}(\mathbf{r}_1, \mathbf{r}_4)h^{(2)}(\mathbf{r}_2, \mathbf{r}_3) \\ &\quad - h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - h^{(2)}(\mathbf{r}_1, \mathbf{r}_3) - h^{(2)}(\mathbf{r}_1, \mathbf{r}_4) \\ &\quad - h^{(2)}(\mathbf{r}_2, \mathbf{r}_3) - h^{(2)}(\mathbf{r}_2, \mathbf{r}_4) - h^{(2)}(\mathbf{r}_3, \mathbf{r}_4) \\ &\quad - 1. \end{aligned} \quad (\text{A.10})$$

From here it's straightforward to express $g^{(n)}$ via $h^{(m)}$, where $m \leq n$ (in [27] such expressions were presented for $n \leq 3$).

A.3. Expressed via $g^{(n)}$ through $g^{(1)}$

For $n = 2$:

$$h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - g^{(1)}(\mathbf{r}_1)g^{(1)}(\mathbf{r}_2) \quad (\text{A.11})$$

For $n = 3$:

$$\begin{aligned} h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)g^{(1)}(\mathbf{r}_3) \\ &\quad - g^{(2)}(\mathbf{r}_1, \mathbf{r}_3)g^{(1)}(\mathbf{r}_2) - g^{(2)}(\mathbf{r}_2, \mathbf{r}_3)g^{(1)}(\mathbf{r}_1) \\ &\quad + 2g^{(1)}(\mathbf{r}_1)g^{(1)}(\mathbf{r}_2)g^{(1)}(\mathbf{r}_3). \end{aligned} \quad (\text{A.12})$$

For $n = 4$:

$$\begin{aligned} h^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) &= \\ &= g^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \\ &\quad - g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)g^{(1)}(\mathbf{r}_4) - g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_4)g^{(1)}(\mathbf{r}_3) \\ &\quad - g^{(3)}(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_4)g^{(1)}(\mathbf{r}_2) - g^{(3)}(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)g^{(1)}(\mathbf{r}_1) \\ &\quad - g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)g^{(2)}(\mathbf{r}_3, \mathbf{r}_4) - g^{(2)}(\mathbf{r}_1, \mathbf{r}_3)g^{(2)}(\mathbf{r}_2, \mathbf{r}_4) \\ &\quad - g^{(2)}(\mathbf{r}_1, \mathbf{r}_4)g^{(2)}(\mathbf{r}_2, \mathbf{r}_3) \\ &\quad + 2[g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)g^{(1)}(\mathbf{r}_3)g^{(1)}(\mathbf{r}_4) + g^{(2)}(\mathbf{r}_1, \mathbf{r}_3)g^{(1)}(\mathbf{r}_2)g^{(1)}(\mathbf{r}_4) \\ &\quad + g^{(2)}(\mathbf{r}_1, \mathbf{r}_4)g^{(1)}(\mathbf{r}_2)g^{(1)}(\mathbf{r}_3) + g^{(2)}(\mathbf{r}_2, \mathbf{r}_3)g^{(1)}(\mathbf{r}_2)g^{(1)}(\mathbf{r}_4) \\ &\quad + g^{(2)}(\mathbf{r}_2, \mathbf{r}_4)g^{(1)}(\mathbf{r}_1)g^{(1)}(\mathbf{r}_3) + g^{(2)}(\mathbf{r}_3, \mathbf{r}_4)g^{(1)}(\mathbf{r}_1)g^{(1)}(\mathbf{r}_2)] \\ &\quad - 6g^{(1)}(\mathbf{r}_1)g^{(1)}(\mathbf{r}_2)g^{(1)}(\mathbf{r}_3)g^{(1)}(\mathbf{r}_4). \end{aligned} \quad (\text{A.13})$$

Equivalent representations for n -point correlation functions were used in [28] in research on galaxy clustering.

