

Equilibrium properties of electrons in dense systems of correlated scatterers

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The density of electron states in a random Gibbsian field is calculated by means of Feynman path integrals and functional integrals over the fields φ . The correlations of the scattering centers are taken into account by using the analogy between the statistical averaging and the functional averaging of Green functions over the vacuum in quantum field theory. Virial expansions of the density of states and of the free energy are obtained, and also the equation of state for a mixture of classical and quantum particles. The quantum-mechanical virial coefficients are expressed in terms of the Feynman integrals and the phase shifts for scattering of an electron by many centers. The density of states of an impurity electron is calculated at the critical point of the system of scattering centers.

1. INTRODUCTION

The equilibrium and kinetic properties of electrons in a dense system of neutral scattering centers (impurity electrons in dense atomic and molecular gases and liquids; electrons in a dense plasma with a small degree of ionization) have been considered many times, but agreement between the data of theory and experiment is still far from being achieved (cf., e.g., the surveys [1-3]). In the case of a semiconducting plasma, the solution of the problem is made easier by the facts that, firstly, for a sufficiently high density of charged centers, the electrons can be described semi-classically [2], and, secondly, the distribution of impurities can almost always be assumed to be a Poisson or Gaussian distribution. To obtain correct results in a dense system of neutral centers, the scattering of the electrons must be treated quantum-mechanically ($\lambda \sim 10-100 \text{ \AA}$). The problem is also made considerably more complicated by the necessity, in a dense gas, plasma or liquid, of taking into account the Gibbs correlations of the scattering centers, since, e.g., phase transitions in the system of scatterers can give rise to considerable changes in the equilibrium and kinetic characteristics of the electron subsystem.

Below, by means of the method of continuous integration, the equations of state of a mixture of quantum particles (non-degenerate electrons) and classical particles (the scattering centers) will be obtained. The method of continuous integrals is evidently the most natural generalization to the case of quantum systems of the classical methods of thermodynamic averaging, since it enables us to reduce a quantum ensemble to a classical ensemble of Wiener-Feynman trajectories.

Integrals over virtual "paths" (and "fields"-cf. Sec. 2) provide great opportunities for the construction of new perturbation-theory methods, inasmuch as they are always sums of an infinite number of diagrams. Here, the analogy between functional averaging of the Green functions over the vacuum in quantum field theory and averaging over the ensemble of the scattering centers of the Green function of the electron in the random field (written in the form of a Feynman path integral and a functional integral over the "field φ ") turns out to be extremely useful.

We shall consider the solution of the Schrödinger equation (everywhere below, $\hbar = m = k = 1$)

$$\left[-\frac{1}{2} \Delta + \int dr' v(r-r') n(r') \right] \psi(r) = E \psi(r),$$

$$n(r) = \sum_{i=1}^N \delta(r-R_i), \quad V(r) = \sum_{i=1}^N v(r-R_i), \quad (1.1)$$

for electrons in a random field of Gibbsian origin, i.e., we shall assume that the probabilities of different configurations (R_1, R_2, \dots, R_N) of the scattering centers, the density $n(r)$, the binary function g_{12} and the higher correlation functions are determined in Gibbsian fashion (U is the potential energy of interaction of the centers, and τ is the volume of the system),

$$w(R_1, \dots, R_N) = \frac{1}{Z_N} e^{-\beta U}, \quad Z_N = \int d\tau_1 \dots d\tau_N e^{-\beta U}, \quad \beta = \frac{1}{T}, \quad (1.2)$$

$$U = \frac{1}{2} \sum_{ij} u(R_i - R_j), \quad g_{12} = \frac{\tau^2}{Z_N} \int d\tau_3 \dots d\tau_N e^{-\beta U}.$$

