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On the relation between the compressibility and the static structure factor of a fluid with a state-dependent pair-potential

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The compressibility equation of a fluid with an effective, state-dependent, pair-potential is derived. It is shown that the thermodynamic states for which the infinite wavelength limit of the static structure factor diverges are not consistent with the thermodynamic states for which the compressibility diverges whenever the effective potential is density-dependent. This result is in agreement with some recent numerical simulations. © 2003 American Institute of Physics.

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I. INTRODUCTION

In recent years it has become current practice to transpose the well-developed statistical mechanical methods from the theory of simple (atomic) fluids to the complex (say, colloidal) fluids encountered in many soft-matter systems.¹ In many instances the main constituent (say, the colloidal particles) of the complex fluid has characteristic space and time scales which are widely separated from those of the remaining constituents.¹ Under such circumstances it is natural to use a coarse-grained description by first integrating out from the partition function all the degrees of freedom not belonging to the main constituent.^{1,2} This procedure invariably leads to an “effective” Hamiltonian for the main constituent which contains a free-energy term and, hence, is state-dependent.¹ On many occasions this effective Hamiltonian has been further approximated in terms of state-dependent potentials. In the simplest case one then ends up describing the original complex fluid in terms of an “equivalent” simple fluid containing only the main constituent of the complex fluid but interacting now with a more complex, state-dependent, pair-potential. Two well-known examples of such effective pair-potentials are provided by the Debye-Hückel potential used to describe the interaction between two charged colloidal particles and the Asakura-Oosawa depletion potential used in the description of the interaction between two uncharged colloidal particles.^{1,3} Here we will, however, not question⁴ the oversimplifications usually involved in this reduction of the original complex fluid to a simple fluid with an effective pair-potential but, instead, inquire for the consequences of the state-dependence of this effective pair-potential on the statistical mechanical relations describing the corresponding “simple fluid.”

In the following we will thus be concerned solely with the question of how one can transpose the equilibrium statistical mechanical relations between the structure and the thermodynamics of a simple fluid with a pair-potential $V(r)$ to the case where the simple fluid has an effective pair-potential of the general form $V(r; \rho, T)$, where ρ represents the average number density of the uniform fluid and T its tempera-

ture. Henceforth we will design the (simple) fluid with the potential, $V(r)$, as the “simple” fluid, whereas the (simple) fluid with an effective potential, $V(r; \rho, T)$, will for the sake of brevity be simply designed as the “complex” fluid. In Sec. II we first briefly summarize the structure-thermodynamics relations of the simple fluid which will then, in Sec. III, be transposed to the complex fluid. Our conclusions will be gathered in Sec. IV.

II. THE SIMPLE FLUID

The following relations between the structural and thermodynamical properties of a uniform simple fluid are well-known.⁵⁻⁷ For future comparison we nevertheless briefly summarize the relevant material here. To simplify the notation, the T -dependence of the thermodynamic state will not be explicitly indicated but its ρ -dependence will be retained throughout.

A. Structural properties

Only the pair structure will be considered here. Within the present pair-potential approximation the potential energy, $U(\mathbf{x}^N)$, of an N -particle configuration $\{\mathbf{x}^N\} \equiv (\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ can be represented as

$$U(\{\mathbf{x}^N\}) = \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \hat{\rho}_2(\mathbf{r}_1, \mathbf{r}_2; \{\mathbf{x}^N\}) V(r_{12}), \quad (1)$$

where $V(r_{12})$ is the pair-potential, $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, and

$$\hat{\rho}_2(\mathbf{r}_1, \mathbf{r}_2; \{\mathbf{x}^N\}) = \sum_{i=1}^N \sum_{j=1, j \neq i}^N \delta(\mathbf{r}_1 - \mathbf{x}_i) \delta(\mathbf{r}_2 - \mathbf{x}_j), \quad (2)$$

the quantity whose thermal average yields the pair-density $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$,

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \left\langle \sum_{i=1}^N \sum_{j=1, j \neq i}^N \delta(\mathbf{r}_1 - \mathbf{x}_i) \delta(\mathbf{r}_2 - \mathbf{x}_j) \right\rangle, \quad (3)$$

where $\langle \dots \rangle$ represents a grand-canonical thermal average over the configurations $\{\mathbf{x}^N\}$.

