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LOCALLY INHOMOGENEOUS HARD-SPHERE FLUID: SOLUTION OF THE PERCUS-YEVICK EQUATION*

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An inhomogeneous fluid with local density of the form: $n(\boldsymbol{r}) = \varrho\{1+\int dk\, A(k) \cos(\boldsymbol{k}\cdot\boldsymbol{r})\}$, ϱ being the average macroscopic density, is discussed. The amplitude $A(k)$ is assumed to be independent of the direction of the wavevector $\boldsymbol{k}$. Hence, only the local inhomogeneities of the fluctuation type are considered. The solution of the Ornstein–Zernike equation is constructed by means of the generalization of the Baxter method. Detailed calculations are performed for the hard-sphere system with one-mode inhomogeneity, $A(k) \sim \delta(k-k_0)$. It is found that the presence of inhomogeneities strongly affects the equilibrium properties of the fluid. In particular, the hard-sphere fluid becomes macroscopically less compressible than the homogeneous one.

1. Introduction

Statistical-mechanical calculations of the properties of non-uniform systems so far have been devoted mainly to the gas-liquid or fluid-wall interfaces (cf. e.g. [1–3] and references cited there), i.e., to the directed inhomogeneities connected with some externally imposed order. In this paper we will discuss the properties of a fluid with local density nonuniformities of the kind characteristic for spontaneous fluctuations. More specifically, we assume that the local density (one-particle distribution function) $n(\boldsymbol{r})$ can be written in the form:

$$n(\boldsymbol{r}) = \varrho\{1+\int dkA(k)\cos(\boldsymbol{k}\cdot\boldsymbol{r})\}, \tag{1.1}$$

with amplitudes $A(k)$ independent of the directions of wavevectors $\boldsymbol{k}$, and with ϱ being the average (global) density:

$$V_0^{-1}\int_{V_0} d\boldsymbol{r}n(\boldsymbol{r}) = \varrho, \tag{1.2}$$

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where V_0 is some finite volume of the fluid. We shall seek the generalization for the inhomogeneous system of the Baxter solution [4] of the Ornstein–Zernike equation. The latter reads:

$$h(\mathbf{r}_1, \mathbf{r}_2) = c(\mathbf{r}_1, \mathbf{r}_2) + \int d\mathbf{r}_3 h(\mathbf{r}_1, \mathbf{r}_3) n(\mathbf{r}_3) c(\mathbf{r}_3, \mathbf{r}_2), \tag{1.3}$$

where $h(\mathbf{r}_1, \mathbf{r}_2) = g(\mathbf{r}_1, \mathbf{r}_2) - 1$, and g and c denote the two-particle radial and direct correlation functions, respectively. We shall discuss globally uniform fluid with no externally imposed direction so that globally:

$$h(\mathbf{r}_1, \mathbf{r}_2) = h(r_{12}), \quad c(\mathbf{r}_1, \mathbf{r}_2) = c(r_{12}), \quad r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|, \tag{1.4}$$

and locally these functions will depend on the actual position only through the local density $n(\mathbf{r})$.

As an application of the general method, the solution of the Percus–Yevick equation for the nonuniform hard-sphere fluid will be discussed.

2. *Rearrangement of the Ornstein–Zernike equation*

We shall follow the Baxter method [4] of the solution of the (homogeneous) Ornstein–-Zernike equation. Hence, we assume the interparticle potential and the closure relation additional to the Ornstein–Zernike equation to be such that the direct correlation function $c(r)$ is of finite range:

$$c(r) = 0 \quad \text{for} \quad r > a. \tag{2.1}$$

With the assumptions (1.4), the Ornstein–Zernike equation is:

$$h(r) = c(r) + \int d\mathbf{s} h(s) n(\mathbf{s} + \mathbf{R})\, c(|\mathbf{r} - \mathbf{s}|). \tag{2.2}$$

Let $\hat{b}(q)$ denote the three-dimensional Fourier transform of $b(r)$:

$$\hat{b}(q) = \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} b(r) = \frac{4\pi}{q} \int_0^\infty dr r b(r) \sin(qr),$$

$$b(r) = (2\pi)^{-3} \int d\mathbf{q} e^{-i\mathbf{q}\cdot\mathbf{r}} \hat{b}(q) = (2\pi^2 r)^{-1} \int_0^\infty dq q \hat{b}(q) \sin(qr). \tag{2.3}$$