2. THE DENSITY OF STATES

The density of states of an electron interacting with N scattering centers can be expressed in terms of the \hat{S} -operator for N -particle scattering (\hat{K} is the kinetic energy operator):

$$\rho_N(E) = \text{Sp} \delta(E - \hat{H}_N) = \rho_0(E) + \frac{1}{2\pi} \int dt e^{itE} \text{Sp} (e^{-it\hat{K}} \hat{f}), \quad (2.1)$$

$$\hat{f} = \hat{S} - 1, \quad \hat{H}_N = \hat{K} + V, \quad \rho_0(E) = \text{Sp} \delta(E - K),$$

Calculating the trace (2.1) in the plane-wave representation, using the displacement theorem and, in the expansion in powers of \hbar

$$e^{it\hat{K}} v(r - tk - R) e^{-it\hat{K}} = v(r - tk - R) + it [\hat{K} v(r - tk - R)] + \dots \quad (2.2)$$

retaining only the first term, we can take the thermodynamic limit $N \rightarrow \infty$, $\tau \rightarrow \infty$, $N/\tau = n < \infty$ in (2.2) and obtain a closed expression for $\rho(E)$.

First, we shall discuss the classical approximation

$$\rho(E) = \int \frac{dk d\tau}{(2\pi)^3 \tau} \overline{\delta(E - \varepsilon_k - V)}, \quad \varepsilon_k = \frac{k^2}{2}. \quad (2.3)$$

For the averaging (denoted in (2.3) by a line) over the distribution $P(\Phi)$ of the random field Φ (cf. [1])

$$\rho(E) = \int d\Phi \rho_0(E - \Phi) P(\Phi), \quad P(\Phi) = \frac{1}{2\pi} \int dt e^{it\Phi} P(t), \quad (2.4)$$

$$P(t) = \int d\tau_1 \dots d\tau_N e^{-itV} w(R_1, \dots, R_N), \quad N \rightarrow \infty$$

we must calculate the partition function Z_N of a real gas in the external field itV/β .

In (2.4), we go over to a functional integration, using the generalized Fourier transformation (cf., e.g., [4]):

$$\begin{aligned} & \exp \left[-\frac{\beta}{2} \int dr dr' n(r) u_{rr'} n(r') \right] \\ & = \int \delta\varphi K(\varphi) \exp \left[i\beta \int dr n(r) \varphi(r) \right] / \int \delta\varphi K(\varphi), \quad (2.5) \\ & K(\varphi) = \exp \left[-\frac{\beta}{2} \int dr dr' \varphi(r) u_{rr'}^{-1} \varphi(r') \right]; \end{aligned}$$

Here $u_{rr'}^{-1}$ is the matrix in the coordinate representation that is the inverse of the interaction matrix $u_{rr'}$, i.e.,

$$\int dr' u_{rr'}^{-1} u_{r'r''} = \delta(r-r''). \quad (2.5')$$

Then $(\langle \dots \rangle)$ denotes functional integration with weight $K(\varphi)$,

$$P(t) = \left\langle \exp \left[n \int d\tau (hf + h + f) \right] \right\rangle / \left\langle \exp \left(n \int d\tau h \right) \right\rangle \quad (2.6)$$

$$h = e^{i\beta\epsilon} - 1, \quad f = e^{-i\theta} - 1.$$

Thus, the calculation of the Gibbsian average reduces to functional averaging over all possible distributions of the field φ , with a nonlinear self-action.

It is not difficult to generalize the formulas (2.5)–(2.6) to the case of a multi-component mixture of gases (or of a pure gas with allowance for excited states of the centers).