For a uniform and isotropic fluid we have, in the thermodynamic limit, for the one-particle density,

$$\rho_1(\mathbf{r}_1) = \left\langle \sum_{j=1}^N \delta(\mathbf{r}_1 - \mathbf{x}_j) \right\rangle = \rho, \quad (4)$$

while the two-particle density of Eq. (3) can be written as:

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 g(r_{12}; \rho) = \rho^2 [1 + h(r_{12}; \rho)], \quad (5)$$

where $g(r; \rho)$ and $h(r; \rho)$ are, respectively, the pair- and total-correlation function (cf.). Finally, the direct cf., $c(r; \rho)$, can be obtained from $h(r; \rho)$ by using the Ornstein–Zernike equation,⁶ which can be written in Fourier space as

$$1 + \rho \tilde{h}(k; \rho) = [1 - \rho \tilde{c}(k; \rho)]^{-1}, \quad (6)$$

where $\tilde{S}(k; \rho) = 1 + \rho \tilde{h}(k; \rho)$ is the static structure factor and the tilde denotes a Fourier transform.

B. Thermodynamic properties

As is well-known,^{5–7} the thermodynamic properties can be expressed in terms of either $g(r; \rho)$ or $c(r; \rho)$.

1. The free-energy density

Let $f(\rho)$ denote the thermodynamic limit of the (grand-potential) free-energy per unit volume and $f_{\text{ex}}(\rho) = f(\rho) - f_{\text{id}}(\rho)$ its excess value, $f_{\text{id}}(\rho) = k_B T \rho [\ln(\rho \Lambda^3) - 1]$, k_B being Boltzmann’s constant, and Λ the thermal de Broglie wavelength resulting from the system’s kinetic energy. Integrating or “charging” the potential energy of Eq. (1) between the ideal gas ($\lambda = 0$) and the actual system ($\lambda = 1$) by the procedure outlined in, e.g., Ref. 5, one obtains

$$f_{\text{ex}}(\rho) = \frac{1}{2} \rho^2 \int d\mathbf{r} V(r) \int_0^1 d\lambda g^{(\lambda)}(r; \rho), \quad (7)$$

where $g^{(\lambda)}(r; \rho)$ denotes the value of $g(r; \rho)$ calculated for $\lambda V(r)$, instead of $V(r)$ [cf. $g^{(0)}(r; \rho) = 1, g^{(1)}(r; \rho) = g(r; \rho)$]. The theoretical basis for Eq. (7) rests on the fact⁵ that because of Eq. (1) the functional derivative of the free-energy with respect to $V(|\mathbf{r}_1 - \mathbf{r}_2|)$ equals $\rho_2(\mathbf{r}_1, \mathbf{r}_2)/2$. Alternatively, the excess free energy density can also be found by integrating or “charging” the density $\rho_1(\mathbf{r}_1) = \rho$ between the ideal gas ($\lambda = 0$) and the actual system ($\lambda = 1$) following the procedure outlined, e.g., in Ref. 5, yielding instead of Eq. (7):

$$\bar{f}_{\text{ex}}(\rho) = -k_B T \int d\mathbf{r} \int_0^\rho d\rho' \int_0^{\rho'} d\rho'' c(r; \rho''), \quad (8)$$

where, this time, the theoretical basis for Eq. (8) rests on the relation⁵ between the direct cf. and the second functional derivative of the free-energy with respect to $\rho_1(\mathbf{r}_1)$. Note that in a thermodynamically consistent theory we must have, $f_{\text{ex}}(\rho) = \bar{f}_{\text{ex}}(\rho)$, since both Eqs. (7) and (8) are exact. In what follows it will nevertheless be convenient to put a bar on the $f_{\text{ex}}(\rho)$ of Eq. (8).

