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2003 J. Phys.: Condens. Matter 15 S395

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# The compressibility equation for soft-matter liquids

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Received 6 November 2002

Published 16 December 2002

Online at [stacks.iop.org/JPhysCM/15/S395](http://stacks.iop.org/JPhysCM/15/S395)

## Abstract

Effective interactions in soft-matter physics result from a formal contraction of an initial multicomponent system, composed of mesoscopic and small particles, into an effective one-component description. By tracing out in the partition function the degrees of freedom of the small particles, a one-component system of mesoscopic particles interacting with a state-dependent Hamiltonian is found. Although the effective Hamiltonian is not in general pairwise additive, it is usually approximated by a volume term and a pair-potential contribution. In this paper the relation between the structure, for which the volume term plays no role, and the thermodynamics of a fluid of particles interacting with a density-dependent pair potential is analysed. It is shown that the compressibility equation differs from that of atomic fluids. An important consequence is that the infinite-compressibility line derived from the thermodynamics does not coincide with the spinodal line stemming from the divergence of correlations.

## 1. Introduction

The term soft-matter (complex) fluids refers to multicomponent fluids composed of mesoscopic (colloidal) particles dispersed into a solvent of microscopic (atomic) particles which may contain other small constituents such as ions of a dissociated salt or short polymeric chains [1]. Since the size of the colloidal particles exceeds that of the remaining constituents by three or four orders of magnitude, it is natural to contract the initial multicomponent system into a one-component description involving only the mesoscopic particles. This can be formally done [2] by integrating in the partition function the coordinates and momenta of the small particles, leading to an ‘effective’ Hamiltonian for the mesoscopic particles which, together with the direct interactions, contains a free-energy term. This term can be formally expanded [3] as the sum of a ‘volume’ contribution (which does not contain the coordinates of the mesoscopic particles) and  $n$ -particle state-dependent interactions ( $n = 2, 3, \dots$ ). In order to take advantage of the well-known methods developed for simple atomic fluids, this expansion is usually truncated at second order yielding the ‘pair-potential approximation’.

In this paper we analyse the relation between the structure, for which the volume term plays no role, and the thermodynamics of a fluid of colloidal particles interacting with a density-dependent pair potential. In the next section we first review some well-known concepts for atomic fluids.

## 2. Pair correlation and direct correlation routes

The free energy  $F_0$  of a simple atomic fluid of particles interacting with a central pair potential  $V_0(|\mathbf{r} - \mathbf{r}'|)$  can be split into the ideal part,  $F_0^{\text{id}}$ , and the excess contribution,  $F_0^{\text{ex}}$ .

When  $F_0^{\text{ex}}$  is viewed as a functional of the interaction potential,  $F_0^{\text{ex}} = F_0^{\text{ex}}[V_0]$ , the two-particle density is defined as the first functional derivative [4]:

$$\rho_0(\mathbf{r}, \mathbf{r}') = 2 \frac{\delta F_0^{\text{ex}}[V_0]}{\delta V_0(|\mathbf{r} - \mathbf{r}'|)}. \quad (1)$$

Integrating equation (1) following a linear path of potentials  $\lambda V_0(r)$  between the ideal gas ( $\lambda = 0$ ) and the actual fluid ( $\lambda = 1$ ) yields for a uniform phase ( $\rho_0(\mathbf{r}, \mathbf{r}') = \rho^2 g_0(|\mathbf{r} - \mathbf{r}'|; \rho)$ ), where  $\rho$  is the average number density and  $g_0(r; \rho)$  is the pair correlation function (pcf),

$$f_0^{\text{ex}}(\rho) = \frac{1}{2} \rho \int_0^1 d\lambda \int d\mathbf{r} V_0(r) g_0(r; \rho|\lambda), \quad (2)$$

where  $f_0^{\text{ex}}(\rho)$  is the excess free energy per particle and  $g_0(r; \rho|\lambda)$  denotes the pcf for the fluid with potential  $\lambda V_0(r)$ . Note that equation (2) involves a charging process of interactions.