In the self-consistent field approximation, the values of the functional integrals in the numerator and denominator of (2.6) are determined by the fields φ_1 and φ_2 satisfying the conditions that the functionals be stationary:

$$\begin{aligned} \ln(h_1 + 1) &= -n\beta \int dr' u_{rr'} (f + 1) (h_1 + 1), \\ \ln(h_2 + 1) &= -n\beta \int dr' u_{rr'} (h_2 + 1). \end{aligned} \quad (2.7)$$

The practical calculation of the functional integrals can be effected by expanding in powers of φ in the exponent in (2.6) and using the linear functional transformations

$$\varphi(r) \rightarrow \varphi'(r) + i\eta \int dr' u_{rr'} f(r'). \quad (2.8)$$

Another simple method is to expand in semi-invariants:

$$\langle e^x \rangle = \exp \left[\ln(1 + \langle e^x - 1 \rangle) \right] = \exp \left[\langle x \rangle + \frac{1}{2} \langle x^2 \rangle - \langle x \rangle^2 + \dots \right]. \quad (2.9)$$

For a large partition function of the system of centers, the series (2.9) corresponds to the usual virial expansion (M is the mass, μ is the chemical potential, ξ is the activity, and b_l is the cluster integral)

$$Z = \sum_{N=0}^{\infty} \frac{\xi^N}{N!} Z_N = \left\langle \exp \left[\int \frac{d\tau}{\lambda^3} e^{\beta(\mu + i\varphi)} \right] \right\rangle = \exp \left(\tau \sum_{l=1}^{\infty} \xi^l b_l \right), \quad (2.10)$$

$$\lambda^3 = 2\pi\beta/M.$$

In the expansion for $P(t)$

$$P(t) = \exp \left\{ n \int d\tau f + \frac{n^2}{2} \int d\tau_1 d\tau_2 f_1 f_2 \left[\exp(-\beta u(\mathbf{R}_1 - \mathbf{R}_2)) (1 + \dots) - 1 \right] \right\} \quad (2.11)$$

we perform the summation of the subsequence of Mayer diagrams contained in the round brackets, which reduces to the replacement

$$\begin{aligned} & \exp(-\beta u(\mathbf{R}_1 - \mathbf{R}_2)) \left\{ 1 + n \int d\tau' \left[\exp(-\beta u(\mathbf{R}_1 - \mathbf{R}') - 1) \right. \right. \\ & \left. \left. \times \left[\exp(-\beta u(\mathbf{R}_2 - \mathbf{R}') - 1) + \dots \right] \right\} \rightarrow g_{12}, \end{aligned} \quad (2.12)$$

and find, finally ¹⁾,

$$\rho(E) = \int \frac{dk dt}{(2\pi)^4} \exp \left[it(E - \epsilon_k) + n \int d\tau f + \frac{n^2}{2} \int d\tau_1 d\tau_2 f_1 f_2 (g_{12} - 1) \right]. \quad (2.13)$$

In the calculation of the integral over t by the stationary-phase method, terms of order t^3 in the exponent in (2.13) can be omitted, so that

$$\begin{aligned} \rho(E) &= \int \frac{dk dt}{(2\pi)^4} \exp \left[it(E - E_0 - \epsilon_k) - \frac{1}{2} v_0^2 t^2 \right], \quad E_0 = n \int d\tau v(R), \\ v_0^2 &= n \int \frac{dq}{(2\pi)^3} |v_q|^2 S_q, \quad S_q = 1 + n \int dR e^{iqR} [g_{12}(R) - 1]. \end{aligned} \quad (2.14)$$

In the absence of correlations, $g_{12} = 1$, the structure factor $S_q = 1$ and (2.14) coincides with the known results^[1,2]. The terms of order n^2 in (2.13)–(2.14) describe the deviation of the Gibbsian random field from a Poisson field. It is possible to generalize the classical expressions (2.3)–(2.13) to the case of the eikonal approximation (which corresponds to the first term in the expansion (2.2)), by replacing

$$f \rightarrow f' = \exp \left[-i \int_0^t dv v(vk - R) \right] - 1 = \exp \left[i \sum_{j=0}^{\infty} \frac{(-t)^{j+1}}{j!(j+1)} (k\nabla)^j v(R) \right] - 1; \quad (2.15)$$

to pass to the classical approximation, it is sufficient to take into account only the first term in the sum over j in the exponent in (2.15)²⁾.