To compare $f_{\text{ex}}(\rho)$ and $\bar{f}_{\text{ex}}(\rho)$ one can compare their (formal) virial or density expansions. To this end let us write the density expansion of $g(r; \rho)$ and $c(r; \rho)$ as

$$g(r; \rho) = \sum_{p=0}^{\infty} \rho^p g_p(r; [V]), \quad (9)$$

and

$$c(r; \rho) = \sum_{p=0}^{\infty} \rho^p c_p(r; [V]), \quad (10)$$

where, as is well-known,^{6,7} the $g_p(r; [V])$ and $c_p(r; [V])$ can be further expressed in terms of convolutions of Mayer functions. Note also that, for later convenience, we have explicitly indicated (but only in the r.h.s.) the functional dependence (cf. $[V]$) of Eqs. (9)–(10) on $V(r)$. Introducing Eq. (9) into Eq. (7) we obtain

$$f_{\text{ex}}(\rho) = \sum_{n=2}^{\infty} \rho^n B_n([V]), \quad (11)$$

where

$$B_n([V]) = \frac{1}{2} \int d\mathbf{r} V(r) \int_0^1 d\lambda g_{n-2}(r; [\lambda V]), \quad (12)$$

whereas introducing Eq. (10) into Eq. (8) results in

$$\bar{f}_{\text{ex}}(\rho) = \sum_{n=2}^{\infty} \rho^n \bar{B}_n([V]), \quad (13)$$

with

$$\bar{B}_n([V]) = -\frac{k_B T}{n(n-1)} \int d\mathbf{r} c_{n-2}(r; [V]). \quad (14)$$

Using now the explicit representation of Eqs. (9)–(10) in terms of Mayer functions, one can verify explicitly that, at least for the first few n -values, we have $B_n([V]) = \bar{B}_n([V])$, and although we know of no proof for a general n we will henceforth still consider that

$$f_{\text{ex}}(\rho) = \bar{f}_{\text{ex}}(\rho), \quad (15)$$

i.e., that the two descriptions of Eqs. (7)–(8) are thermodynamically consistent.⁸

2. The pressure

Once the free-energy density, $f(\rho)$, is known, the pressure, $p(\rho)$, and the inverse isothermal compressibility, $\partial p(\rho)/\partial \rho$, can be obtained from the thermodynamic relations

$$p(\rho) = \rho \frac{\partial f(\rho)}{\partial \rho} - f(\rho); \quad \frac{\partial p(\rho)}{\partial \rho} = \rho \frac{\partial^2 f(\rho)}{\partial \rho^2}. \quad (16)$$

From Eq. (7) one obtains then

$$p_{\text{ex}}(\rho) = \frac{1}{2} \rho^2 \int d\mathbf{r} V(r) \int_0^1 d\lambda \left[g^{(\lambda)}(r; \rho) + \rho \frac{\partial g^{(\lambda)}(r; \rho)}{\partial \rho} \right], \quad (17)$$

where $p_{\text{ex}}(\rho) = p(\rho) - p_{\text{id}}(\rho)$, with $p_{\text{id}}(\rho) = \rho k_B T$, denotes the excess pressure. Similarly, Eq. (8) yields

$$p_{\text{ex}}(\rho) = -k_B T \int d\mathbf{r} \int_0^\rho d\rho' \rho' c(r; \rho'). \quad (18)$$

From Eq. (18) one can also obtain the inverse isothermal compressibility via $(\beta = 1/k_B T)$

$$\beta \frac{\partial p(\rho)}{\partial \rho} = 1 - \rho \int d\mathbf{r} c(r; \rho), \quad (19)$$

which together with Eq. (6) and $\tilde{h}(k=0, \rho) = \int d\mathbf{r} h(r; \rho)$, yields the compressibility equation

$$\beta \frac{\partial p(\rho)}{\partial \rho} = [\tilde{S}(k=0; \rho)]^{-1}, \quad (20)$$

where

$$\tilde{S}(k=0; \rho) = 1 + \rho \int d\mathbf{r} h(r; \rho) = \left[1 - \rho \int d\mathbf{r} c(r; \rho) \right]^{-1}. \quad (21)$$

Note, finally, that because Eq. (17) involves the density derivative of $g^{(\lambda)}(r; \rho)$ its practical utility is limited and one often uses instead the so-called virial equation^{6,7}

$$p_{\text{ex}}(\rho) = \left\langle - \left[\frac{\partial U(\{\alpha^{1/3} \mathbf{x}\}^N)}{\partial \alpha} \right]_{\alpha=1} \right\rangle, \quad (22)$$

which results from rescaling ($\mathbf{x} \rightarrow \alpha^{1/3} \mathbf{x}$) the configuration space ($V \rightarrow \alpha V$), and which when evaluated with the aid of Eq. (1) yields

$$p_{\text{ex}}(\rho) = - \frac{1}{6} \rho^2 \int d\mathbf{r} g(r; \rho) r \frac{\partial V(r)}{\partial r}, \quad (23)$$

which no longer involves any density derivative of $g(r; \rho)$. Since Eq. (23) is exact it has also to be equivalent to Eqs. (17)–(18), although we know of no explicit proof of their equality.