When a single-particle external field potential  $\phi(\mathbf{r})$  is added to the Hamiltonian,  $F_0^{\text{ex}}$  is a unique functional of the local density  $\rho(\mathbf{r})$ ,  $F_0^{\text{ex}} = F_0^{\text{ex}}[\rho]$ , for a given interaction potential. The Ornstein–Zernike direct correlation function (dcf) is defined as the second functional derivative [4]:

$$c_0(\mathbf{r}, \mathbf{r}') = - \frac{\delta^2 \beta F_0^{\text{ex}}[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')}, \quad (3)$$

where  $\beta = 1/k_B T$ , with  $k_B$  Boltzmann's constant and  $T$  the temperature. Integrating equation (3) twice following a linear path in the space of density functions  $\xi \rho(\mathbf{r})$  ( $0 \leq \xi \leq 1$ ) yields for a uniform phase ( $\phi(\mathbf{r}) = 0$ ,  $\rho(\mathbf{r}) = \rho$ ,  $c_0(\mathbf{r}, \mathbf{r}') = c_0(|\mathbf{r} - \mathbf{r}'|; \rho)$ , where the dcf becomes an ordinary function of the average number density),

$$\beta f_0^{\text{ex}}(\rho) = \rho \int_0^1 d\xi (\xi - 1) \int d\mathbf{r} c_0(r; \xi \rho), \quad (4)$$

where  $c_0(r; \xi \rho)$  is the dcf for the fluid with average number density  $\xi \rho$ . Note that equation (4) involves a charging process of the density between the ideal gas ( $\xi = 0$ ) and the actual fluid ( $\xi = 1$ ). Note also that the cornerstone of the theory of simple fluids is that equations (2) and (4) are equivalent, i.e. they generate the same thermodynamics.

The dcf  $c_0(r; \rho)$  and the total correlation function (tcf)  $h_0(r; \rho) = g_0(r; \rho) - 1$  satisfy the Ornstein–Zernike equation [4], which for a fluid phase in Fourier space reads

$$1 - \rho \tilde{c}_0(k; \rho) = [1 + \rho \tilde{h}_0(k; \rho)]^{-1}, \quad (5)$$

where the tilde denotes a Fourier transform.

From the thermodynamic relation

$$p_0(\rho) = \rho^2 \frac{\partial f_0(\rho)}{\partial \rho}, \quad (6)$$

where  $p_0(\rho)$  is the pressure,  $f_0(\rho) = k_B T [\ln(\rho \Lambda^3) - 1] + f_0^{\text{ex}}(\rho)$ , and  $\Lambda$  is the thermal de Broglie wavelength, from equations (4) and (5) the compressibility equation follows:

$$\beta \frac{\partial p_0(\rho)}{\partial \rho} = 1 - \rho \tilde{c}_0(0; \rho) = [1 + \rho \tilde{h}_0(0; \rho)]^{-1}. \quad (7)$$

It is seen from equation (7) that the line of diverging correlations  $\tilde{h}_0(0; \rho) = \infty$  ( $\rho \tilde{c}_0(0; \rho) = 1$ ) coincides with the infinite-compressibility line  $\partial p_0(\rho)/\partial \rho = 0$ .

### 3. Soft-matter fluids

We now consider a fluid of mesoscopic particles interacting with a density-dependent pair potential  $V(r; \rho)$ . Since  $\rho$  appears in the Hamiltonian as a parameter, the procedure of section 2 which consists in charging the interactions from the ideal gas to the actual fluid can be easily transposed. Indeed, when the excess free energy of the colloidal fluid  $F^{\text{ex}}$  is viewed as a functional of the interaction potential,  $F^{\text{ex}} = F^{\text{ex}}[V(\rho)]$ , the two-particle density is

$$\rho(\mathbf{r}, \mathbf{r}') = 2 \frac{\delta F^{\text{ex}}[V(\rho)]}{\delta V(|\mathbf{r} - \mathbf{r}'|; \rho)}, \quad (8)$$

and following the same steps as in the previous section, the excess free energy per particle  $f^{\text{ex}}(\rho)$  for a uniform phase reads

$$f^{\text{ex}}(\rho) = \frac{1}{2} \rho \int_0^1 d\lambda \int d\mathbf{r} V(r; \rho) \bar{g}(r; \rho|\lambda), \quad (9)$$

where  $\bar{g}(r; \rho|\lambda)$  is the pcf for the fluid with potential  $\lambda V(r; \rho)$ .

