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ON THE EXISTENCE OF FLUCTUATION-TYPE SOLUTIONS IN THE EQUILIBRIUM THEORY OF FLUIDS*

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It is shown that the first equation of the equilibrium BBGKY hierarchy possesses locally inhomogeneous solutions of the fluctuation type, which branch off smoothly from the uniform solution, i.e., which can appear spontaneously in an initially uniform fluid. Initial fluctuations are of the form of separate modes; in the subsequent steps these modes are broadened and mixed together. Discussed in more detail are: fluids of hard spheres and of adhesive hard spheres, and two-component plasma. For these fluids, solutions of the considered type exist in sufficiently dense systems only.

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1. *Introduction*

The first equation of the well-known equilibrium BBGKY hierarchy [1] reads:

$$\frac{\partial}{\partial \boldsymbol{r}} \ln n_1(\boldsymbol{r}) = -\beta \int d\boldsymbol{s} n_1(\boldsymbol{s}) g(\boldsymbol{r}, \boldsymbol{s}) \frac{\partial}{\partial \boldsymbol{r}} u(|\boldsymbol{r}-\boldsymbol{s}|), \tag{1.1}$$

with $g(\boldsymbol{r}, \boldsymbol{s}) = n_2(\boldsymbol{r}, \boldsymbol{s})/n_1(\boldsymbol{r})n_1(\boldsymbol{s})$, $n_1(\boldsymbol{r})$ and $n_2(\boldsymbol{r}, \boldsymbol{s})$ being, respectively, one- and two-particle distribution functions, $u(r)$ — two-particle interaction potential, $\beta = 1/k_BT$ — inverse temperature in energy units. It is also well-known that Eq. (1.1) has always a constant solution $n_1(\boldsymbol{r}) = \varrho$, corresponding to the uniform, translationally and rotationally invariant fluid with local density $n_1(\boldsymbol{r})$ equal to the average (global) number density ϱ. For such a fluid, the pair correlation function becomes also translationally and rotationally invariant:

$$g(\boldsymbol{t}, \boldsymbol{s}) = g(r), \quad r = |\boldsymbol{t}-\boldsymbol{s}|. \tag{1.2}$$

The function $g(r)$ is called the radial distribution function (RDF). The question arises whether the equation (1.1) with RDF can possess non-constant solutions for $n_1(\boldsymbol{r})$, i.e., whether an initially uniform fluid can evolve spontaneously an inhomogeneity of some kind. This

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question was recently examined [2–10], mainly from the point of view of crystallization. Several articles were published, investigating the existence and properties of the solutions to Eq. (1.1), or to other related equations [2, 7], which branch off from the constant solution, and which possess crystalline-like symmetries. Also liquid-crystalline solutions for angular singlet probability density have been found [9]. However, the problems of stability of these solutions and of their symmetries are not fully understood so far [2, 7, 10].

In this paper we propose to investigate nonconstant nonperiodic rotationally invariant solutions of Eq. (1.1), which can be interpreted as density fluctuations. The existence of solutions for the local density of the form:

$$n_1(\boldsymbol{r}) = n_1(r) \neq \text{const} \tag{1.3}$$

means that in an initially locally homogeneous fluid with the property (1.2) a local density inhomogeneity can appear spontaneously. Such solutions do not destroy the global fluid symmetry, guaranteed by the invariance of the Hamiltonian, and hence no external field is needed to choose particular (local) broken symmetry solution. Also, one does not expect the spontaneous local fluctuation to lower the global (the more the local) free energy, so that the problems of stability, haunting the phase-transition theory, become meaningless here.

2. *Expansion in the parameter of smallness*

We first cast Eq. (1.1) into a more suitable form [2, 3, 5]. Write:

$$n_1(\boldsymbol{r}) = \varrho[1+h(\boldsymbol{r})], \tag{2.1}$$

with

$$\lim_{V\to\infty} \frac{1}{V}\int\limits_V d\boldsymbol{r} h(\boldsymbol{r}) = 0, \tag{2.2}$$

and

$$\frac{\partial}{\partial \boldsymbol{r}} \psi(\boldsymbol{r}, \boldsymbol{s}) = g(\boldsymbol{r}, \boldsymbol{s}) \frac{\partial}{\partial \boldsymbol{r}} u(|\boldsymbol{r}-\boldsymbol{s}|), \tag{2.3}$$

