REGULARIZATION OF THE SELF-CONSISTENT FIELD METHOD IN STATISTICAL MECHANICS

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REGULARIZATION OF THE SELF-CONSISTENT FIELD METHOD IN STATISTICAL MECHANICS

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One of the most effective methods for the statistical study of many-particle systems is the method of correlation distribution functions $F_s(q_1, q_2, \dots, q_s)$ $(s = 1, 2, \dots, N)$, which determine (when multiplied by V^{-s}) the probability density of finding a given group of s particles, respectively in unit volumes near the points with radius vectors $q_1, q_2, \dots, q_s$ (the Cartesian coordinates of the vector q are denoted by q^α, where $\alpha = 1, 2, 3$; N is the number of particles in the volume V).

The distribution functions $F_s(q_1, q_2, \dots, q_s)$ are connected with one another by the chain of Bogolyubov equations ([1]). The first equation of this chain—the equation for the one-particle distribution function $F_1(q)$—has the form:

$$\theta \frac{\partial F_1(q)}{\partial q^\alpha} + \frac{1}{v} \int \frac{\partial \Phi(|q - q'|)}{\partial q^\alpha} F_2(q, q')\, dq' = 0 \tag{1}$$

($\theta = kT$; T is the absolute temperature; $v = V/N$, $\Phi(|q-q'|)$ is the pair-interaction potential).

Solving equation (1) is not possible, since, in addition to $F_1(q)$, it also contains the unknown binary distribution function $F_2(q, q')$.

If, neglecting the pair correlation between particles, one sets

$$F_2(q, q') = F_1(q) F_1(q'), \tag{2}$$

then after substituting (2) into (1) we obtain, for the density of the number of particles $\rho(q) = \frac{1}{v} F_1(q)$, the Vlasov equation with a self-consistent field ([2])

$$\theta \ln \lambda \rho(q) + \int \Phi(|q - q'|) \rho(q')\, dq' = 0, \tag{3}$$

where λ is determined from the normalization condition

$$\int \rho(q)\, dq = N, \tag{4}$$

and $\int \Phi(|q-q'|)\rho(q')\, dq' = u(q)$ is called the self-consistent potential.

Equation (3) has the physical defect that, when calculating the interaction energy between the particles of the system, it leads to taking into account the self-energy of these particles. Therefore, when applying equation (3) to statistical systems, this defect must be eliminated.

In ([3]) it was shown that equation (3) is a good approximation not only for a plasma but also for a crystal, since, owing to the "rigid"localization of its particles near the lattice sites, the motion of each particle is determined by interaction not with any one neighboring particle, but by simultaneous collective interaction with all–

by the particles surrounding it. The physical defect of equation (3) is thereby eliminated automatically.

The application of equation (3) to a spatially homogeneous system (liquid, gas), even after its modification, leads to results that are correct only qualitatively and in order of magnitude [4]. This is connected with the impossibility, in this case, of eliminating unambiguously the defect of equation (3).

For a more consistent application of the distribution-function method to a liquid and a gas, it is necessary to take into account correlations at small distances between particles, i.e., to regularize the self-consistent-field equation at these distances.* To this end, let us represent the potential $\Phi(r)$ of the pair interaction between particles as the sum of the potential $\Phi_0(r)$ of "short-range" forces and the potential $\Phi_1(r)$ of "long-range" forces [6, 7]:

$$\Phi(r) = \Phi_0(r) + \Phi_1(r). \tag{5}$$

At small distances ($|q-q'| \leq \sigma$), where the "short-range" forces manifest themselves, the binary distribution function is determined by the Boltzmann formula

$$F_2(q,q') \approx e^{-\Phi(|q-q'|)/\theta}, \tag{6}$$

whereas in the region of action of the "long-range" forces ($|q-q'| > \sigma$) it is equal to (2). Both of these expressions for $F_2(q,q')$ can be taken into account simultaneously and thereby, to a certain extent, the self-consistent-field method can be regularized if one sets

$$F_2(q,q') = e^{-\Phi_0(|q-q'|)/\theta} F_1(q) F_1(q'). \tag{7}$$

Substituting (7) into the exact equation (1), we obtain

$$\theta\frac{\partial}{\partial q^\alpha}\ln F_1(q)-\frac{\theta}{v}\int_{|q-q'|\le\sigma}\frac{\partial}{\partial q^\alpha}\left(e^{-\Phi_0(|q-q'|)/\theta}\right)F_1(q')\,dq'+$$

$$+\frac{1}{v}\frac{\partial}{\partial q^\alpha}\int_{|q-q'|>\sigma}\Phi_1(|q-q'|)F_1(q')\,dq'=0. \tag{8}$$