3. USE OF CONTINUOUS PATH INTEGRALS

If the scattering of an electron by a center is essentially quantum in character, it is necessary to take into account all the terms in the expansion (2.2), so that it is not possible to pass to the thermodynamic limit directly in (2.1). In this case, we can obtain a closed expression for the density of electron states with allowance for the correlation of the scattering centers by writing (2.1) with the aid of a continuous path integral^[11]:

$$\rho(E) = \frac{1}{2\pi} \int dr dt e^{iEt} \oint \delta r(v) e^{i\epsilon_0 r'}, \quad s_0 = \frac{1}{2} \int_0^t dv [r(v)]^2, \quad (3.1)$$

$$\rho' = \exp \left(-i \sum_{j=1}^N \theta_j \right), \quad \theta_j = \int_0^t dv v(r(v) - R_j).$$

The continuous integral is taken over all closed trajectories with $\mathbf{r}(0) = \mathbf{r}(t) = \mathbf{r}$; for $\mathbf{r}(0) = \mathbf{r}$ and $\mathbf{r}(t) = \mathbf{r}'$, the path integral in (3.1) defines the corresponding Green function $G_t(\mathbf{r}, \mathbf{r}')$. The averaging over the configurations and the passage to the thermodynamic limit in (3.1) are carried out in exactly the same way as in Sec. 2. In place of (2.6)–(2.13), we find

$$\begin{aligned} \rho' &= \left\langle \exp \left\{ n \int d\tau [h(e^{-i\theta} - 1) + h + e^{-i\theta} - 1] \right\} \right\rangle / \left\langle \exp \left(n \int d\tau h \right) \right\rangle \\ &\approx \exp \left[n \int d\tau (e^{-i\theta} - 1) + \frac{n^2}{2} \int d\tau_1 d\tau_2 (e^{-i\theta_1} - 1) (e^{-i\theta_2} - 1) (g_{12} - 1) \right]. \end{aligned} \quad (3.2)$$

If we expand $e^{-i\theta}$ in a series in powers of v and confine ourselves to terms no higher than v^2 in the exponent in (3.2), we obtain

$$\rho' = \exp \left[-itE_0 - \int_0^t dv_1 dv_2 \Omega(v_1, v_2) \right], \quad (3.3)$$

$$\Omega(v_1, v_2) = \frac{n}{2} \int \frac{dq}{(2\pi)^3} |v_q|^2 S_q \exp[iq\mathbf{r}(v_1) - iq\mathbf{r}(v_2)].$$

The averaging in (3.1) was performed, without allowance for the correlations ($g_{12} = 1$), by Edwards and Gulyaev^[12]; the possibility of taking pair correlations into account in the case of a Gaussian random field in the nv^2 -approximation has been discussed by Lukes^[13] and Chaplik^[14]. The integrals in (3.2)–(3.3) can be calculated directly if we use the analogy between Eq. (1.1) and, e.g., an equation of the Klein-Gordon type for a scalar charged particle in a quantized electromagnetic field. Then the procedure for averaging over the configurations of the scattering centers (or, after the thermodynamic limit has been taken, over the random field

φ) in (3.2) corresponds to the functional quantum-field averaging (in the nv^2 -approximation, $|v_q|^2 S_q$ in our case plays the role of the causal field function D_q). We remark that, in contrast to (3.2), in the usual linear formulation of quantum field theory the averaging can be carried out exactly, since the integrals are Gaussian (if we exclude the contribution of the polarization loops).