or

$$\frac{d}{dr} \psi(r) = g(r) \frac{d}{dr} u(r) \tag{2.3a}$$

for the uniform fluid. Hence Eq. (1.1) can be integrated:

$$\ln[1+h(\boldsymbol{r})] = \ln C_h - \beta\varrho \int d\boldsymbol{s} h(\boldsymbol{s}) \psi(\boldsymbol{r}, \boldsymbol{s}), \tag{2.4}$$

$$C_h^{-1} = \lim_{V\to\infty} \frac{1}{V} \int\limits_V d\boldsymbol{r} \exp\left\{-\beta\varrho \int d\boldsymbol{s} h(\boldsymbol{s}) \psi(\boldsymbol{r}, \boldsymbol{s})\right\}. \tag{2.5}$$

It is seen that $h(\boldsymbol{r}) = 0$ is always a solution to Eq. (2.4), i.e., to Eq. (1.1).

Consider now a uniform fluid (Eq. (1.2)) and look for rotationally invariant solutions of the type (1.3), i.e., for $h(\mathbf{r}) = h(r)$, $r = |\mathbf{r}|$. In this case the integrals in Eqs. (2.4), (2.5) can be written in the form:

$$I(r) = \beta\varrho \int d\mathbf{s}h(s)\psi(|\mathbf{r}-\mathbf{s}|) = \beta\varrho \int d\mathbf{t}h(|\mathbf{r}+\mathbf{t}|)\psi(t)$$

$$= \frac{2\pi\beta\varrho}{r}\int\limits_0^\infty dxx\psi(x)\int\limits_{|r-x|}^{r+x} dyyh(y) = \frac{2\pi\beta\varrho}{r}\int\limits_0^\infty dxxh(x)\int\limits_{|r-x|}^{r+x} dyy\psi(y). \tag{2.6}$$

Formal properties of the branching of non-constant solutions of Eq. (2.4), especially in the connection with the eigenvalues of the Fréchet derivative of Eq. (2.4), were discussed in the quoted literature in a rather detailed manner and will not be repeated here. Eq. (2.4) can also be dealt with in another way [7–9]. When we are interested in the birth of an inhomogeneity in initially homogeneous fluid, it is reasonable to begin with $h(\mathbf{r})$ different from zero but in some sense (for example in norm, or in amplitude) small. Let us expand formally $h(\mathbf{r})$ in powers of a formal smallness parameter α:

$$h(\mathbf{r}) = \alpha h^{(1)}(\mathbf{r})+\alpha^2 h^{(2)}(\mathbf{r})+ \ldots \tag{2.7}$$

(α can be interpreted also as a measure of the distance from the bifurcation point). Insert the expansion (2.7) into (2.4) and collect terms of the same order in α:

$$h^{(1)}(\mathbf{r}) = -\beta\varrho \int d\mathbf{s}h^{(1)}(\mathbf{s})\psi(\mathbf{r}, \mathbf{s}), \tag{2.8}$$

$$h^{(2)}(\mathbf{r}) = -\beta\varrho \int d\mathbf{s}h^{(2)}(\mathbf{s})\psi(\mathbf{r}, \mathbf{s})+\tfrac{1}{2}\,[h^{(1)}(\mathbf{r})]^2 \tag{2.9}$$

$$h^{(3)}(\mathbf{r}) = -\beta\varrho \int d\mathbf{s}h^{(3)}(\mathbf{s})\psi(\mathbf{r}, \mathbf{s})+h^{(1)}(\mathbf{r})h^{(2)}(\mathbf{r})-\tfrac{1}{3}\,[h^{(1)}(\mathbf{r})]^3 \tag{2.10}$$

etc. Constants, which should appear in the above equations, are, because of the assumed smallness of $h(\mathbf{r})$, identically equal to zero. For ψ uniform, h rotationally invariant, Eq. (2.8) — with Eq. (2.6) — has the solution:

$$h^{(1)}(r) = \sum_i A_i^{(1)} \sin(k_i r)/r, \tag{2.11}$$

where the amplitudes $A_i^{(1)}$, which are arbitrary, can be connected, for example, with the expansion parameter α. The allowed values k_i of the wavenumber k are determined as the solutions of the equation:

$$1+\beta\varrho\hat{\psi}(k) = 0, \tag{2.12}$$

with $\hat{\psi}(k)$ being the three-dimensional Fourier transform of $\psi(r)$:

$$\hat{\psi}(k) = \frac{4\pi}{k}\int\limits_0^\infty drr\sin(kr)\psi(r) = \int d\mathbf{r}e^{i\mathbf{k}\cdot\mathbf{r}}\psi(r), \tag{2.13a}$$

or, integrating by parts and making use of Eq. (2.3a),

$$\hat{\varphi}(k) = \frac{4\pi}{k^3} \int_0^\infty dr [kr \cos (kr) - \sin (kr)] g(r) u'(r). \tag{2.13b}$$