To simplify notation, let's denote $(\mathbf{r}_1, \dots, \mathbf{r}_n) = (1, \dots, n)$. And let's group similar terms under summation signs. Then $h^{(3)}$ and $h^{(4)}$ can be rewritten as

$$\begin{aligned} h^{(3)}(1, 2, 3) &= g^{(3)}(1, 2, 3) - \sum_{\mathbf{l}=\left\{\begin{smallmatrix} 1,2,3 \\ 1,3,2 \\ 2,3,1 \end{smallmatrix}\right\}} g^{(2)}(l_1, l_2)g^{(1)}(l_3) \\ &\quad + 2g^{(1)}(1)g^{(1)}(2)g^{(1)}(3). \end{aligned} \quad (\text{A.14})$$

$$\begin{aligned} h^{(4)}(1, 2, 3, 4) &= g^{(4)}(1, 2, 3, 4) - \sum_{\mathbf{l}=\left\{\begin{smallmatrix} 1,2,3,4 \\ 1,2,4,3 \\ 1,3,4,2 \\ 2,3,4,1 \end{smallmatrix}\right\}} g^{(3)}(l_1, l_2, l_3)g^{(1)}(l_4) \\ &\quad - \sum_{\mathbf{l}=\left\{\begin{smallmatrix} 1,2,3,4 \\ 1,3,2,4 \\ 1,4,2,3 \end{smallmatrix}\right\}} g^{(2)}(l_1, l_2)g^{(2)}(l_3, l_4) \\ &\quad + 2 \sum_{\mathbf{l}=\left\{\begin{smallmatrix} 1,2,3,4 \\ 1,3,2,4 \\ 2,3,1,4 \\ 2,4,1,3 \\ 3,4,1,2 \end{smallmatrix}\right\}} g^{(2)}(l_1, l_2)g^{(1)}(l_3)g^{(1)}(l_4) \\ &\quad - 6g^{(1)}(1)g^{(1)}(2)g^{(1)}(3)g^{(1)}(4). \end{aligned} \quad (\text{A.15})$$

The sums extend over all distinct argument lists in which each point appears exactly once. E.g. $g^{(3)}(1, 2, 3)$ and $g^{(3)}(3, 2, 1)$ are not considered distinct, and terms such as $g^{(2)}(1, 2)g^{(2)}(2, 3)$ do not appear [28].

A.4. Fourier components of total correlation functions

The following generic notation is used for the Fourier components of the total correlation function:

$$\begin{aligned} \hat{h}^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_n) & \quad (\text{A.16}) \\ &= \int \exp(-i\mathbf{k}_1\mathbf{r}_1 - \dots - i\mathbf{k}_n\mathbf{r}_n)h^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)d\mathbf{r}_1 \dots d\mathbf{r}_n \end{aligned}$$

By properly selecting the origin, it can be shown that for a homogeneous isotropic system:

$$g^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = g^{(n)}(\mathbf{r}_1 - \mathbf{r}_n, \dots, \mathbf{r}_{n-1} - \mathbf{r}_n) \quad (\text{A.17})$$

and applying a proper change of variables it can be written as:

$$g^{(n)} = g^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_{n-1}) \quad (\text{A.18})$$

Thus,

$$h^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) \Rightarrow h^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_{n-1}) \quad (\text{A.19})$$

It enables us to write the following expressions for the Fourier components $\hat{h}^{(n)}(\mathbf{k}^n)$:

$$\frac{1}{V}\hat{h}^{(n)}(\mathbf{k}^n) = \hat{h}^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_{n-1})\delta_{\mathbf{k}_1+\dots+\mathbf{k}_n} \quad (\text{A.20})$$

where

$$\begin{aligned} \hat{h}^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_{n-1}) \\ = \int \exp(-i\mathbf{k}_1\mathbf{r}_1 - \dots - i\mathbf{k}_{n-1}\mathbf{r}_{n-1}) h^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_{n-1}) d\mathbf{r}_1 \dots d\mathbf{r}_{n-1} \end{aligned} \quad (\text{A.21})$$

In particular, for $n = 1$:

$$\hat{h}^{(1)}(\mathbf{k}) = \int \exp(-i\mathbf{k}\mathbf{r}) h^{(1)}(\mathbf{r}) d\mathbf{r} = \int \exp(-i\mathbf{k}\mathbf{r}) d\mathbf{r} \quad (\text{A.22})$$

$$\frac{1}{V} \hat{h}^{(1)}(\mathbf{k}) = \delta_{\mathbf{k}} \quad (\text{A.23})$$

For $n = 2$:

$$\frac{1}{V} \hat{h}^{(2)}(\mathbf{k}_1, \mathbf{k}_2) = \hat{h}^{(2)}(\mathbf{k}_1) \delta_{\mathbf{k}_1 + \mathbf{k}_2} \quad (\text{A.24})$$

A.5. Fourier transform of the radial correlation function for the hard-spheres system

From [17] (see Eqs. (3)-(5) therein) an explicit expression for $\hat{h}^{(2)}(k)$ can be calculated in the Percus-Yevick approximation. Figure 13 shows the dependency of $\hat{h}^{(2)}(k)/\sigma^3$ on $k\sigma$. Figure 14 shows the dependency of $\hat{h}^{(2)}(0)/\sigma^3$ on packing fraction η .