Integrating (8), we obtain for $\rho(q)$ the equation:

$$-T\left[-k\ln\rho(q)+k\int_{|q-q'|\le\sigma}\left(e^{-\Phi_0(|q-q'|)/\theta}-1\right)\rho(q')\,dq'\right]+$$

$$+\int_{|q-q'|>\sigma}\Phi_1(|q-q'|)\rho(q')\,dq'+\lambda=0 \tag{9}$$

(λ is a constant of integration). Here the first term in square brackets, $-k\ln\rho(q)=-k(\rho\ln\rho/e)'$, is the derivative with respect to ρ of the density of the configurational part of the entropy of an ideal gas, while the entire square bracket is correspondingly the derivative with respect to ρ of the density of the configurational part of the entropy $s_0(\rho)$ of a system of particles with short-range forces. Therefore (9) leads to the following regularized self-consistent-field equation for $\rho(q)$:

$$\int\Phi(|q-q'|)\rho(q')\,dq'-T\frac{ds_0(\rho)}{d\rho}+\lambda=0. \tag{10}$$

Here $\Phi(|q-q'|)\equiv\Phi_1(|q-q'|)$ is the potential of the "long-range forces."

In paper [3] it was shown that the solution of equation (3) is equivalent to a variational problem of finding the minimum, depending on the self-consistent—

* In the theory of electrolytes, such a regularization was successfully carried out in paper [5].

of the self-consistent potential $u(q)$ of the free-energy functional of the system $F(u)$. Replacing in this functional, with the aid of (3) and taking (4) into account, the self-consistent potential $u(q)$ by $\rho(q)$, we obtain a free-energy functional $F(\rho)$ depending on ρ.

Analogously, the regularized equation with a self-consistent field (10) can be obtained by minimizing the free-energy functional

$$F(\rho)=\frac{1}{2}\int\Phi(|q-q'|)\rho(q)\rho(q')\,dq\,dq'-T\int s_0(\rho)\,dq \tag{11}$$

under the additional condition (4).

For a spatially homogeneous system, the free energy, according to (11), has the form

$$F(\rho) = \int \left(\frac{1}{2} K_0 \rho^2 - T s_0(\rho) \right) dq, \tag{12}$$

where

$$K_0 = \int \Phi(|q - q'|) dq' = 4\pi \int_\sigma^\infty \Phi(r) r^2 \, dr.$$

Consequently, the free-energy density of the spatially homogeneous phase is

$$f(\rho) = \tfrac{1}{2} K_0 \rho^2 - T s_0(\rho). \tag{13}$$

The critical state, as is known, lies on the boundary of stability of the spatially homogeneous phase, when the second and third derivatives of the free energy (13) vanish. Therefore from (13) we find:

$$T_\text{k} = \frac{4\pi}{s_0''(\rho_\text{k})} \int_\sigma^\infty \Phi(r) r^2 \, dr, \tag{14}$$

$$s_0'''(\rho_\text{k}) = 0. \tag{15}$$

The criterion for the critical transition (14) coincides with the criterion found in [4] (with a proper choice of the cutoff parameter d of the total interaction potential at zero) and corresponds to the criterion for branching of the solution of equation (3) about the spatially homogeneous solution, identified in [2] with crystallization. From [4] and, additionally, from what has been presented here, it is clear that the branching and the branching solution of the corrected equation with a self-consistent field (both (3) and (10)) physically correspond to the critical transition.

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Note: Figure translations are in progress. See original paper for figures.