Eq. (2.8) is isomorphic with the linear eigenvalue problem for the Fréchet derivative of the nonlinear equation (2.4) (cf. Refs. [5, 8]). Hence, only these solutions (2.11) of Eq. (2.8) which are of odd multiplicity, (i.e., with odd number of corresponding solutions of Eq. (2.12)), will be the branching points of nonconstant solutions of the nonlinear equation (2.4).

The three-dimensional Fourier decomposition of the solution (2.12) has the form of separate modes:

$$\hat{h}^{(1)}(k) = \int dr e^{ik\cdot r} h^{(1)}(r) = 2\pi^2 \sum_i A_i^{(1)} \delta(k-k_i)/k_i. \tag{2.14}$$

This form of fluctuations has been used earlier in our model description of the influence of fluid inhomogeneities on the critical properties and on the equation of state [11].

The solution (2.12) for $h^{(1)}(r)$ allows us to find an analytical form of the solution for $h^{(2)}(r)$. Fourier-transforming Eq. (2.9) with the use of Eqs. (2.6) and (2.12), we get:

$$\hat{h}^{(2)}(q) [1+\beta\varrho\hat{\varphi}(q)] = \frac{1}{8\pi^2 q} \int_0^\infty dp p \hat{h}^{(1)}(p) \int_{p-q}^{p+q} dt t \hat{h}^{(1)}(t)$$

$$= \frac{\pi^2}{2q} \sum_{i,j} A_i^{(1)} A_j^{(1)} [\theta(k_i + k_j - q) - \theta(|k_i - k_j| - q)], \tag{2.15}$$

with $\theta(x)$ being the step-function. Now, at $q = k_i$, $1+\beta\varrho\hat{\varphi}(q) = 0$. Hence, $\hat{h}^{(2)}(q = k_i) \sim \delta(q-k_i)$ (compare with an analogous form of Eq. (2.8), and with Eq. (2.14)). The solution of Eq. (2.9) thus is:

$$rh^{(2)}(r) = \sum_i A_i^{(2)} \sin (k_i r) + \tfrac{1}{4} \sum_{i,j} A_i^{(1)} A_j^{(2)} \mathrm{PP} \int_{|k_i - k_j|}^{k_i + k_j} \frac{\sin (qr) dq}{1+\beta\varrho\hat{\varphi}(q)}, \tag{2.16}$$

where PP means the principal part of the integral. Again, $A_i^{(2)}$ are arbitrary. Hence, the first term of the right-hand side of the solution (2.16) adds up to the solution for $h^{(1)}(r)$ and causes only the renormalization of the amplitudes of unmixed modes. Second term of the solution (2.16) broadens and mixes different initial modes.

3. *Hard spheres and adhesive hard spheres*

Denoting:

$$f(r) = \exp [-\beta u(r)] - 1, \tag{3.1}$$

and

$$g(r) = [1 + f(r)] y(r), \tag{3.2}$$

Eq. (2.3a) can be written in the form:

$$-\beta \frac{d}{dr}\psi(r) = y(r)\frac{d}{dr}f(r). \tag{3.3}$$

For the fluid of hard spheres of diameter σ,

$$f(r) = -\theta(\sigma-r), \quad df(r)/dr = \delta(r-\sigma), \tag{3.4}$$

so that

$$\beta\psi(r) = y(\sigma)\theta(\sigma-r) = g(\sigma+0)\theta(\sigma-r), \quad r \geqslant 0, \tag{3.5}$$

Integration constant which should appear in the above relation can be set equal to zero: addition of a constant to $\psi(r)$ does not change the initial equation, Eq. (2.4) with (2.5).