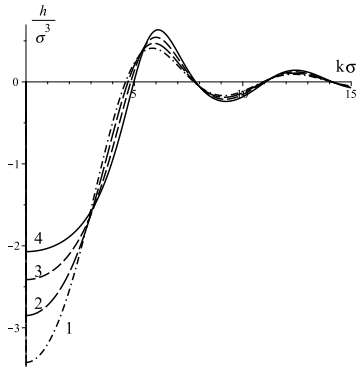


Figure 13. Fourier transform of the total correlation function $\hat{h}^{(2)}(k)/\sigma^3$ as a function of $k\sigma$. 1 - $\eta = 0.05$, 2 - $\eta = 0.1$, 3 - $\eta = 0.15$, and 4 - $\eta = 0.2$.

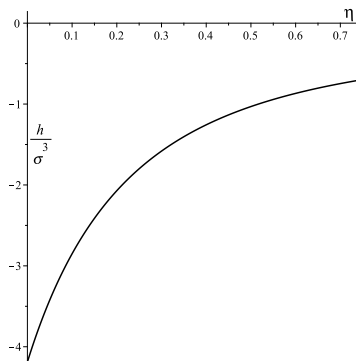


Figure 14. Fourier transform of the total correlation function $\hat{h}^{(2)}(k)/\sigma^3$ as a function of packing fraction η at $\mathbf{k} = 0$

A.6. Some recurrence relations for correlation functions

In this section, some recurrence relations for the total correlation functions $h^{(n)}$ will be derived. Let's use equations for the n -particle density from [18] (Eq. (A7) therein):

$$\begin{aligned} \left. \frac{\partial \rho^{(n)}}{\partial \rho} \right|_T = \\ = \frac{n\rho^{(n)} + \int \{\rho^{(n+1)}(\mathbf{r}_1, \dots, \mathbf{r}_{n+1}) - \rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)\rho^{(1)}(\mathbf{r}_{n+1})\} d\mathbf{r}_{n+1}}{(1/V) \int \rho^{(1)}(\mathbf{r}_1) d\mathbf{r}_1 + \int \{\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)\} d\mathbf{r}_1} \end{aligned}$$

which is rewritten in terms of the n -particle distribution functions as (Eq. (A8) in [18])

$$\begin{aligned} \left. \frac{\partial (\rho^n g^{(n)})}{\partial \rho} \right|_T = \\ = \frac{n\rho^{n-1}g^{(n)} + \rho^n \int \{g^{(n+1)}(\mathbf{r}_1, \dots, \mathbf{r}_{n+1}) - g^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)\} d\mathbf{r}_{n+1}}{1 + \rho \int \{g^2(\mathbf{r}_1, \mathbf{r}_2) - 1\} d\mathbf{r}_1} \end{aligned} \quad (\text{A.25})$$

First, consider $n = 2$ and rewrite (A.25) in terms of correlation functions:

$$\begin{aligned} \frac{\partial}{\partial \rho} \left(\rho^2 h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + \rho^2 \right) = \\ = \frac{2\rho(h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + 1)}{1 + \rho \hat{h}^{(2)}(0)} \\ + \frac{\int (h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + h^{(2)}(\mathbf{r}_1, \mathbf{r}_3) + h^{(2)}(\mathbf{r}_2, \mathbf{r}_3)) d\mathbf{r}_3}{1 + \rho \hat{h}^{(2)}(0)} \end{aligned} \quad (\text{A.26})$$

Then apply the following Fourier transformation to the above equation:

$$\mathcal{F}_2(\dots) = \iint e^{-i\mathbf{k}_1\mathbf{r}_1 - i\mathbf{k}_2\mathbf{r}_2} \dots d\mathbf{r}_1 d\mathbf{r}_2 \quad (\text{A.27})$$