Introduce also functions $B(r)$ and $\hat{B}(q)$, defined by

$$B(r) = \int_r^\infty dt t b(t) = (2\pi^2)^{-1} \int_0^\infty dq \hat{b}(q) \cos(qr),$$

$$\hat{B}(q) = 4\pi \int_0^\infty dr b(r) \cos(qr) = \int_q^\infty dk k \hat{b}(k), \tag{2.4}$$

i.e.,

$$\hat{b}(q) = 4\pi \int_0^\infty dr \cos(qr) B(r),$$

$$b(r) = (2\pi^2)^{-1} \int_0^\infty dq \cos(qr) \hat{B}(q). \tag{2.5}$$

The Fourier transform of Eq. (2.1) is:

$$\hat{h}(q) = \hat{c}(q)+\varrho\hat{h}(q)[\hat{c}(q)+\hat{D}(q;\boldsymbol{R})], \tag{2.6a}$$

$$= \hat{c}(q)+\varrho\hat{c}(q)[\hat{h}(q)+\hat{G}(q;\boldsymbol{R})], \tag{2.6b}$$

where

$$\hat{D}(q;\boldsymbol{R}) = \tfrac{1}{2}\int dkA(k)e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\hat{c}(|\boldsymbol{q}+\boldsymbol{k}|)+e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}\hat{c}(|\boldsymbol{q}-\boldsymbol{k}|)$$

$$= \frac{1}{2q}\int\limits_0^\infty dk\phi(k;\boldsymbol{R})\,[\hat{C}(|q-k|)-\hat{C}(q+k)], \tag{2.7a}$$

and similarly

$$\hat{G}(q;R) = \frac{1}{2q}\int\limits_0^\infty dk\phi(k;\boldsymbol{R})\,[\hat{H}(|q-k|)-\hat{H}(q+k)], \tag{2.7b}$$

with

$$\phi(k,\boldsymbol{R}) = 4\pi kA(k)\cos(\boldsymbol{k}\cdot\boldsymbol{R}). \tag{2.7c}$$

Multiplying Eq. (2.6a) by ϱ, adding to both sides the term $1-\varrho\hat{D}$, and regrouping, we get:

$$[1+\varrho\hat{h}(q)]\,[1-\varrho\hat{c}(q)-\varrho\hat{D}(q;\boldsymbol{R})] = 1-\varrho\hat{D}(q;\boldsymbol{R}). \tag{2.8a}$$

Adding only 1, we can get another form of the above relation:

$$[1+\varrho\hat{h}(q)]\,[1-\hat{c}(q)] = 1+\varrho\hat{c}(q)\varrho\hat{G}(q;\boldsymbol{R}). \tag{2.8b}$$

Eqs. (2.8) show that the well-known simple relation between the isothermal compressibility K_T and $\hat{c}(0)$ does not hold in the presence of inhomogeneities. Indeed, the relation

$$k_BT\left(\frac{\partial\varrho}{\partial p}\right)_T \equiv K_T = 1+\varrho\hat{h}(0) \tag{2.9}$$

(p — pressure, T — temperature, k_B — Boltzmann constant) implies now that

$$K_T = \frac{1-\varrho\hat{D}(0;\boldsymbol{R})}{1-\varrho\hat{c}(0)-\varrho\hat{D}(0;\boldsymbol{R})} = \frac{1+\varrho\hat{c}(0)\varrho\hat{G}(0;\boldsymbol{R})}{1-\varrho\hat{c}(0)}, \tag{2.10}$$

i.e., the isothermal compressibility is now connected not only with the value of the Fourier transform of the direct correlation function at $q = 0$, but also with its values at nonzero wavenumbers.

Because the right-hand sides (rhs) of Eqs. (2.8) are now functions of q, we cannot use the original Baxter's argument that rhs is never equal to zero, and hence expressions in both brackets of the lhs of these equations separately always have a constant sign, which in turn permits us to introduce a new function $\hat{Q}(q)$ with appropriate properties. We must then proceed in a slightly different manner. Multiply both sides of Eq. (2.6b) by ϱ and by some new function $\hat{E}(q)$, and add a constant $K > 0$, such that

$$\hat{E}\varrho\hat{h} = 1+\varrho\hat{h}+\varrho\hat{G}-K. \tag{2.11}$$

After rearrangements, we now get:

$$[1-\hat{E}(q)\varrho\hat{c}(q)]\,[1+\varrho\hat{h}(q)+\varrho\hat{G}(q;\boldsymbol{R})] = K > 0. \tag{2.12}$$