The well-known relation (cf. e.g. Refs. [8, 12]) between $g(\sigma)$ and the pressure p of the fluid of hard spheres:

$$\beta_p/\varrho = 1+2\pi g(\sigma+0)/3, \tag{3.6}$$

together with the best known hard-sphere equation of state [12, 13]:

$$\beta_p/\varrho = (1+\eta+\eta^2-\eta^3)/(1-\eta)^3, \quad \eta = \pi\varrho\sigma^3/6, \tag{3.7}$$

give

$$\gamma = 4\pi\varrho\sigma^3 g(\sigma+0) = 8\eta^2(2-n)/\pi(1-\eta)^3. \tag{3.8}$$

Eq. (2.12) for the fluid of hard spheres is thus:

$$[\sin(k\sigma)-k\sigma\cos(k\sigma)]/(k\sigma)^3 = -1/\gamma. \tag{3.9}$$

This equation has solutions for $(1/\gamma) \lesssim 0.0267\ldots$ (cf. Fig. 1), i.e., for $\eta \gtrsim 0.534\ldots$ (cf. Fig. 2), i.e., for rather high densities, near to the densities of the hard-sphere solid. Besides, these

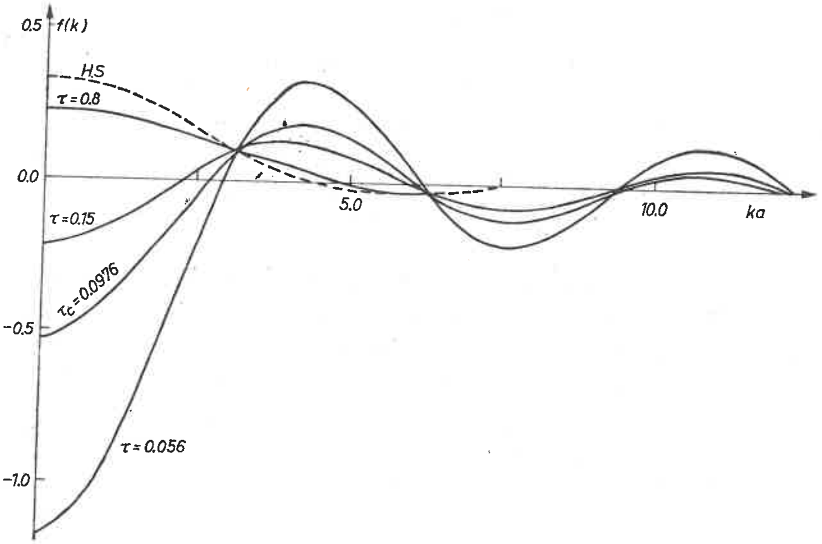

Fig. 1. Left-hand side of Eq. (3.19) as the function of the wavenumber ka, for different temperatures τ. Dashed line corresponds to the fluid of hard spheres

solutions are of multiplicity two. This result seems to suggest that in the fluid of classical hard spheres there are no density fluctuations which can branch off continuously from the uniform solution.

Consider now the fluid of hard spheres with attraction:

$$f(r) = \begin{cases} -1 & r < \sigma \\ E & \sigma < r < a, \qquad E = e^{\beta\varepsilon}-1, \\ 0 & a < r \end{cases} \tag{3.10}$$

i.e.,

$$\begin{aligned} f(r) &= -\theta(\sigma-r)+E\theta(r-\sigma)\theta(a-r) \\ f'(r) &= \delta(r-\sigma)\,[1+E\theta(a-\sigma)]-\delta(r-a)\theta(a-\sigma)E, \end{aligned} \tag{3.11}$$

where ε is the depth of the potential well of the width $(a-\sigma)$. Hence,

$$\beta\psi(r) = y(\sigma)\,(1+E)\theta(\sigma-r)-y(a)E\theta(a-r), \tag{3.12}$$

and Eq. (2.12) has the form:

$$\begin{aligned} &4\pi\varrho\{y(\sigma)\,(1+E)\,[\sin{(k\sigma)}-k\sigma\cos{(k\sigma)}] \\ &-y(a)E[\sin{(ka)}-ka\cos{(ka)}]\}/k^3+1 = 0. \end{aligned} \tag{3.13}$$