As a result, after some algebraic manipulations, the following relations between $\hat{h}^{(3)}$ and $\hat{h}^{(2)}$ are obtained:

$$\begin{aligned} \hat{h}^{(3)}(\mathbf{k}_1, \mathbf{k}_2, 0) = 2\hat{h}^{(2)}(0)\hat{h}^{(2)}(\mathbf{k}_1, \mathbf{k}_2) + \frac{\partial \hat{h}^{(2)}(\mathbf{k}_1, \mathbf{k}_2)}{\partial \rho} (1 + \rho \hat{h}^{(2)}(0)), \\ \hat{h}^{(3)}(k, -k) = 2\hat{h}^{(2)}(0)\hat{h}^{(2)}(k) + \frac{\partial \hat{h}^{(2)}(k)}{\partial \rho} (1 + \rho \hat{h}^{(2)}(0)). \end{aligned} \quad (\text{A.28})$$

Similarly, the relations between $\hat{h}^{(4)}$ and $\hat{h}^{(3)}$ are following:

$$\begin{aligned}\hat{h}^{(4)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, 0) &= 3\hat{h}^{(2)}(0)\hat{h}^{(3)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) \\ &+ \frac{\partial\hat{h}^{(3)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)}{\partial\rho}(1 + \rho\hat{h}^{(2)}(0)), \\ \hat{h}^{(4)}(\mathbf{k}_1, \mathbf{k}_2, 0) &= 3\hat{h}^{(2)}(0)\hat{h}^{(3)}(\mathbf{k}_1, \mathbf{k}_2) \\ &+ \frac{\partial\hat{h}^{(3)}(\mathbf{k}_1, \mathbf{k}_2)}{\partial\rho}(1 + \rho\hat{h}^{(2)}(0))\end{aligned}\quad (\text{A.29})$$

The relations (4.18) and (4.19) for cumulants follow directly from (A.28) and (A.29), respectively.

B. Cumulants calculation

For the sake of simplicity, in this Appendix we will omit the subscript 0 at the notation for averages, $\langle \dots \rangle_0 \Rightarrow \langle \dots \rangle$, and also will understand $\Psi_N \equiv \Psi_N(\mathbf{r}^N)$.

B.1. $n = 1$

$$\mathfrak{M}_1(\mathbf{k}) = \langle \hat{\rho}_{\mathbf{k}} \rangle. \quad (\text{B.1})$$

$$\begin{aligned}\langle \hat{\rho}_{\mathbf{k}} \rangle &= \Xi_0^{-1} \sum_{N=0}^{\infty} \frac{z_0^N}{N!} \int \sum_{j=1}^N \exp(-i\mathbf{k}\mathbf{r}_j) \exp(-\beta\Psi_N) \mathbf{dr}^N \\ &= \Xi_0^{-1} \sum_{N=0}^{\infty} \frac{z_0^N}{N!} \int \exp(-i\mathbf{k}\mathbf{r}') \sum_{j=1}^N \delta(\mathbf{r}' - \mathbf{r}_j) \exp(-\beta\Psi_N) \mathbf{dr}^N \mathbf{dr}' \\ &= \int \exp(-i\mathbf{k}\mathbf{r}') \left\langle \sum_{j=1}^N \delta(\mathbf{r}' - \mathbf{r}_j) \right\rangle \mathbf{dr}'\end{aligned}\quad (\text{B.2})$$

It can be shown that (see Eq (2.5.11) and p.40 in [25])

$$\left\langle \sum_{j=1}^N \delta(\mathbf{r}' - \mathbf{r}_j) \right\rangle = \rho^{(1)}(\mathbf{r}') \quad (\text{B.3})$$

where $\rho^{(1)}(\mathbf{r})$ is the equilibrium single-particle density.