At this point, we consider a simple example which shows that the compressibility equation for density-dependent pair potentials differs from equation (7). Let us assume that  $V(r; \rho)$  can be expanded as a series in the density:

$$V(r; \rho) = V_0(r) + \rho V_1(r) + O(\rho^2). \quad (10)$$

Integrating now equation (8) following the linear path of potentials  $V(r; \rho|\lambda) \equiv V_0(r) + \lambda[V(r; \rho) - V_0(r)]$ , the free energy per particle  $f(\rho)$  can be written as

$$f(\rho) = f_0(\rho) + \frac{1}{2} \rho \int_0^1 d\lambda \int d\mathbf{r} [V(r; \rho) - V_0(r)] g(r; \rho|\lambda), \quad (11)$$

where  $g(r; \rho|\lambda)$  denotes the pcf for the fluid with potential  $V(r; \rho|\lambda)$ . Note that  $f(\rho)$  and  $f_0(\rho)$  only differ in the density derivatives of  $V(r; \rho)$ . A simple approximation for  $f(\rho)$  can be obtained by truncating at second order in the density the last term in the rhs of equation (11), with  $g(r; \rho|\lambda) \simeq \exp[-\beta V_0(r)]$ , giving

$$f(\rho) = f_0(\rho) - \rho^2 a, \quad (12)$$

where

$$a = -\frac{1}{2} \int d\mathbf{r} V_1(r) \exp[-\beta V_0(r)]. \quad (13)$$

Note that equation (12) resembles the van der Waals equation for atomic fluids, leading to

$$\frac{\partial p(\rho)}{\partial \rho} = \frac{\partial p_0(\rho)}{\partial \rho} - 6\rho^2 a, \quad (14)$$

where  $p(\rho)$  is the (osmotic) pressure of the colloidal fluid.

With this simplification in mind, let us assume that both  $V(r; \rho)$  and  $V_0(r)$  are repulsive pair potentials. Since for the density-independent pair potential  $V_0(r)$  the pressure is an

increasing function of the density ( $\partial p_0(\rho)/\partial\rho > 0$ ), equation (14) shows that, whenever  $a > 0$ , thermodynamic states can be found for which  $\partial p(\rho)/\partial\rho \leq 0$ . In other words, the density dependence of the potential may produce van der Waals loops in the pressure yielding a vapour–liquid transition. This is the case for the Debye–Hückel potential:

$$V(r; \rho) = \frac{Z^2 e^2 \exp[-\kappa(\rho)r]}{\epsilon r}, \quad (15)$$

describing the effective pair-potential interaction between two point colloidal particles with total charge  $-Ze$ . In equation (15),  $\epsilon$  is the dielectric constant of the solvent and  $\kappa(\rho)$  denotes the Debye screening parameter:

$$\kappa^2(\rho) = \frac{4\pi e^2}{\epsilon k_B T} (Z\rho + 2\rho_s), \quad (16)$$

where  $\rho_s$  is the density of the ions of an added monovalent salt. It is seen from equations (15) and (16) that

$$\rho V_1(r) = -\frac{Z^2 e^2}{2\epsilon} \left( \frac{Z\rho}{2\rho_s} \right) \kappa(0) \exp[-\kappa(0)r] < 0, \quad (17)$$