Baxter [14] (cf. also Ref. [15]) several years ago proposed to consider the model of adhesive hard spheres, i.e., the potential (3.10) for which the well depth goes to infinity and the well width goes to zero in such a way that

$$E = a/12\tau(a-\sigma), \qquad \sigma \to a-0 \tag{3.14}$$

(τ being a dimensionless measure of the temperature), and

$$\lim_{\sigma\to a-0} f(r) = -1+\frac{a}{12}\delta(r-a+0). \tag{3.15}$$

This model has the advantage that for it the Percus-Yevick approximation [16] can be solved exactly [14] and the obtained solution reveals qualitative features of the gas-liquid phase transition. Especially, in the Percus-Yevick approximation in the limit (3.14), the function $y(r)$ becomes continuous at the point $\sigma = a-0$, and is equal to [14]:

$$y(a) = y(\sigma) = \frac{2+\eta}{2(1-\eta)^2}-\frac{\eta\lambda}{1-\eta}+\frac{\eta\lambda^2}{12}, \tag{3.16}$$

where the parameter λ is to be calculated from the second relation, equivalent to the Percus-Yevick approximation:

$$y(a) = \lambda\tau \tag{3.17}$$

(from the two positive roots for λ, the smaller is physical [14]). The solution (3.16) possesses the critical point at:

$$\tau_c = (2-\sqrt{2})/6 \simeq 0.0976..., \qquad \eta_c = (3\sqrt{2}-4)/2 \simeq 0.1213, \tag{3.18}$$

below which in the $\tau-\eta$ plane there is a region in which exist no real solutions for the parameter λ, and this region is interpreted as the gas-liquid transition.

Expanding the left-hand side of Eq. (3.13) into powers of $(a-\sigma)$ and taking the limit (3.14), we get, after some rearrangements:

$$[(1-k^2a^2/12\tau)\sin(ka)-ka\cos(ka)]/(ka)^3 = -1/\gamma, \tag{3.19}$$

where now

$$\gamma = 4\pi\varrho a^3 y(a) = 24\lambda\tau\eta. \tag{3.20}$$

The shape of the left-hand side of Eq. (3.19), as the function of ka, is shown in Fig. 1 for a few values of the temperature τ, whereas Fig. 2 shows the shape of the right-hand side of Eq. (3.19), as the function of η, for the same values of τ. Dashed curves in these figures correspond to the fluid of hard spheres without attraction ($\tau \to \infty$). Dot-dashed fragment of the isotherm $\tau = 0.056$ in Fig. 2 corresponds to the unphysical part of the isotherm, where $(\partial p/\partial\varrho) < 0$. For $\tau = 0.056$, for $0.02 \lesssim \eta \lesssim 0.20$, there are no real solutions for λ.

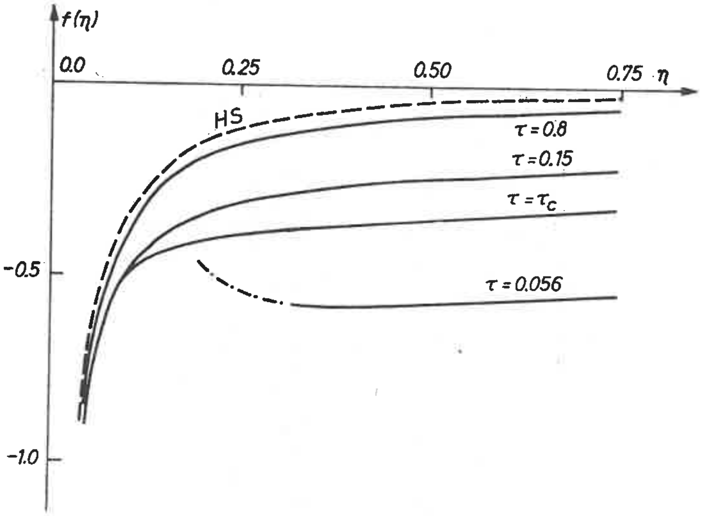

Fig. 2. Right-hand side of Eq. (3.19) as the function of the reduced density η

Loci of the solutions of Eq. (3.19), in the $ka-\eta$ plane, are shown in Fig. 3. It is seen that for temperatures τ lower than about 0.15 (which is still fairly above the critical temperature), Eq. (3.19) has always one single solution. This means that the attractive part of the potential, even of the extremely short range, is able to produce the density fluctuation

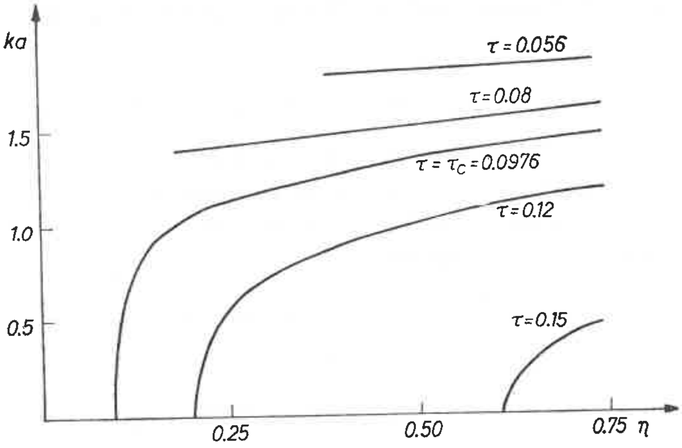

Fig. 3. Solutions of Eq. (3.19)