For a homogeneous system (uniform fluid):

$$\rho^{(1)}(\mathbf{r}) = \frac{\langle N \rangle}{V} \quad (\text{B.4})$$

Thus

$$\langle \hat{\rho}_{\mathbf{k}} \rangle = \frac{\langle N \rangle}{V} \int \exp(-i\mathbf{k}\mathbf{r}') \mathbf{dr}' = \langle N \rangle \delta_{\mathbf{k}}. \quad (\text{B.5})$$

$$\boxed{\mathfrak{M}_1(\mathbf{k}) = \langle N \rangle \delta_{\mathbf{k}}.} \quad (\text{B.6})$$

B.2. $n = 2$

$$\mathfrak{M}_2(\mathbf{k}_1, \mathbf{k}_2) = \langle \hat{\rho}_{\mathbf{k}_1} \hat{\rho}_{\mathbf{k}_2} \rangle - \langle \hat{\rho}_{\mathbf{k}_1} \rangle \langle \hat{\rho}_{\mathbf{k}_2} \rangle. \quad (\text{B.7})$$

$$\begin{aligned}\langle \hat{\rho}_{\mathbf{k}_1} \hat{\rho}_{\mathbf{k}_2} \rangle &= \\ &= \Xi_0^{-1} \sum_{N=0}^{\infty} \frac{z_0^N}{N!} \int \sum_{i=1}^N \exp(-i\mathbf{k}_1\mathbf{r}_i) \sum_{j=1}^N \exp(-i\mathbf{k}_2\mathbf{r}_j) \exp(-\beta\Psi_N) \mathbf{dr}^N\end{aligned}$$

Let's single out the term with $i = j$:

$$\begin{aligned}\langle \hat{\rho}_{\mathbf{k}_1} \hat{\rho}_{\mathbf{k}_2} \rangle &= \Xi_0^{-1} \sum_{N=0}^{\infty} \frac{z_0^N}{N!} \int \left[\sum_{i=1}^N \exp(-i(\mathbf{k}_1 + \mathbf{k}_2)\mathbf{r}_i) \right. \\ &\quad \left. + \sum_{i=1}^N \exp(-i\mathbf{k}_1\mathbf{r}_i) \sum_{\substack{j=1 \\ j \neq i}}^N \exp(-i\mathbf{k}_2\mathbf{r}_j) \right] \exp(-\beta\Psi_N) \mathbf{dr}^N\end{aligned}$$

The first term is $\langle \hat{\rho}_{\mathbf{k}_1 + \mathbf{k}_2} \rangle$ and thus is equal to $\langle N \rangle \delta_{\mathbf{k}_1 + \mathbf{k}_2}$. Let's rewrite the second term via δ -functions:

$$\begin{aligned}\langle \hat{\rho}_{\mathbf{k}_1} \hat{\rho}_{\mathbf{k}_2} \rangle &= \langle N \rangle \delta_{\mathbf{k}_1 + \mathbf{k}_2} \\ &+ \Xi_0^{-1} \sum_{N=0}^{\infty} \frac{z_0^N}{N!} \int e^{-i\mathbf{k}_1\mathbf{r}'} e^{-i\mathbf{k}_2\mathbf{r}''} \\ &\times \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \delta(\mathbf{r}' - \mathbf{r}_i) \delta(\mathbf{r}'' - \mathbf{r}_j) \exp(-\beta\Psi_N) \mathbf{dr}^N \mathbf{dr}' \mathbf{dr}'' \\ &= \langle N \rangle \delta_{\mathbf{k}_1 + \mathbf{k}_2} \\ &+ \iint e^{-i\mathbf{k}_1\mathbf{r}'} e^{-i\mathbf{k}_2\mathbf{r}''} \left\langle \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \delta(\mathbf{r}' - \mathbf{r}_i) \delta(\mathbf{r}'' - \mathbf{r}_j) \right\rangle \mathbf{dr}' \mathbf{dr}''\end{aligned}$$

From [25] (see Eq (2.5.13) and the last paragraph on p.40 therein) it follows

$$\left\langle \sum_{i=1}^N \delta(\mathbf{r}' - \mathbf{r}_i) \sum_{\substack{j=1 \\ j \neq i}}^N \delta(\mathbf{r}'' - \mathbf{r}_j) \right\rangle = \rho^{(2)}(\mathbf{r}', \mathbf{r}'') \quad (\text{B.8})$$

where $\rho^{(2)}(\mathbf{r}', \mathbf{r}'')$ is the equilibrium 2-particle density, or just the pair density

$$\langle \hat{\rho}_{\mathbf{k}_1} \hat{\rho}_{\mathbf{k}_2} \rangle = \langle N \rangle \delta_{\mathbf{k}_1 + \mathbf{k}_2} + \iint e^{-i\mathbf{k}_1 \mathbf{r}'} e^{-i\mathbf{k}_2 \mathbf{r}''} \rho^{(2)}(\mathbf{r}', \mathbf{r}'') d\mathbf{r}' d\mathbf{r}'' \quad (\text{B.9})$$