and, hence,  $a > 0$ . Computer simulations [5] show that in the high-salt limit ( $2\rho_s \gg Z\rho$ ) the phase diagram contains only a fluid phase; that is, according to equation (17), the amplitude of  $\rho V_1(r)$  is so weak that the ‘attractive’ contribution in equation (14) is negligible, i.e.,  $\partial p(\rho)/\partial\rho \simeq \partial p_0(\rho)/\partial\rho > 0$ . On the other hand, in the low-salt limit ( $2\rho_s \ll Z\rho$ ) the phase diagram obtained by Monte Carlo simulations [6] contains a vapour–liquid transition; that is, the ‘attractive’ contribution in equation (14) drives the fluid towards a phase separation and the compressibility diverges for certain thermodynamic states, i.e.,  $\partial p(\rho)/\partial\rho = 0$ . But since the lack of attractions precludes the divergence of correlations, the equivalent to the compressibility equation (7) no longer holds. This result agrees with recent numerical simulations [7] and could explain the thermodynamic inconsistencies found in [8]<sup>1</sup>.

#### 4. Compressibility equation

As stated in equation (4), the basis of the compressibility equation for density-independent interactions consists in a charging process of the density. For density-dependent pair potentials a change of density simultaneously induces a change of interactions and when the excess free energy per particle is determined from the direct correlation route, pair correlation terms also contribute to  $f^{\text{ex}}(\rho)$ . This can be formally shown by introducing equation (4) into (11) and using the identity

$$\tilde{c}_0(0; \xi\rho) = \tilde{c}(0; \xi\rho) - \int_0^1 d\lambda \tilde{c}'(0; \xi\rho|\lambda), \quad (18)$$

<sup>1</sup> During the conference to which this Special Issue is devoted, a different opinion was expressed by Louis. According to this author an effective density-dependent pair potential cannot be properly interpreted without reference to the coarse-graining procedure by which it was derived. This is illustrated in [8] with a number of explicit examples. Note, however, that some of the inconsistencies discussed by this author in [8] result from the use of the standard compressibility equation whereas, as shown here, thermodynamically consistent results can be obtained within the pair-potential approximation only when the compressibility equation is modified as indicated below. To further illustrate this point it may also be observed here that the results of the simulations of an effective pair potential by Dijkstra and van Roij [6] are not compatible with the standard compressibility equation.

<sup>2</sup> Note that for density-independent potentials the fluid can be charged with interactions at constant density and vice versa. For density-dependent potentials the fluid can be charged with interactions at constant density but cannot be charged with density with constant interactions.

where  $\tilde{c}(0; \xi\rho|\lambda)$  is the zero-wavevector Fourier transform of the dcf for the fluid with potential  $V(r; \xi\rho|\lambda)$  (the prime denoting the derivative with respect to  $\lambda$ ) [9], giving

$$\beta f^{\text{ex}}(\rho) = \rho \int_0^1 d\xi (\xi - 1) \int d\mathbf{r} c(r; \xi\rho) + b(\rho), \quad (19)$$

with

$$b(\rho) = -\rho \int_0^1 d\xi (\xi - 1) \int_0^1 d\lambda [1 + \xi\rho\tilde{h}(0; \xi\rho|\lambda)]^{-2} \tilde{h}'(0; \xi\rho|\lambda) \\ + \frac{1}{2}\rho\beta \int_0^1 d\lambda \int d\mathbf{r} [V(r; \rho) - V_0(r)]g(r; \rho|\lambda), \quad (20)$$

where  $\tilde{h}(0; \xi\rho|\lambda)$  is the tcf related to  $\tilde{c}(0; \xi\rho|\lambda)$  through the Ornstein–Zernike equation. The compressibility equation then reads

$$\beta \frac{\partial p(\rho)}{\partial \rho} = 1 - \rho\tilde{c}(0; \rho) + \rho \left[ 2 \frac{\partial}{\partial \rho} + \rho \frac{\partial^2}{\partial \rho^2} \right] b(\rho), \quad (21)$$

showing that the infinite-compressibility line  $\partial p(\rho)/\partial \rho = 0$  does not coincide with the line of diverging correlations  $\rho\tilde{c}(0; \rho) = 1$ . Since equation (19) is an exact transformation of equations (11) or (9), it is seen that the pair correlation and the direct correlation routes are equivalent for density-dependent pair potentials<sup>3</sup>. Note that if  $b(\rho)$  were omitted in (19), the two routes would not generate the same thermodynamics.