After a displacement in the functional space, $r(\nu) \rightarrow \omega(\nu) + k$, the density of states (3.1)–(3.2) can be written in the form^[15,16]

$$\rho(E) = \frac{1}{\pi} \text{Im} \int \frac{dk}{(2\pi)^2} G(k, E),$$

$$G(k, E) = i \int_0^\infty dt \exp[it(E - \epsilon_k + i\eta)] c \int \delta\omega(v) \exp\left[-\frac{i}{2} \int_0^t dv \omega^2(v)\right] \rho', \quad (3.4)$$

$$\eta \rightarrow 0, \quad c \int \delta\omega(v) \exp\left(-\frac{i}{2} \int_0^t dv \omega^2(v)\right) = 1.$$

Here ρ' is defined according to (3.3), but with

$$0 = \int_0^t dv v(r(v) - R), \quad r(v) = vk + \int_0^t dv' \omega(v'). \quad (3.5)$$

If in the integration in (3.4)–(3.5) we confine ourselves to rectilinear paths $r(\nu) = \nu k$ we obtain the eikonal approximation (2.15), and with $\theta = tv(R)$ we find the classical result (2.13).

In the discussion of the infrared asymptotic behavior of the Green functions in quantum field theory in^[16], an approximation going beyond the framework of perturbation theory (and connected with a regrouping of the corresponding series) was proposed for integrals of the type (3.4)–(3.5) in the nv^2 -approximation. We introduce

$$w_1 = \langle\langle \Omega(v_1, v_2) \rangle\rangle, \quad w_2 = \langle\langle \Omega(v_1, v_2) \Omega(v_1', v_2') \rangle\rangle, \dots \quad (3.6)$$

($\langle\langle \dots \rangle\rangle$ denotes the Feynman averaging (3.4)). It is not difficult to calculate the averages in (3.6) by means of linear transformations of the type $\omega \rightarrow \omega' + q\Theta(\nu_2 - \nu)\Theta(\nu - \nu_1)$ ($\Theta(x) = 0$ for $x < 0$ and $\Theta(x) = 1$ for $x > 0$). Specifically,

$$w_1 = \frac{n}{2} \int \frac{dq}{(2\pi)^2} |v_q|^2 S_q \exp[i(\epsilon_k - \epsilon_{k-q}) |v_1 - v_2|]. \quad (3.7)$$

Cumbersome expressions for w_2, w_3 , etc. can be obtained by performing calculations analogous to those of Barbashov^[16]. In the so-called "modified" perturbation theory, the expansion is performed not in Ω but in the difference $\Omega - w_1$; terms of order v^2 then vanish. In the next approximation, we have (allowance for further terms in the exponent leads to the complete cancellation of the terms of order v^2 and v^4 and the partial cancellation of terms of higher order)

$$e^{i\epsilon_0} \rho' = \exp\left\{-\int_0^t dv_1 dv_2 w_1 - \frac{1}{2} \int_0^t dv_1 dv_2 dv_1' dv_2' [w_2 - w_1(v_1, v_2) w_1(v_1', v_2')] (1 + \dots)\right\}, \quad (3.8)$$

and so on (cf. ^[16]). In fact, the expansion (3.8) coincides with the cumulant expansion (2.9).

By comparing (3.3) and (3.7), it can be seen that taking the functional argument ω into account leads to a quadratic dependence on the virtual momenta. If the product $|v_q|^2 S_q$ is small for large q , then $\epsilon_{k-q} - \epsilon_k \approx k \cdot q$ and the dependence of Ω on ω can be neglected (the eikonal approximation).

We put

$$\int_0^t dv_1 dv_2 w_1 = tn \int \frac{dq}{(2\pi)^2} |v_q|^2 S_q \int_0^t dt' \left(1 - \frac{t'}{t}\right) \exp[it'(\epsilon_k - \epsilon_{k-q})] = t\Sigma + I(k, t). \quad (3.9)$$

Since the integrand in the integral over t

$$G(k, E) = i \int_0^\infty dt \exp[it(E - E_0 - \epsilon_k + i\eta) - t\Sigma - I] \quad (3.10)$$

is bounded, the possible singularities of G are associated with the integration over the large t . Near the "mass" surface $\epsilon_k \approx E - E_0 = \epsilon$, we find in the limit $t \rightarrow \infty$

$$\lim_{t \rightarrow \infty} \Sigma = \Gamma - i\Delta = \pi n \int \frac{dq}{(2\pi)^2} |v_q|^2 S_q \delta(\epsilon - \epsilon_{k-q}) - in \int \frac{dq}{(2\pi)^2} \frac{|v_q|^2 S_q}{\epsilon - \epsilon_{k-q}}, \quad (3.10')$$

which corresponds to the usual Σ -approximation^[3].