Because $\hat{h}(q)$: finite, $\forall\, q \in R$, hence

$$1-\hat{E}(q)\varrho\hat{c}(q) \neq 0, \qquad \forall\, q \in R \tag{2.13}$$

and now we can repeat Baxter's arguments: relation (2.13) implies that there exists some function $\hat{Q}(q) : \forall\, q \in C$,

$$\begin{aligned} &(i) && \varrho\hat{c}(q)\hat{E}(q) = 1-\hat{Q}(q)\hat{Q}(-q),\\ &(ii) && \hat{Q}(0) > 0,\\ &(iii) && \hat{Q}(q_j) = 0 \quad \text{for} \quad \operatorname{Im} q_j < 0,\\ &(iv) && \hat{Q}(q) = 1-2\pi\varrho \int_0^{a'} dr e^{iqr} Q(r), \ \forall\ r \in R. \end{aligned} \tag{2.14}$$

The last relation defines the function $Q(r)$ for $r \in (0, a')$. This definition is completed by:

$$Q(a') = 0, \qquad Q(r) = 0 \quad \text{for } r \text{ outside } (0, a'). \tag{2.14a}$$

We shall prove below that $a' = a$, i.e., that the range of $Q(r)$ is equal to the range of the direct correlation function.

From Eqs. (2.12) and (2.14) we have:

$$\hat{Q}(q)\,[1+\varrho\hat{h}(q)+\varrho\hat{G}(q;\boldsymbol{R})] = K[\hat{Q}(-q)]^{-1}. \tag{2.15}$$

Multiplying the above relation by e^{-iqr}, $r > 0$, and integrating over q along the whole real axis, we shall get the rhs equal to zero: The contour on the rhs can be closed in the lower half-plane, where $\hat{Q}(-q)$ has no zeros, $K[\hat{Q}(-q)]^{-1}$ is regular, and e^{-iqr} vanishes on the lower great half-circle for $r > 0$. Integration of the lhs thus gives:

$$-Q(r)+H(r)-2\pi\varrho \int_0^{a'} dt Q(t) H(|r-t|)+\Delta(r;\boldsymbol{R}) = 0, \qquad r > 0 \tag{2.16}$$

with

$$\Delta(r;\boldsymbol{R}) = F(r;\boldsymbol{R})-2\pi\varrho \int_0^{a'} dt Q(t) F(|r-t|;\boldsymbol{R}), \tag{2.17}$$

$$F(r;\boldsymbol{R}) = (2\pi)^{-2} \int_{-\infty}^{+\infty} dq e^{-iqr}\hat{G}(q;\boldsymbol{R})$$

$$= \frac{1}{2\pi}\int_0^{\infty} dk\phi(k;\boldsymbol{R}) \int_0^{\infty} ds h(s) \int_{-\infty}^{+\infty} dq q^{-1} e^{-iqr}\{\cos(qs-ks)-\cos(qs+ks)\}. \tag{2.18}$$

Hence,

$$\frac{\partial}{\partial r}F(r;\boldsymbol{R}) = -\int\limits_0^\infty dk\phi(k;\boldsymbol{R})\sin(kr)h(r), \qquad r > 0 \tag{2.19}$$

and the differentiation of Eq. (2.16) with respect to r leads to the relation between $h(r)$ and $Q(r)$:

$$\psi(r)h(r) = -Q'(r)+2\pi\varrho\int\limits_0^{a'} dtQ(t)\psi(r-t)h(|r-t|), \qquad r > 0, \tag{2.20}$$

where

$$\psi(r) = r+\int\limits_0^\infty dk\phi(k;\boldsymbol{R})\sin(kr), \tag{2.21}$$

and $Q'(r) = \partial Q(r)/\partial r$.

The relation between $c(r)$ and $Q(r)$ can be found from Eq. (2.14). To this end, the function $\hat{E}(q)$ must be eliminated. Multiply Eq. (2.14) and Eq. (2.11) by e^{-iqr} and integrate over q, for $r > 0$. The result is:

$$2\pi\int\limits_0^{a'} dsC(s)M(r,s) = Q(r)-2\pi\varrho\int\limits_0^{a'} dtQ(t)Q(t-r), \tag{2.22}$$

$$2\pi\int\limits_0^{a'} dsH(s)M(r,s) = H(r)+\int\limits_0^\infty dk\phi(k;\boldsymbol{R})\int\limits_0^\infty dsh(s)(2\pi)^{-1}$$