Taking into account the definition (A.1) of the n -particle distribution function $g^{(n)}$, and the relationship between $\rho^{(n)}$ and $g^{(n)}$ for a homogeneous system

$$\rho^{(n)}(\mathbf{r}^n) = \rho^n g^{(n)}(\mathbf{r}^n) \quad (\text{B.10})$$

where $\rho = \langle N \rangle / V$ is the particle density, one arrives at

$$\begin{aligned} \langle \hat{\rho}_{\mathbf{k}_1} \hat{\rho}_{\mathbf{k}_2} \rangle &= \langle N \rangle \delta_{\mathbf{k}_1 + \mathbf{k}_2} \\ &+ \rho^2 \iint e^{-i\mathbf{k}_1 \mathbf{r}'} e^{-i\mathbf{k}_2 \mathbf{r}''} g^{(2)}(\mathbf{r}', \mathbf{r}'') d\mathbf{r}' d\mathbf{r}'' \end{aligned} \quad (\text{B.11})$$

Here $g^{(2)}(\mathbf{r}', \mathbf{r}'')$ is called the pair distribution function. Taking into account the definition (A.3) for the pair (total) correlation function $h^{(2)}$, one has

$$\begin{aligned} \langle \hat{\rho}_{\mathbf{k}_1} \hat{\rho}_{\mathbf{k}_2} \rangle &= \langle N \rangle \delta_{\mathbf{k}_1 + \mathbf{k}_2} + \rho^2 \iint e^{-i\mathbf{k}_1 \mathbf{r}'} e^{-i\mathbf{k}_2 \mathbf{r}''} h^{(2)}(\mathbf{r}', \mathbf{r}'') d\mathbf{r}' d\mathbf{r}'' \\ &+ \frac{\langle N \rangle^2}{V^2} \iint e^{-i\mathbf{k}_1 \mathbf{r}'} e^{-i\mathbf{k}_2 \mathbf{r}''} d\mathbf{r}' d\mathbf{r}'' \end{aligned} \quad (\text{B.12})$$

The last term is equal to $\langle N \rangle^2 \delta_{\mathbf{k}_1} \delta_{\mathbf{k}_2}$. For isotropic system $h^{(2)}(\mathbf{r}', \mathbf{r}'') = h^{(2)}(|\mathbf{r}' - \mathbf{r}''|)$, and the second term becomes

$$\begin{aligned} \frac{\langle N \rangle^2}{V^2} \iint e^{-i\mathbf{k}_1 \mathbf{r}'} e^{-i\mathbf{k}_2 \mathbf{r}''} d\mathbf{r}' d\mathbf{r}'' &= \left. \begin{array}{l} \text{Change of variables:} \\ \mathbf{r} = \mathbf{r}' - \mathbf{r}''; \quad \mathbf{R} = \mathbf{r}'' \\ \mathbf{r}' = \mathbf{R} + \mathbf{r}; \quad \mathbf{r}'' = \mathbf{R} \\ d\mathbf{r}' d\mathbf{r}'' = d\mathbf{r} d\mathbf{R} \end{array} \right| \\ &= \frac{\langle N \rangle^2}{V^2} \int \exp(-i(\mathbf{k}_1 + \mathbf{k}_2)\mathbf{R}) d\mathbf{R} \int \exp(-i\mathbf{k}_1 \mathbf{r}) h^{(2)}(r) d\mathbf{r} \\ &= \frac{\langle N \rangle^2}{V} \hat{h}^{(2)}(\mathbf{k}_1) \delta_{\mathbf{k}_1 + \mathbf{k}_2} = \langle N \rangle \rho \hat{h}^{(2)}(\mathbf{k}_1) \delta_{\mathbf{k}_1 + \mathbf{k}_2}. \end{aligned} \quad (\text{B.13})$$