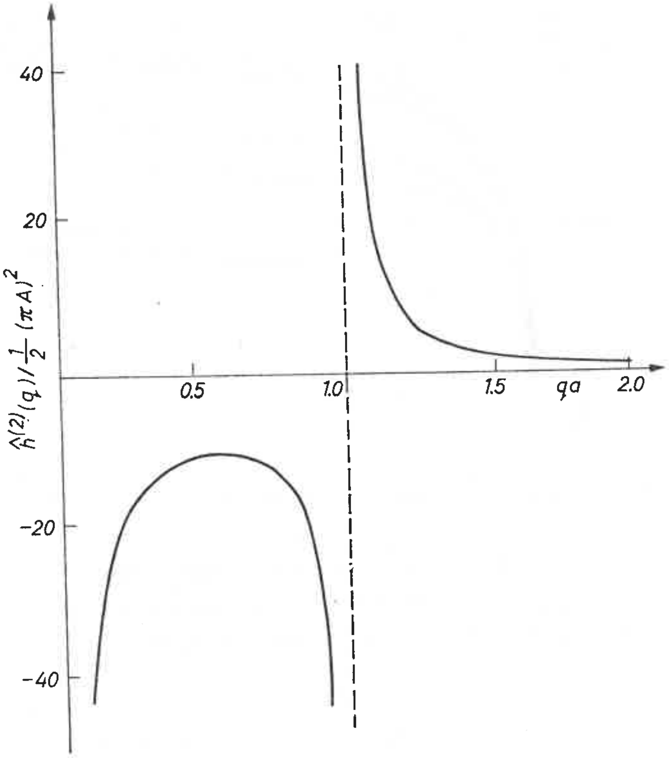

Fig. 4. Second-order fluctuation spectrum for adhesive hard spheres, for $\tau = \tau_c$, $\eta = 0.17$. Dashed line denotes the position of the starting mode

branching off smoothly from the uniform fluid. However, for low densities and/or high temperatures, there are no such solutions.

The above results show that the density fluctuations appear first in the form of one single mode. This single mode is broadened subsequently by the higher-order terms of the expansion (2.7) (cf. formula (2.15)). The shape of the second-order fluctuation spectrum, $\hat{h}^{(2)}(q)$, is shown in Fig. 4, for $\tau = \tau_c$ and $\eta = 0.17$. Dashed line in Fig. 4 denotes the position of the starting mode. It is seen that the second-order fluctuation spectrum covers now the whole range between $q = 0$ and $q = 2k_0$, i.e., all wavelengths λ longer than π/k_0, where k_0 is the starting mode wavenumber, with however the k_0-mode strongly pronounced.

4. *Two-component system: monovalent plasma*

Most of the formulas and results of first two sections of this paper can be easily extended to N-component systems simply by treating quantities like $n(r)$, $h(r)$, $h^{(i)}(r)$ as N-component column matrices, and quantities like $\psi(r)$ as $N\times N$ square matrices, with components $n_j(r)$, $\psi_{jk}(r)$, etc., subscripts j, k indicating different species of the mixture. Especially, Eq. (2.8) has now the form:

$$h_i^{(1)}(r) = -\beta \sum_{j=1}^{N} \varrho_i \int ds h_j^{(1)}(s)\psi_{ij}(r, s), \quad i = 1, \dots, N, \tag{4.1a}$$

or, for initially uniform fluid,

$$h_i^{(1)}(r) = -\frac{2\pi\beta}{r} \sum_{j=1}^{N} \varrho_j \int_0^{\infty} dx x\psi_{ij}(x) \int_{|r-x|}^{r+x} dy y h_j(y), \quad i = 1, \dots, N \tag{4.1b}$$

with

$$\frac{d}{dr}\psi_{ij}(r) = g_{ij}(r)\frac{d}{dr}u_{ij}(r), \tag{4.2}$$

and ϱ_j being the average number density of the species j. This system of equations has again the solution in the form of m separate modes:

$$rh_i^{(1)}(r) = \sum_{l=1}^{m} A_{il}^{(1)} \sin(k_{il}r), \quad i = 1, \dots, N \tag{4.3}$$

with the conditions

$$k_{1l} = k_{2l} = \dots = k_{Nl} \equiv k_l \tag{4.4}$$

(the same modes for all species), and with

$$A_{il}^{(1)} + \sum_{j=1}^{N} \beta\varrho_j A_{jl}^{(1)} \Phi_{ij}(k_l) = 0, \quad i = 1, \dots, N, \quad l = 1, \dots, m \tag{4.5}$$

determining the mode wavenumbers, and relating amplitudes of the same mode of different species.

The overall density fluctuation is decribed by the function

$$h_\varrho(r) = \sum_{l=1}^{N} h_i(r), \tag{4.6}$$

and we have, from Eq. (4.3),

$$rh_\varrho^{(1)}(r) = \sum_{l=1}^{m} A_{\varrho l}^{(1)} \sin(k_l r), \qquad A_{\varrho l}^{(1)} = \sum_{i=1}^{N} A_{il}^{(1)}. \tag{4.7}$$

As an example, consider two-component diluted monovalent plasma (hydrogen plasma, for example) with components denoted e and p. The same considerations will apply to diluted solution of monovalent electrolyte, when fluctuations of the solvent density are not taken into account. In this case we have:

$$u_{ee}(r) = u_{pp}(r) = e^2/r, \qquad u_{ep}(r) = u_{pe}(r) = -e^2/r, \tag{4.8}$$

and (cf. e.g. Ref. [17])

$$\begin{aligned} g_{ee}(r) = g_{pp}(r) &= 1 - \frac{\beta e^2}{r}(1-e^{-ar}) \\ & \qquad\qquad a^2 = 8e^2\pi\beta\varrho, \\ g_{ep}(r) = g_{pe}(r) &= 1 + \frac{\beta e^2}{r}(1-e^{-ar}) \end{aligned} \tag{4.9}$$

with $\varrho_e = \varrho_p = \varrho$. Hence

$$\begin{aligned} \hat{\varphi}_{ee}(k) = \hat{\varphi}_{pp}(k) &= \frac{4\pi e^2}{k^2} + \frac{2\pi\beta e^4}{k}\left[\frac{a^2+k^2}{k^2}\operatorname{arc\,tg}\frac{k}{a} - \frac{\pi}{2} - \frac{a}{k}\right], \\ \hat{\varphi}_{ep}(k) = \hat{\varphi}_{pe}(k) &= -\frac{4\pi e^2}{k^2} + \frac{2\pi\beta e^4}{k}\left[\frac{a^2+k^2}{k^2}\operatorname{arc\,tg}\frac{k}{a} - \frac{\pi}{2} - \frac{a}{k}\right], \end{aligned} \tag{4.10}$$

and Eqs. (4.5) read

$$\left.\begin{aligned} 1+\beta\varrho\hat{\varphi}_{ee}(k)+\xi\beta\varrho\hat{\varphi}_{ep}(k) = 0 \\ 1+\beta\varrho\hat{\varphi}_{ee}(k)+\xi^{-1}\beta\varrho\hat{\varphi}_{ep}(k) = 0 \end{aligned}\right\}, \qquad \xi = A_p/A_e. \tag{4.11}$$

Both above equations must hold simultaneously, which gives

$$\xi = \pm 1, \quad \text{or} \quad A_p = \pm A_e, \tag{4.12}$$

i.e.,

$$k^2+a^2 = 0 \quad \text{for} \quad A_p = -A_e, \tag{4.13}$$

and

$$-\frac{a}{k}\left[\frac{a^2+k^2}{k^2}\operatorname{arc\,tg}\frac{k}{a} - \frac{\pi}{2}\right] = \frac{2}{\beta e^2 a} + \frac{a^2}{k^2}, \quad \text{for} \quad A_p = A_e. \tag{4.14}$$

Neither Eq. (4.13) nor Eq. (4.14) has solutions for real positive k, i.e., according to the BBGKY hierarchy equations, threre are no fluctuations in a dilute plasma, which fulfill the expansion (2.7), i.e., which branch off continuously from the uniform solution.