$$\times\int\limits_{-\infty}^{+\infty} dqe^{-iqr}q^{-1}\{\cos(qs-ks)-\cos(qs+ks)\}, \qquad r > 0, \tag{2.23}$$

where the upper limits on the integrals in left- and right-hand sides of Eq. (2.22) result from (2.1) and (2.14), respectively, and where $M(r,s) = E(|r-s|)+E(r+s)$, $E(r)$ being the inverse Fourier transform of $\hat{E}(q)$. The integral over s in the rhs of Eq. (2.23) can be written in the form ($\lim\limits_{r\to\infty} h(r) = 0$):

$$I = \int\limits_0^\infty dsh(s)sN(q,k;s) = \int\limits_0^\infty dsH(s)\frac{\partial}{\partial s}N(q,k;s),$$

$$N(q,k;s) = s^{-1}\{\cos(qs-ks)-\cos(qs+ks)\},$$

so that Eq. (2.23) can be cast into the form:

$$\int\limits_0^\infty dsH(s)W(s,r) = 0, \tag{2.24}$$

with

$$W(s,r) = 2\pi M(r,s)-\delta(r-s)-\frac{1}{2\pi}\int\limits_0^\infty dk\phi(k;\boldsymbol{R})\int\limits_{-\infty}^{+\infty} dqe^{-iqr}\frac{\partial}{\partial s}N(q,k;s). \tag{2.25}$$

Eq. (2.24) must be fulfilled for every $r \in (0, \infty)$, which implies

$$W(s, r) = 0 \quad \text{for all} \quad (r, s) \in (0, \infty). \tag{2.26}$$

Introducing relations (2.26) and (2.25) into (2.22), differentiating with respect to r, and integrating over q and over s, we get the desired relation between $c(r)$ and $Q(r)$:

$$\psi(r)c(r) = -Q'(r) + 2\pi\varrho \int_r^{a'} dt Q'(t)Q(t-r), \qquad r > 0. \tag{2.27}$$

Incidentally, because $c(r) = 0$ for $r > a$, Eq. (2.27) proves that also $Q'(r) = 0$ for $r > a$. This means that, without the loss of generality, we can put $a' = a$, so that also $Q(r) = 0$ for $r > a$.

The function $\hat{D}$, appearing in the relations between $\hat{c}(q)$ and $\hat{h}(q)$, and in the formulas for the isothermal compressibility, and given by Eq. (2.7), can be now cast into the form which will be more convenient in further calculations. We have from Eqs. (2.7) and (2.3)–(2.5):

$$\hat{D}(q; \boldsymbol{R}) = \frac{4\pi}{q} \int_0^\infty dk\phi(k; \boldsymbol{R}) \int_0^a dr c(r) \sin(qr) \sin(kr),$$

so that, from Eq. (2.20):

$$\hat{c}(q) + \hat{D}(q; \boldsymbol{R}) = \hat{\mu}(q; \boldsymbol{R}) = \frac{4\pi}{q} \int_0^a dr[\psi(r)c(r)] \sin(qr), \tag{2.28}$$

and

$$K_T = 1 + \varrho\hat{c}(0)/[1 - \varrho\hat{\mu}(0; \boldsymbol{R})], \tag{2.29}$$

$$\hat{h}(q) = \hat{c}(q)/[1 - \varrho\hat{\mu}(q; \boldsymbol{R})]. \tag{2.30}$$

3. Hard-sphere fluid in the Percus–Yevick approximatiou

For the hard-sphere fluid we have

$$h(r) = -1, \quad \text{for} \quad r < \sigma, \tag{3.1}$$

σ being the particle diameter, and the Percus–Yevick approximation means in this case that the cut-off a of the relation (2.1) is now equal to σ. In the foregoing we put, for simplicity, $\sigma = a = 1$. Relations (2.20) and (3.1) determine the function $Q'(r)$:

$$Q'(r) = \alpha r + \beta + \int_0^\infty dkk\phi(k) [\zeta(k) \cos(kr) - \xi(k) \sin(kr)], \tag{3.2}$$

with

$$\alpha = 1-2\pi\varrho \int_0^1 dt Q(t), \quad \beta = 2\pi\varrho \int_0^1 dt t Q(t),$$

$$\zeta(k) = \frac{2\pi\varrho}{k} \int_0^1 dt Q(t) \sin(kt), \quad \xi(k) = \frac{2\pi\varrho}{k} \int_0^1 dt Q(t) \cos(kt) \tag{3.3}$$

and

$$Q(r) = \tfrac{1}{2}\alpha(r^2-1)+\beta(r-1)+ \int_0^\infty dk \phi(k) \{\zeta(k)[\sin(kr)-\sin k] + \xi(k)[\cos(kr)-\cos k]\}. \tag{3.4}$$