One arrives at the final expression for $\langle \hat{\rho}_{\mathbf{k}_1} \hat{\rho}_{\mathbf{k}_2} \rangle$:

$$\langle \hat{\rho}_{\mathbf{k}_1} \hat{\rho}_{\mathbf{k}_2} \rangle = \langle N \rangle \delta_{\mathbf{k}_1 + \mathbf{k}_2} + \langle N \rangle \rho \hat{h}^{(2)}(\mathbf{k}_1) \delta_{\mathbf{k}_1 + \mathbf{k}_2} + \langle N \rangle^2 \delta_{\mathbf{k}_1} \delta_{\mathbf{k}_2}.$$

And for the cumulant \mathfrak{M}_2 the final expression is

$$\boxed{\mathfrak{M}_2(\mathbf{k}_1, \mathbf{k}_2) = \langle N \rangle \delta_{\mathbf{k}_1 + \mathbf{k}_2} (1 + \rho \hat{h}^{(2)}(\mathbf{k}_1))} \quad (\text{B.14})$$

The quantity $1 + \rho \hat{h}^{(2)}(\mathbf{k})$ is equal to the static structure factor of the uniform fluid (see [25], Eq. (3.6.10)):

$$S(\mathbf{k}) = 1 + \hat{h}^{(2)}(\mathbf{k}) \quad (\text{B.15})$$

$$\mathfrak{M}_2(\mathbf{k}_1, \mathbf{k}_2) = \langle N \rangle \delta_{\mathbf{k}_1 + \mathbf{k}_2} S(\mathbf{k}_1). \quad (\text{B.16})$$

The structure factor is related to the thermodynamic properties via the following relationship (see Eqs. (2.6.12), (3.5.14), and (3.6.11) in [29]):

$$S(0) = 1 + \rho \hat{h}^{(2)}(0) = \rho \chi_T / \beta = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle}, \quad (\text{B.17})$$

where χ_T is the isothermal compressibility. Thus for $\mathbf{k}_1 = \mathbf{k}_2 = 0$:

$$\boxed{\mathfrak{M}_2(0, 0) = \langle N^2 \rangle - \langle N \rangle^2} \quad (\text{B.18})$$

C. A method of calculation for cumulants at $\mathbf{k}_i = 0$

It follows from (3.7) and (3.4), that

$$\begin{aligned} \mathfrak{M}_n(0, \dots, 0) &= \frac{1}{(-i2\pi)^n} \frac{\partial^n \ln \langle \exp(-i2\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \hat{\rho}_{\mathbf{k}}) \rangle_0}{\partial \omega_0^n} \Big|_{\omega_{\mathbf{k}_i} = 0} \\ &= \frac{\partial^n \ln \Xi_0}{\partial (\beta \mu_0)^n} = \frac{\partial^{n-1} \langle N \rangle_0}{\partial (\beta \mu_0)^{n-1}} = \frac{\partial^{n-1} \mathfrak{M}_1(0)}{\partial (\beta \mu_0)^{n-1}} \\ &= \frac{\partial \mathfrak{M}_{n-1}(0, \dots, 0)}{\partial (\beta \mu_0)}. \end{aligned} \quad (\text{C.1})$$

Then from (2.33) one derives

$$\frac{\partial \langle N \rangle_0}{\partial (\beta \mu_0)} = \langle N^2 \rangle_0 - \langle N \rangle_0^2, \quad (\text{C.2})$$

$$\frac{\partial \langle N^2 \rangle_0}{\partial (\beta \mu_0)} = \langle N^3 \rangle_0 - \langle N^2 \rangle_0 \langle N \rangle_0, \quad (\text{C.3})$$

$$\frac{\partial \langle N^3 \rangle_0}{\partial (\beta \mu_0)} = \langle N^4 \rangle_0 - \langle N^3 \rangle_0 \langle N \rangle_0, \quad (\text{C.4})$$

and so on, to give in general:

$$\frac{\partial \langle N^n \rangle_0}{\partial (\beta \mu_0)} = \langle N^{n+1} \rangle_0 - \langle N^n \rangle_0 \langle N \rangle_0. \quad (\text{C.5})$$

Thus the equation for $\mathfrak{M}_2(0, 0)$ is obtained immediately

$$\begin{aligned} \mathfrak{M}_2(0, 0) &= \frac{\partial \langle N \rangle_0}{\partial (\beta \mu_0)} = \langle N^2 \rangle_0 - \langle N \rangle_0^2 \\ &= \langle (N - \langle N \rangle_0)^2 \rangle_0. \end{aligned} \quad (\text{C.6})$$