For the correction function $I(k, t)$ we can use approximations that ensure the correct asymptotic behavior. For example, for $I(k, t) \approx \text{Beit}^b$ we have

$$\rho(E) = \frac{1}{\pi} \int \frac{dk}{(2\pi)^2} \left[\frac{\Gamma}{A_0^2 + \Gamma^2} + \sum_{m=1}^\infty \frac{|-B|^m}{m!} \frac{\Gamma_m \cos(m \arg B) - A_m \sin(m \arg B)}{A_m^2 + \Gamma_m^2} \right], \quad (3.10'')$$

where $A_m = E + \Delta - E_0 + m \text{Re} b$, and $\Gamma_m = \Gamma + m \text{Im} b$. Thus, the correction function $I(k, t)$ takes into account the contribution, proportional to $|B|^m/m!$, of the singularities of the Green function that are displaced by $m \text{Re} b$ from the principal (for $|B| \ll 1$) pole corresponding to the Σ -approximation.

The results obtained make it possible to study the change in the density of states of the impurity electrons near the critical point (T_c, n_c) of the system of scatterers, when we can use the Ornstein-Zernike approximation³⁾ $S_q = S_0(1 + L^2 q^2)^{-1}$ for the structure factor (at the critical point, the correlation length $L(T, n) \rightarrow \infty$). It follows from (3.7) that

$$\int_0^t dv_1 dv_2 w_1 = F(t) - F(0) - tF'(0), \quad (3.11)$$

$$F(t) = -n \int \frac{dq}{(2\pi)^2} \frac{|v_q|^2 S_q}{(\epsilon_k - \epsilon_{k-q})^2} \exp[it(\epsilon_k - \epsilon_{k-q})].$$

In the particular case $|v_q|^2 = v_1^2 \exp(-2qR_0)$ (which corresponds to the polarization interaction $v(R) \sim (R^2 + R_0^2)^{-2}$), in the classical approximation $\rho' \approx \exp[-itE_0 - 1/2 t^2 F''(0)]$ we obtain ($\alpha_0 \rightarrow 0$; $C = 0.577$ is the Euler constant)

$$F''(0) = Q^2 = Q_c^2 [1 - 1/2 \pi \alpha_0 + \alpha_0^2 \ln \alpha_0 - (C-1) \alpha_0^2 + \dots], \quad (3.12)$$

$$Q_c^2 = n S_0 v_1^2 / 4\pi^2 R_0 L^2, \quad \alpha_0 = 2R_0/L.$$

Since $Q_c = Q(n_c, T_c) > Q(n, T)$ and the function $\rho(\delta) \sim |\delta|^{-3/2} \exp(-\delta^2/2Q^2)$ for $\delta = E - E_0 \rightarrow -\infty$, the density of states in the "tail" increases sharply in the critical region—it behaves like $\sim \exp(-\pi \alpha_0 \delta^2/4Q_c^2)$. For $\delta \rightarrow \infty$, the density of states at the critical point has a minimum ($(\rho - \rho_c)/\rho_c \approx \pi \alpha_0 Q_c^2/4\delta^2$). When $Q \rightarrow Q_c$ for any δ , it is not difficult to find ($D_p(z)$ is the parabolic cylinder function)

$$\frac{\rho - \rho_c}{\rho_c} = -\frac{1}{8} \pi \alpha_0 + \frac{\pi \alpha_0 \delta}{4Q_c} D_{-1/2} \left(-\frac{\delta}{Q_c}\right) \left[D_{-1/2} \left(-\frac{\delta}{Q_c}\right)\right]^{-1}. \quad (3.13)$$