Inserting Eq. (3.4) into definitions (3.3) and performing integrations we get the set of two linear algebraic and two linear integral equations for unknowns α, β, $\zeta(k)$, and $\xi(k)$, which can be solved numerically by standard methods. The explicit form of the direct correlation function may be obtained by inserting Eqs. (3.2)–(3.4) into Eq. (2.27) and performing integrations. Subsequently, $\hat{\mu}(q)$ can be calculated analytically. All these calculations are tedious and the resulting formulae are rather lengthy. Moreover, the function $\hat{c}(q)$ must be calculated numerically, after the evaluation of numerical values of the coefficients α–ξ. For this purpose, the detailed form of the amplitude $A(k)$ must be first specified. We are thus not presenting all formulae for the general case. Instead, in the next Section we shall discuss in detail the simplest special case of one-mode inhomogeneity, assuming the amplitude to be:

$$A(k) = (4\pi k_0^2)^{-1} A_0 \delta(k-k_0). \tag{3.5}$$

In this case,

$$Q(r) = Q_0+\beta r+\tfrac{1}{2}\alpha r^2+\gamma k^{-1}\cos(kr)+\varepsilon k^{-1}\sin(kr) \tag{3.6}$$

(for simplicity, we drop out the index 0 from k_0), with:

$$Q_0 = -\tfrac{1}{2}\alpha-\beta-\gamma k^{-1}\cos k-\varepsilon k^{-1}\sin k,$$

$$\gamma = 2\pi\varrho\phi \int_0^1 dt Q(t)\cos(kt), \quad \varepsilon = 2\pi\varrho\phi \int_0^1 dt Q(t)\sin(kt). \tag{3.7}$$

Now, the insertion of Eq. (3.6) into definitions of the coefficients α–ε leads to the set of four linear inhomogeneous algebraic equations, the solution of which is trivial (coefficients of these equations are listed in the Appendix). Insertion of Eq. (3.6) into Eq. (2.27) gives the explicit formula for the direct correlation function:

$$\psi(r)c(r) = c_0+c_1 r+c_2 r^2+c_4 r^4+c_s\sin(kr)+c_c\cos(kr)+c_r r\sin(kr), \tag{3.8}$$

$$\psi(r) = r+\phi\sin(kr), \quad \phi = \phi(k, \boldsymbol{R}) = k^{-1}A\cos(\boldsymbol{k}\cdot\boldsymbol{R}) \tag{3.9}$$

(coefficients $c_0 \ldots c_r$ are listed in the Appendix). Calculation of the function $\hat{\mu}(q)$ from Eqs. (3.8) and (2.28) is again trivial; however, the function $\hat{c}(q)$ still must be computed numerically, after determining the values of the coefficients α–ε.

It should be remarked that previously Hutchinson [5], in the critique of Temperley's proposition [6] argued that the direct correlation function cannot contain terms proportional to trigonometric functions, like (3.8). Hutchinson's arguments state that such terms mean that $1-\varrho\hat{c}(q) = 0$ for some values of $q = q_i$ (q_i real). Now, the relation

$$1+\varrho\hat{h}(q) = [1-\varrho c(q)]^{-1} \tag{3.10}$$

implies that in this case either $1+\varrho\hat{h}(q)$ has double roots at the real axis at $q = q_i$, or $\hat{h}(q_i) = \infty$, which implies in turn that the radial distribution function $g(r)$ would become divergent. Now, Eq. (3.10) is valid for a homogeneous fluid only. In the presence of inhomogeneities it is replaced by one of Eqs. (2.8), and Hutchinson's arguments cease to hold.