Explicit calculation for $\mathfrak{M}_3(0, 0, 0)$ leads to

$$\begin{aligned} \mathfrak{M}_3(0, 0, 0) &= \frac{\partial}{\partial (\beta \mu_0)} (\langle N^2 \rangle_0 - \langle N \rangle_0^2) \\ &= \langle (N - \langle N \rangle_0)^3 \rangle_0. \end{aligned} \quad (\text{C.7})$$

And for $\mathfrak{M}_4(0, 0, 0, 0)$:

$$\begin{aligned} \mathfrak{M}_4(0, 0, 0, 0) &= \frac{\partial}{\partial (\beta \mu_0)} (\langle N^3 \rangle_0 - 3 \langle N^2 \rangle_0 \langle N \rangle_0 + 2 \langle N \rangle_0^3) \\ &= \langle (N - \langle N \rangle_0)^4 \rangle_0 - 3 \langle (N - \langle N \rangle_0)^2 \rangle_0^2. \end{aligned} \quad (\text{C.8})$$

D. Notation

The list of notations used throughout the work follows.

\mathbf{r} - the coordinate in three-dimensional space;

$r \equiv |\mathbf{r}|$ - the absolute value of \mathbf{r} .

\mathbf{k} - the wave vector in the reciprocal space.

$k \equiv |\mathbf{k}|$ - the absolute value of the wave vector \mathbf{k} .

$\delta(\dots)$ - the Dirac's δ -function.

δ_{\dots} - the Kronecker's δ -symbol.

V - the volume.

N - the number of particles.

ρ - the particle density.

η - the packing fraction.

$n(\mathbf{r})$ - the microscopic particle density.

$\hat{\rho}_{\mathbf{k}}$ - the Fourier component of the microscopic particle density.

$\rho_{\mathbf{k}}, \rho_0$ - the collective variables.

Ξ - the grand partition function.

z - the activity.

μ - the chemical potential.

Ξ_0, z_0, μ_0 - the grand partition function, activity, and chemical potential of the reference system, respectively.

Z_N - the configuration integral.

β - the inverse temperature.

Λ - the de Broglie thermal wavelength.

$\rho^{(n)}(\mathbf{r}^n)$ - the equilibrium n -particle density.

$g^{(n)}(\mathbf{r}^n)$ - the n -particle distribution function.

$h^{(n)}(\mathbf{r}^n)$ - the n -particle total correlation function.

$\hat{h}^{(n)}(\mathbf{k}^n)$ - the Fourier component of the n -particle total correlation function.

$U(r_{ij})$ - the full pairwise interaction potential between two particles i and j at distance r_{ij} .

$U_N(\mathbf{r}^N), U_N$ - the potential energy of the interparticle interaction.

$\Psi(r_{ij})$ - the repulsive part of the full interaction potential.

$\Psi_N(\mathbf{r}^N), \Psi_N$ - the potential energy of the short-range repulsive interaction.

$\Phi(r_{ij})$ - the attractive part of the full interaction potential.

$\Phi_N(\mathbf{r}^N), \Phi_N$ - the potential energy of the long-range attractive interaction.

σ - the hard-sphere diameter.

$J(\rho - \hat{\rho})$ - the Jacobian for transformation from $\hat{\rho}_{\mathbf{k}}$ to $\rho_{\mathbf{k}}$.

$\omega_{\mathbf{k}}, \omega_0$ - the variables conjugate to collective variables $\rho_{\mathbf{k}}, \rho_0$.

$\mathfrak{M}_n(\mathbf{k}^n)$, $\mathfrak{m}_n(\mathbf{k}^{n-1})$ - the cumulants (semi-invariants).
 $\mathfrak{J}(\rho)$ - the Jacobian $J(\rho - \hat{\rho})$ averaged over the reference system.
 $\mathfrak{J}(\omega)$ - the part of Jacobian $\mathfrak{J}(\rho)$ dependent on $\omega_{\mathbf{k}}$.

Abbreviations

The following abbreviations were used throughout the work.

GPF - Grand Partition Function.
 HS - Hard Spheres.
 MF - Mean Field.
 RS - Reference System.

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