The main question now concerns the way in which the above relations can be transposed to a fluid with an effective, state-dependent, pair-potential.

III. THE COMPLEX FLUID

When in the above fluid the pair-potential $V(r)$ is replaced by an effective pair-potential of the general form $V(r; \rho, T)$, or since we do not indicate the T -dependence explicitly, $V(r; \rho)$, all of the above quantities will acquire a supplementary ρ -dependence induced by the density-dependence of $V(r; \rho)$. In order to formally distinguish these two types of ρ -dependencies, we will call in the following the ρ -dependence of Sec. II the “explicit” ρ -dependence, while the dependence induced via $V(r; \rho)$ will be designed as the “implicit” ρ -dependence, although, of course, in the end both dependencies are equally explicit.

A. Structural properties

The implicit ρ -dependence of the structural properties considered in Sec. II, results from the fact that the potential energy of an N -particle configuration $\{\mathbf{x}^N\}$ now becomes

$$U(\{\mathbf{x}^N\}; \rho) = \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \hat{\rho}_2(\mathbf{r}_1, \mathbf{r}_2; \{\mathbf{x}^N\}) V(r_{12}; \rho), \quad (24)$$

instead of Eq. (1). Note that in Eq. (24) the ρ -dependence of U is not formally related to $\{\mathbf{x}^N\}$, i.e., ρ appears only as a parameter in the system’s Hamiltonian. Therefore Eqs. (9)–(10) can be formally transposed as

$$g(r; \rho) = \sum_{p=0}^{\infty} \rho^p g_p(r; [V(\rho)]), \quad (25)$$

and

$$c(r; \rho) = \sum_{p=0}^{\infty} \rho^p c_p(r; [V(\rho)]), \quad (26)$$

indicating that the Mayer functions are now evaluated with $V(r; \rho)$ and hence become density dependent. In other words, Eqs. (25)–(26) are now formal density expansions with respect to the explicit ρ -dependence but not yet with respect to the implicit ρ -dependence of $g(r; \rho)$ and $c(r; \rho)$. In order to stress this point it will be convenient for what follows to introduce the auxiliary functions

$$g(r; \rho; [V(\rho_0)]) = \sum_{p=0}^{\infty} \rho^p g_p(r; [V(\rho_0)]), \quad (27)$$

and

$$c(r; \rho; [V(\rho_0)]) = \sum_{p=0}^{\infty} \rho^p c_p(r; [V(\rho_0)]), \quad (28)$$

where ρ is the system’s density and ρ_0 the parameter which appears in the system’s Hamiltonian Eq. (24). Note that Eqs. (27)–(28) are still related by an Ornstein–Zernike equation of the form⁹

$$1 + \rho \tilde{h}(k; \rho; [V(\rho_0)]) = (1 - \rho \tilde{c}(k; \rho; [V(\rho_0)]))^{-1}, \quad (29)$$

in close analogy with Eq. (6). Of course, Eqs. (27)–(28) reduce to Eqs. (25) and (26) when $\rho_0 = \rho$, i.e., $g(r; \rho) = g(r; \rho; [V(\rho)])$ and $c(r; \rho) = c(r; \rho; [V(\rho)])$ and these $g(r; \rho)$ and $c(r; \rho)$ functions obey the same equation Eq. (6). In other words, $c(r; \rho; [V(\rho_0)])$ is the direct cf. conjugated to $g(r; \rho; [V(\rho_0)])$, and $c(r; \rho)$ the direct cf. conjugated to $g(r; \rho)$.