4. *Hard-sphere fluid with one-mode inhomogeneity*

Numerical computations need as input the values of three parameters: density ϱ, amplitude A, and wavevector k. The values of these parameters are limited by the following obvious inequalities:

$$0 < \varrho(r) < \varrho_{\max},$$

i.e.,

$$0 < 1+\phi \sin(kr)/r < \varrho_{\max}/\varrho, \tag{4.1}$$

$\varrho_{\max}$ being the close-packing density. Because the inequalities (4.1) must hold for all r, we have

$$-1 < k\phi < (\varrho_{\max}-\varrho)/\varrho. \tag{4.2}$$

Because $\phi = A\cos(\boldsymbol{k}\cdot\boldsymbol{R})/k$, and again (4.2) must hold for all $\boldsymbol{R}$, we have also

$$|A| < 1, \quad \text{and} \quad |A| < (\varrho_{\max}-\varrho)/\varrho \tag{4.3}$$

and because $|k\phi| \leqslant |A|$, inequalities (4.3) hold also for $k\phi$. It is worth mentioning that the above conditions also ensure that $\psi(r) > 0$ (cf. Eq. (3.9)), which in turn guarantees finiteness of $c(r)$ (cf. Eq. (3.8)) and hence of $\hat{c}(q)$, and the latter property is necessary for condition (2.13) to be fulfilled.

Figures 1–3 show the direct correlation functions for a few values of density, wavenumber, and local amplitude $k\phi$, in comparison with $c(r)$ calculated for uniform hard spheres of the same mean density. For convenience, the curves are labelled by the conventional dimensionless density $\eta = \pi\varrho a^3/6$, and by the wavelength $\lambda = 2\pi/k$ rather than by ϱ and k. Direct correlation functions were subsequently integrated numerically to $\hat{c}(0)$, and the compressibility K_T was calculated. The local values of the pressure P (local compressibility equation of state) was obtained by the numerical integration of K_T^{-1} as the function of density. Local pressure is shown in Fig. 4 for a few values of λ and $k\phi$ (dashed lines), as compared with the uniform compressibility equation of state (dot-dashed line).

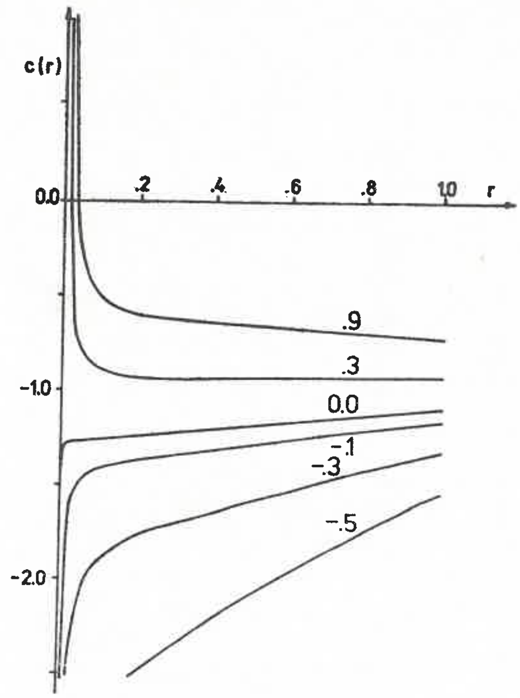

Fig. 1. Direct correlation function of non-uniform hard-sphere fluid. $\lambda = 4a$, $\eta = 0.03$. The numbers labelling different curves denote values of the effective (local) amplitude $k\phi = A \cos (\boldsymbol{k} \cdot \boldsymbol{R})$. $k\phi = 0$ corresponds to the uniform fluid

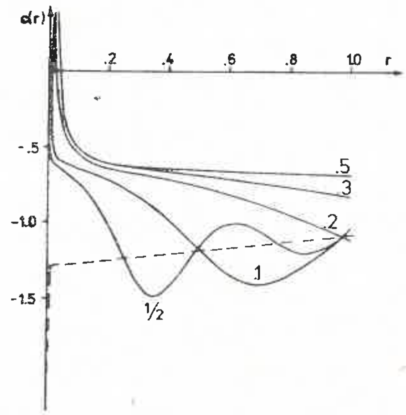

Fig. 2. Direct correlation function of non-uniform hard-sphere fluid. $k\phi = 0.9$, $\eta = 0.03$. The numbers labelling different curves denote values of the wavelength λ in units of the particle diameter. The dashed line denotes $c(r)$ for homogeneous fluid