In order to see whether such fluctuations will appear at higher densities, let us approximate roughly the shape of the radial distribution functions by:

$$g_{ee}(r) = g_{pp}(r) = b[1-\cos(ar)]/ar,$$

$$g_{ep}(r) = g_{pe}(r) = b\sin(ar)/ar, \tag{4.15}$$

where parameters a and b are functions of temperature and density. Relations (4.11) and (4.12), which are valid for all densities, give now

$$1+\frac{\pi}{4}B\lambda[\lambda^2-(\lambda^2-1)\theta(\lambda-1)]\pm B\lambda\left[(\lambda^2-1)\ln\left|\frac{\lambda+1}{\lambda-1}\right|-\lambda\right] = 0, \tag{4.16}$$

with $\lambda = a/k$, $B = 2\pi\beta\varrho be^2/a^2$, and with upper and lower signs referring to $A_p = \pm A_e$. For $A_p = A_e$, i.e., for the density mode, Eq. (4.16) has double solutions for $B \gtrsim 1.149...$ For $A_p = -A_e$, i.e., for the charge mode, Eq. (4.16) has one single solution for every positive value of B, for $\lambda \gtrsim 1.6...$

5. *Final remarks*

Lovett a.o. [19] proposed the following, claimed to be generally valid, relation between local density $n_1(\boldsymbol{r})$ and two-particle direct correlation function $c(r)$:

$$\frac{\partial}{\partial \boldsymbol{r}}\ln n_1(\boldsymbol{r}) = \int d\boldsymbol{s}c(|\boldsymbol{r}-\boldsymbol{s}|)\frac{\partial}{\partial \boldsymbol{s}}n_1(\boldsymbol{s}). \tag{5.1}$$

This equation is formally very similar to Eq. (1.1) and thus its solutions can be analysed in a manner analogous to those of Eq. (1.1). Indeed, on the basis of Eq. (5.1), Lovett [7] discussed the problem of crystallization in analogy to an earlier analysis of Eq. (1.1) performed by Raveché and Stuart [5]. Discussion of fluctuation-type behaviour leads in the case of Eq. (5.1) again to the solutions in the form of formulas and equations (2.7)–(2.13a), with function $-\beta\psi(r)$ replaced by the function $c(r)$. Consequently, the equation (2.12) determining the wavenumbers k_i of the arising initial modes is now:

$$1-\varrho\hat{c}(k) = 0. \tag{5.2}$$

However, this condition means that Eq. (5.1) admits fluctuation-type solutions only at the points of mechanical instability. For the fluid of hard spheres, Eq. (5.2) is never fulfilled (cf. e.g. Ref. [7]). From the thermodynamic arguments, Eq. (5.2) has always solution $k = 0$, but solely at the critical point and on the spinodal line, i.e., at the limit of stability with respect to the gas-liquid phase transition. For adhesive hard spheres, Eq. (5.2) has no solutions for $k \neq 0$, at least when $c(r)$ is calculated in the Percus-Yevick approximation [14]. Hence, it seems that Eq. (5.1) does not describe the appearance of small spontaneous fluctuations in an otherwise stable, globally uniform fluid.

On the other hand, the results of the preceding Sections show that indeed the BBGKY hierarchy, Eq. (1.1), admits inhomogeneous solutions of the fluctuation type, which branch off smoothly from the uniform solution, i.e., which can appear spontaneously in an initially uniform fluid. However, both for short-range and for long-range interparticle interactions, discussed in more detail in this paper, such solutions do not exist in diluted fluids and appear solely above some threshold density. This observation is valid only for initially small fluctuations, evolving in accordance with the expansion (2.7) from the uniform fluid, and hence the question of the existence of gross fluctuations in diluted systems is not answered here. The same remark is true for the discussion of Eq. (5.1).

The lowest density at which fluctuation of the type discussed in this paper can appear is determined by the first zero of Eq. (2.12) (or Eqs. (4.5)). The appearance of such a zero was sometimes interpreted as the instability (the so-called Kirkwood instability) with respect to the crystal formation. This problem — for hard spheres, Eq. (3.9) — was discussed by Kunkin and Frisch [18] who showed that such interpretation is incorrect, and especially that such zeros do not describe the instability, in the nonuniform fluid, with respect to the perturbation of wavelength greater than the critical one. However, they were not able to find any consistent interpretation of such instabilities. The results presented in this work suggest that these zeros can be interpreted as the bifurcation points of spontaneous fluctuations arising in the uniform fluid, i.e., points at which the initially homogeneous fluid becomes unstable with respect to the spontaneous formation of inhomogeneities of appropriate wavelength.

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