B. Thermodynamic properties

1. The free-energy density

Because of Eq. (24) the functional derivative of the free-energy with respect to $V(|\mathbf{r}_1 - \mathbf{r}_2|; \rho)$ is still given by $\rho_2(\mathbf{r}_1, \mathbf{r}_2)/2$ and hence the procedure which consists in charging the potential ($\lambda V(r; \rho); 0 \leq \lambda \leq 1$) is unaltered and yields here instead of Eq. (7)

$$f_{\text{ex}}(\rho) = \frac{1}{2} \rho^2 \int d\mathbf{r} V(r; \rho) \int_0^1 d\lambda g^{(\lambda)}(r; \rho), \quad (30)$$

where we have, formally, for $g^{(\lambda)}(r; \rho)$ [cf. Eq. (25)]

$$g^{(\lambda)}(r; \rho) = \sum_{p=0}^{\infty} \rho^p g_p(r; [\lambda V(\rho)]), \quad (31)$$

and hence

$$f_{\text{ex}}(\rho) = \sum_{n=2}^{\infty} \rho^n B_n([V(\rho)]), \quad (32)$$

where

$$B_n([V(\rho)]) = \frac{1}{2} \int d\mathbf{r} V(r; \rho) \int_0^1 d\lambda g_{n-2}(r; [\lambda V(\rho)]), \quad (33)$$

in agreement with Eq. (12). Note, however, that Eq. (32) contains now the virial expansion of $f_{\text{ex}}(\rho)$ with respect to its explicit ρ -dependence only. To obtain the full virial expansion of $f_{\text{ex}}(\rho)$ one still has to introduce the virial expansion of Eq. (33) into Eq. (32).

The alternative procedure leading to $\bar{f}_{\text{ex}}(\rho)$, which consists in charging the density $[\lambda \rho_1(\mathbf{r}); 0 \leq \lambda \leq 1]$ is, however, less straightforward. It is indeed not clear a priori whether the functional derivatives of the free-energy with respect to $\rho_1(\mathbf{r})$, which is at the basis of this method, has to take into account also the implicit density dependence via $V(r; \rho)$. To avoid this ambiguity with the functional derivative of $V(r; \rho)$, we will exploit the equality, $B_n([V]) = \bar{B}_n([V])$, and proceed as follows. In the same way as Eq. (32) is a straightforward transposition of Eq. (11), we will transpose Eq. (13) here as

$$\bar{f}_{\text{ex}}(\rho) = \sum_{n=2}^{\infty} \rho^n \bar{B}_n([V(\rho)]), \quad (34)$$

where from Eq. (14),

$$\bar{B}_n([V(\rho)]) = -\frac{k_B T}{n(n-1)} \int d\mathbf{r} c_{n-2}(r; [V(\rho)]). \quad (35)$$

Now, since $\bar{B}_n([V(\rho)])$ is the same functional of $V(r; \rho)$ as $\bar{B}_n([V])$ was of $V(r)$, and similarly for $B_n([V(\rho)])$ and $B_n([V])$ [cf. Eq. (33) and Eq. (12)], the equality $\bar{B}_n([V]) = B_n([V])$, implies the equality of $\bar{B}_n([V(\rho)]) = B_n([V(\rho)])$ for all ρ , and hence $\bar{f}_{\text{ex}}(\rho) = f_{\text{ex}}(\rho)$, i.e., Eq. (15). Therefore, if the potential-charging and density-charging procedures have to be mutually consistent, then the density charging will correspond to Eq. (34), or equivalently

$$\bar{f}_{\text{ex}}(\rho) = -k_B T \int d\mathbf{r} \int_0^\rho d\rho' \int_0^{\rho'} d\rho'' c(r; \rho'', [V(\rho)]), \quad (36)$$

where

$$c(r; \rho''; [V(\rho)]) = \sum_{\rho=0}^{\infty} (\rho'')^\rho c_\rho(r; [V(\rho)]) \quad (37)$$

[cf. also Eq. (28)]. Hence, while in Eq. (30) the potential is being charged at constant density, in Eq. (36) the density is being charged at constant potential. In other words, the density charging operates only on the explicit density dependence while the density appearing in the system's Hamiltonian is treated as an external parameter. This somewhat subtle point is forced upon us if we want to maintain Eq. (15). Indeed, if Eq. (36) was evaluated with $c(r; \rho''; [V(\rho'')])$, $\bar{f}_{\text{ex}}(\rho)$ would differ from $f_{\text{ex}}(\rho)$ already at order- ρ^3 , i.e., Eq. (15) would no longer hold. Note finally

that while $f_{\text{ex}}(\rho)$ of Eq. (30) requires the knowledge of Eq. (31), or, say, of $g(r; \rho; [\lambda V(\rho)])$ for $0 \leq \lambda \leq 1$, Eq. (36) requires the knowledge of Eq. (37), or, say, of $c(r; \lambda \rho; [V(\rho)])$, or equivalently, of $g(r; \lambda \rho; [V(\rho)])$ for $0 \leq \lambda \leq 1$.