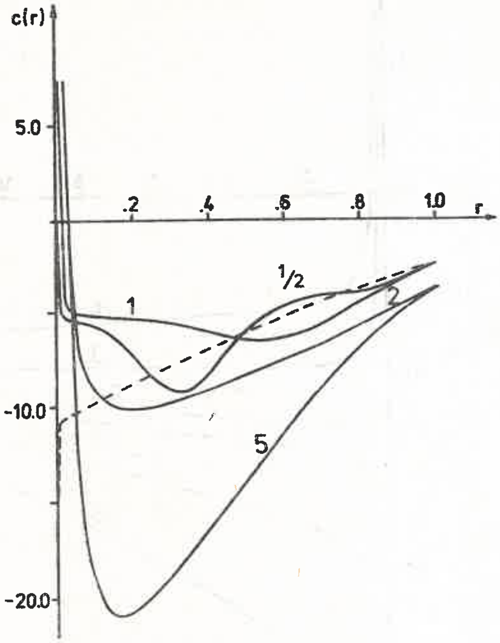

Fig. 3. The same as in Fig. 2, for $\eta = 0.3$

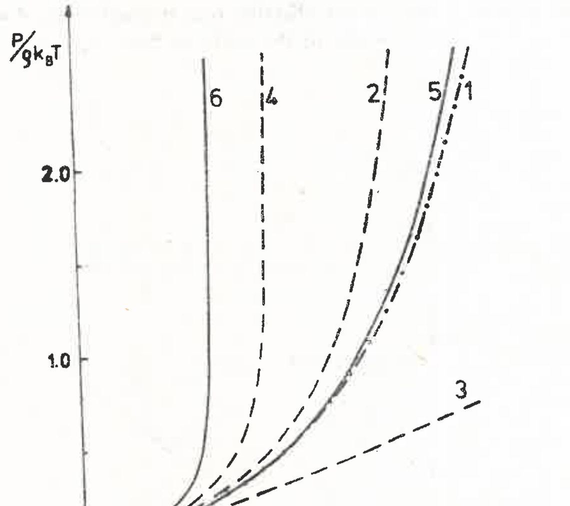

Fig. 4. Compressibility equation of state of inhomogeneous fluid of hard spheres: $(P/\varrho k_B T)$ vs. density. Dot-dashed line, curve *1* — homogeneous fluid. Dashed lines: local pressure. Curve *2* — $\lambda = 1$, $k\phi = A \cos(\boldsymbol{k} \cdot \boldsymbol{R}) = 0.9$; *3* — $\lambda = 5$, $k\phi = 0.9$; *4* — $\lambda = 5$, $k\phi = -0.3$. Full lines: global pressure calculated from averaged compressibility. Curve *5* — $\lambda = 5$, $A = 0.18$; *6* — $\lambda = 5$, $A = 0.9$

Usually we are interested in global rather than in local properties of an inhomogeneous system, especially when the inhomogeneity range is of the order of a few molecular diameters. Hence, the local values of K_T were averaged over R, over the volume V_0 defined by the condition (1.3), which for $A(k)$ from Eq. (3.5) gives:

$$\int_{V_0} d\boldsymbol{r} \cos(\boldsymbol{k}\cdot\boldsymbol{r}) = \frac{4\pi}{k}\int_0^{R_0} dRR\sin(kR) = 0,$$

i.e., the volume V_0 is a sphere of radius R_0, determined by the solution of the equation

$$\sin(kR_0) - kR_0\cos(kR_0) = 0. \tag{4.4}$$

First nonzero solution appears at

$$R_0 = 0.715148\ldots(2\pi/k). \tag{4.5}$$

The averaging proceeds now as follows: K_T is a function of R through its dependence on $k\phi = A\cos(\boldsymbol{k}\cdot\boldsymbol{R})$. Consider a function $f(A\cos(\boldsymbol{k}\cdot\boldsymbol{R}))$. Its average over $\boldsymbol{R}$ is:

$$\bar{f} \equiv \frac{1}{V_0}\int_{V_0} d\boldsymbol{R} f(A\cos(\boldsymbol{k}\cdot\boldsymbol{R}))$$

and it is easy to find that the above three-dimensional integral can be reduced to the single one:

$$\bar{f} = \frac{3}{2x_0}\int_0^{x_0} dx(x_0^2 - x^2) f(A\cos x), \qquad x_0 = kR_0. \tag{4.6}$$

The average (global) value $\overline{K_T}$ was thus computed by numerical integration of local K_T considered as the function of $k\phi = A\cos(kR_0)$, according to the formula (4.6). Global equation of state was obtained again by the numerical integration of $(\overline{K_T})^{-1}$. The resulting values of the global pressure are also shown in Fig. 4 (full lines). The averaging of K_T seems to be more proper than the direct averaging of pressure, because it means the averaging over fluctuation in density, the magnitude of which, as is well-known, is directly connected with the value of the isothermal compressibility. The earlier averaging of $c(r)$, or the later averaging of P itself lead to slightly different results for the compressibility equation of state.