A different interpretation of the compressibility equation for density-dependent pair potentials has also been recently considered [10]. We first note that when  $V_0(r)$  is replaced by a density-dependent pair potential  $V(r; \rho)$ , all the thermodynamical and structural quantities acquire a supplementary  $\rho$ -dependence induced by the effective potential. Let us call the  $\rho$ -dependence of section 2 ‘explicit’ and call the  $\rho$ -dependence induced via  $V(r; \rho)$  ‘implicit’. In order to distinguish between these  $\rho$ -dependences, we denote the pcf of the colloidal fluid by  $g(r; \rho; [V(\rho)])$ , where the first argument refers to the explicit  $\rho$ -dependence whereas the implicit  $\rho$ -dependence has been indicated through the functional dependence  $[V(\rho)]$ . Let  $c(r; \rho; [V(\rho)])$  denote the dcf related through the Ornstein–Zernike equation to  $g(r; \rho; [V(\rho)])$ . As noted in section 2, equations (2) and (4) are equivalent, i.e. when we perform the virial expansion of the excess free energy using the pair correlation and the direct correlation routes, we obtain the same virial coefficients in terms of Mayer functions involving the density-independent potential  $V_0(r)$ . In this case the charging process of the density in equation (4) operates on the explicit dependence (the unique  $\rho$ -dependence for density-independent potentials). If we assume that for density-dependent potentials the charging process of the density only operates on the explicit dependence, we obtain for both routes, by hypothesis, the same virial coefficients in terms of Mayer functions involving now the density-dependent potential  $V(r; \rho)$ , i.e. the same thermodynamics. Thus, if we want to maintain the equivalence of the two procedures, we propose to generalize the direct correlation route as

$$\beta f^{\text{ex}}(\rho) = \rho \int_0^1 d\xi (\xi - 1) \int d\mathbf{r} c(r; \xi\rho; [V(\rho)]); \quad (22)$$

<sup>3</sup> The basic difference between equations (4) and (19) is that for density-dependent pair potentials there is an additional term  $b(\rho)$ .

in other words, the  $\rho$  appearing in  $V(r; \rho)$  is treated as an external parameter<sup>4</sup>. From equation (22) we recover the compressibility equation (21), which reads in this formulation

$$\beta \frac{\partial p(\rho)}{\partial \rho} = 1 - \rho \tilde{c}(0; \rho; [V(\rho)]) - 2\rho \int_0^\rho d\rho' \frac{\partial \tilde{c}(0; \rho', [V(\rho)])}{\partial \rho} - \rho \int_0^\rho d\rho' \int_0^{\rho'} d\rho'' \frac{\partial^2 \tilde{c}(0; \rho'', [V(\rho)])}{\partial \rho^2}. \quad (23)$$

In summary, we have shown that the pair correlation and the direct correlation routes are equivalent for density-dependent pair potentials when the parameter  $\rho$  appearing in  $V(r; \rho)$  is interpreted either as an ‘active’ or as a ‘passive’ variable [11] in the charging process of the density. The resulting compressibility equation indicates that the thermodynamic states for which the compressibility diverges are different from the thermodynamic states for which the tcf is long ranged.

### Acknowledgments

The author acknowledges financial support from the Ministerio de Ciencia y Tecnología (Spain), reference: BFM2001-1017-C03-03. I wish to thank M Baus, G Ruiz, E Lomba and N G Almarza for many useful discussions and A A Louis for communicating with me [8] prior to publication.

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<sup>4</sup> In this formulation the direct correlation route does not contain additional terms. The difference between equations (22) and (19) arises since in equation (19) the charging process of the density operates on the global density (explicit and implicit).