2. The pressure

It is now an easy matter to obtain the (osmotic) pressure from Eq. (16). Note, however, that in order to obtain the pressure of the actual system, the density parameter (say, ρ_0) appearing in the system's Hamiltonian must be taken equal to the system's density (say, ρ) and the density derivative appearing in Eq. (16) must operate on both the explicit and the implicit density dependencies. Computing the excess pressure from Eq. (30) thus yields

$$p_{\text{ex}}(\rho) = \frac{1}{2} \rho^2 \int d\mathbf{r} V(r; \rho) \int_0^1 d\lambda \times \left[g^{(\lambda)}(r; \rho) + \rho \frac{\partial g^{(\lambda)}(r; \rho)}{\partial \rho} \right] + \frac{1}{2} \rho^3 \int d\mathbf{r} \frac{\partial V(r; \rho)}{\partial \rho} \int_0^1 d\lambda g^{(\lambda)}(r; \rho), \quad (38)$$

where, as stated, the density dependence of $g^{(\lambda)}(r; \rho)$ now contains two types of contributions:

$$\frac{\partial g^{(\lambda)}(r; \rho)}{\partial \rho} = \left[\frac{\partial g^{(\lambda)}(r; \rho; [\lambda V(\rho_0)])}{\partial \rho} + \frac{\partial g^{(\lambda)}(r; \rho_0; [\lambda V(\rho)])}{\partial \rho} \right]_{\rho_0=\rho}, \quad (39)$$

where we have used the more explicit notation of Eq. (27). Similarly Eq. (36) yields

$$p_{\text{ex}}(\rho) = -k_B T \int d\mathbf{r} \int_0^\rho d\rho' \rho' c(r; \rho'; [V(\rho)]) - k_B T \int d\mathbf{r} \int_0^\rho d\rho' \int_0^{\rho'} d\rho'' \rho \frac{\partial c(r; \rho''; [V(\rho)])}{\partial \rho}, \quad (40)$$

using Eq. (28). An important consequence of Eq. (40) is that

$$\beta \frac{\partial p(\rho)}{\partial \rho} = 1 - \rho \int d\mathbf{r} c(r; \rho; [V(\rho)]) - 2\rho \int d\mathbf{r} \int_0^\rho d\rho' \frac{\partial c(r; \rho'; [V(\rho)])}{\partial \rho} - \rho \int d\mathbf{r} \int_0^\rho d\rho' \int_0^{\rho'} d\rho'' \frac{\partial^2 c(r; \rho''; [V(\rho)])}{\partial \rho^2}, \quad (41)$$

and therefore the conditions

$$\beta \frac{\partial p(\rho)}{\partial \rho} = 0 \quad (42)$$

and

$$\bar{\zeta}(k=0;\rho) = \left[1 - \rho \int d\mathbf{r} c(r;\rho;[V(\rho)]) \right]^{-1} = \infty \quad (43)$$

do not coincide, i.e., Eq. (20) no longer holds.¹⁰ In other words, for the complex fluid the thermodynamic states for which the compressibility diverges are different from the thermodynamic states for which the infinite wavelength limit of the static structure factor diverges, i.e., for which the pair cf. becomes long-ranged [see Eq. (29)]. Note that this general result is consistent with the numerical simulations performed in Ref. 11 for the particular case (cf. Ref. 12) when $V(r;\rho)$ is of the inverse-power type with a density-dependent index [viz. $V(r;\rho) = V_{\text{HS}}(r) - \epsilon(\sigma/r)^{n(\rho)}$, ϵ and σ being some constant energy and length scales, and $V_{\text{HS}}(r)$ the hard-sphere potential for particles of diameter σ] and in Ref. 13 for the case of the point Yukawa potential.