The above results show that the presence of the fluctuation-like local inhomogeneities influences the equilibrium properties of a fluid rather strongly. In particular, the fluid, at least that of hard spheres, is macroscopically stiffer, less compressible: The average pressure is higher and the isothermal compressibility is lower than in the absence of density fluctuations.

APPENDIX

Equations for coefficients α–ε are:

$$Bt = s, \tag{A.1}$$

with elements:

$$t_1 = \alpha, \quad t_2 = \beta, \quad t_3 = \gamma, \quad t_4 = \varepsilon, \quad s_1 = -v, \quad s_2 = s_3 = s_4 = 0, \tag{A.2}$$

and ($v = 1/\eta$, $\eta = \pi\varrho a^3/6$, $a = 1$)

$$\begin{aligned}
&B_{11} = 4-v, \quad B_{12} = 6, \quad B_{21} = 3, \quad B_{22} = 4+2v,\\
&B_{13} = 12(k\cos k-\sin k)/k^2, \quad B_{14} = 12(k\sin k-1+\cos k)/k^2,\\
&B_{23} = 12[2-2k\sin k-(2-k^2)\cos k]/k^3, \quad B_{24} = 12[2k\cos k-(2-k^2)\sin k]/k^3,\\
&B_{31} = 12\phi(\sin k-k\cos k)/k^3, \quad B_{32} = 12\phi(1-\cos k)/k^2,\\
&B_{33} = v-6\phi(k-\sin k\cos k)/k^2, \quad B_{34} = 6\phi\sin^2 k/k^2,\\
&B_{41} = 6\phi(k^2+2-2\cos k-2k\sin k)/k^3, \quad B_{42} = 12\phi(k-\sin k)/k^2,\\
&B_{43} = 6\phi[\cos k(2-\cos k)-1]/k^2, \quad B_{44} = v+6\phi[\sin k(2-\cos k)-k]/k^2.
\end{aligned} \tag{A.3}$$

Coefficients in Eq. (3.8) are:

$$\begin{aligned}
c_0 &= -\beta-6\eta[Q_0^2+(Q_0+\tfrac{1}{2}\alpha+\beta)^2+(12\eta/k^2)\,[\beta\varepsilon-\alpha\gamma/k\\
&\quad+(\alpha+\beta)\,(\varepsilon\cos k-\gamma\sin k)-\alpha(\gamma\cos k+\varepsilon\sin k)/k],\\
c_1 &= -\alpha+2\eta[\alpha+3\beta+6Q_0+6(\gamma\sin k+\varepsilon-\varepsilon\cos k)/k^2],\\
c_2 &= 6\eta(\beta^2-2\alpha Q_0), \quad c_4 = -\tfrac{1}{2}\eta\alpha^2,
\end{aligned} \tag{A.4}$$

$$\begin{aligned}
c_s = \gamma+12\eta\Bigg\{&\frac{\alpha\varepsilon}{k^3}+\frac{\beta\gamma}{k^2}-\frac{2Q_0\varepsilon+\gamma^2+\varepsilon^2}{2k}-(\alpha+\beta)\frac{\gamma\cos k+\varepsilon\sin k}{k^2}\\
&+\alpha\frac{\gamma\sin k-\varepsilon\cos k}{k^3}-\gamma\varepsilon\left(\frac{\cos k}{k}\right)^2+\tfrac{1}{2}(\gamma^2-\varepsilon^2)\frac{\sin k\cos k}{k^2}\Bigg\},
\end{aligned} \tag{A.5}$$

$$\begin{aligned}
c_c = -\varepsilon+12\eta\Bigg\{&\frac{\alpha\gamma}{k^3}-\frac{\beta\varepsilon}{k^2}-\frac{Q_0\gamma}{k}+(\alpha+\beta)\frac{\gamma\sin k-\varepsilon\cos k}{k^2}\\
&+\alpha\frac{\gamma\cos k+\varepsilon\sin k}{k^3}+\gamma\varepsilon\frac{\sin k\cos k}{k^2}+\tfrac{1}{2}(\varepsilon^2-\gamma^2)\left(\frac{\sin k}{k}\right)^2\Bigg\},
\end{aligned} \tag{A.6}$$

$$c_r = 6\eta(\gamma^2+\varepsilon^2)/k. \tag{A.7}$$

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