Note, finally, that it is not clear how Eq. (22) should be transposed to the complex fluid. If the potential energy of Eq. (24) is rescaled as $U(\{\alpha^{1/3}\mathbf{x}\}^N; \rho/\alpha)$ one obtains instead of Eq. (23) the well-known⁶ result

$$p_{\text{ex}}(\rho) = -\frac{1}{2}\rho^2 \int d\mathbf{r} g(r;\rho;[V(\rho)]) \times \left[\frac{1}{3}r \frac{\partial}{\partial r} - \rho \frac{\partial}{\partial \rho} \right] V(r;\rho), \quad (44)$$

the validity of which has been questioned in, e.g., Ref. 4. In view of the above, it is indeed not clear whether it is consistent to relate the configuration $\{\mathbf{x}^N\}$ and the density-parameter ($\rho_0 = \rho$) appearing in the Hamiltonian in the same rescaling process ($\mathbf{x} \rightarrow \alpha^{1/3}\mathbf{x}, \rho \rightarrow \rho/\alpha$) or whether the rescaling should be performed at constant density ($\mathbf{x} \rightarrow \alpha^{1/3}\mathbf{x}, \rho_0 \rightarrow \rho_0$), i.e., whether the density parameter appearing in the Hamiltonian should be treated as an external parameter. If the latter is the case then there will be no density derivative in Eq. (44). One way to find this out could consist in comparing Eq. (44) with Eq. (38). Indeed, even if Eq. (23) is equivalent to Eq. (17) or (18), this does not imply that Eq. (44) will also be equivalent to Eq. (38) or (40) because this time Eq. (44) is a different functional of $V(r;\rho)$ than Eq. (23) was of $V(r)$. Hence, the status of Eq. (44) cannot be investigated by the same method as used above and will have to form the subject of a separate investigation.¹⁴

IV. CONCLUSIONS

We have assumed that both for a simple and a complex fluid the expression of the free-energy in terms of either its pair cf. or its direct cf. are mutually consistent. Since the

expression in terms of the pair cf. is easily transposed to the case of a complex fluid with a state dependent pair-potential, we have constructed an equivalent expression in terms of the direct cf. of the complex fluid. On this basis it has been shown that the infinite wavelength limit of the static structure factor of the complex fluid is no longer proportional to its isothermal compressibility, i.e., that the so called compressibility equation no longer holds for the complex fluid. An alternative conclusion could, of course, also be that describing the complex fluid in terms of an effective pair-potential only, i.e., without adding higher-order effective many-body interactions, does not yield a thermodynamically satisfactory description of the complex fluid.

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¹ See, e.g., C. N. Likos, Phys. Rep. **348**, 267 (2001), and references therein.

² A. König and N. W. Ashcroft, Phys. Rev. E **63**, 041203 (2001).

³ Note that when the densities of the different constituents can be varied independently, the density dependence of the effective potential can be transformed away by working in the semi-grand ensemble as illustrated in, e.g., M. Dijkstra, R. van Roij and R. Evans, Phys. Rev. E **59**, 5744 (1999).

⁴ See, e.g., A. A. Louis, J. Phys.: Condens. Matter **14**, 9187 (2002).

⁵ R. Evans, Adv. Phys. **28**, 143 (1979).

⁶ J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1986).

⁷ D. A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1976).

⁸ Of course, in many cases this condition of thermodynamic consistency has already been verified numerically.

⁹ Approximate integral equation theories for complex fluids should be generalized in the same way and then be closed with the generalized Ornstein-Zernike equation (29).

¹⁰ The crucial point here is again provided by Eq. (36). If Eq. (36) was evaluated with $c(r;\rho'';[V(\rho'')])$, the compressibility equation (Eq. (20)) would hold but the theory would not be thermodynamically consistent [i.e., Eq. (15) would not hold]. Our treatment favors thus the latter property over the former one. That a problem should arise with Eq. (20) can also be inferred from the standard textbook derivation (cf. Ref. 6) of the compressibility equation since the latter is based on derivatives with respect to the fugacity which now also operate on the effective potential.

¹¹ N. G. Almarza, E. Lomba, G. Ruiz, and C. F. Tejero, Phys. Rev. Lett. **86**, 2038 (2001).

¹² C. F. Tejero and M. Baus, Phys. Rev. E **57**, 4821 (1998).

¹³ M. Dijkstra and R. van Roij, J. Phys.: Condens. Matter **10**, 1219 (1998).

¹⁴ After this paper was submitted we did learn about related work [F. Stillinger, H. Sakai, and S. Torquato, J. Chem. Phys. **117**, 288 (2002)] where similar conclusions were reached.