By analogy with the results (3.2)–(3.4), we can calculate the averaged two-particle Green function, which describes the kinetic properties of the electrons with the correlation of the scattering centers taken into account. A virial expansion for $\rho(E)$ can be obtained either by expanding the exponential in (3.2) in powers of the den-

sity n , or directly from (2.1)–(2.2) with the aid of the series

$$\hat{f} = \sum_i \hat{f}_i + \frac{1}{2!} \sum_{ij} (\hat{f}_{ij} - \hat{f}_i - \hat{f}_j) + \frac{1}{3!} \sum_{ijk} (\hat{f}_{ijk} - \hat{f}_{ij} - \hat{f}_{ik} - \hat{f}_{jk} + \hat{f}_i + \hat{f}_j + \hat{f}_k) + \dots$$

$$\hat{f}_i = \exp(it\hat{K}) \exp\{-it[\hat{K} + v(\mathbf{r} - \mathbf{R}_i)]\} - 1. \quad (3.14)$$

The expansion (3.14) of the nonunitary \hat{f} -operator for scattering at many centers in terms of the operators for scattering at one, two, etc. centers is analogous to the representations used by Luttinger and Kohn^[17] for the collision T-operator and the density operator $e^{-\beta\hat{H}}$ (cf. also^[11]). We note that for the one-particle density operator $e^{-\beta(\hat{K} + \hat{V})}$ and the electron free energy we can use the results of Secs. 2 and 3, by replacing (it) by β . For example, in place of (3.1)–(3.2) we find

$$\overline{\text{Sp}[\exp\{-\beta(\hat{K} + \hat{V})\}]} = \left\langle \exp \left[n \int d\mathbf{R}_1 f_{1e} + \frac{n^2}{2} \int d\mathbf{R}_1 d\mathbf{R}_2 f_{12} f_{1e} f_{2e} + \dots \right] \right\rangle, \quad (3.15)$$

$$f_{12} = \exp[-\beta u(R_{12})] - 1, \quad f_{1e} = \exp \left[- \int_0^\beta dv v(\mathbf{r}(v) - \mathbf{R}_1) \right] - 1.$$

4. EQUATIONS OF STATE FOR A MIXTURE OF CLASSICAL AND QUANTUM PARTICLES

We shall discuss in more detail the virial expansions for the free energy, density of states and equilibrium properties of a mixture of $N_1 + N_2$ classical particles (atoms and ions) and N_3 quantum particles (a nondegenerate electron gas). In the case of a classical mixture, the grand partition function

$$Z = \sum_{N_1, N_2, N_3} \frac{\exp[\beta(\mu_1 N_1 + \mu_2 N_2 + \mu_3 N_3)]}{N_1! N_2! N_3!} \text{Sp}[\exp(-\beta\hat{H}_{N_1, N_2, N_3})], \quad (4.1)$$

which enables us to calculate the densities, partial pressures, etc. from the conditions of equilibrium and quasi-neutrality, can be written analogously to (2.10). In place of the virial expansion of the partition function (2.10) and the corresponding quantum expression (cf. [4]), it is simpler to use (4.1) directly with

$$\text{Sp}[\exp(-\beta\hat{H}_{N_1, N_2, N_3})] = \int \frac{d^N \mathbf{R}_1 d^N \mathbf{P}_1 d^N \mathbf{R}_2 d^N \mathbf{P}_2}{(2\pi)^{3(N_1 + N_2)}} e^{-\beta H_{12}}$$

$$\times \int d^N \mathbf{r} \oint \delta^N \mathbf{r}(v) \exp \left\{ - \int_0^\beta dv \sum_{\alpha=1}^{N_1} \left[\frac{1}{2} r_{\alpha}^2(v) + \sum_{i=1}^{N_1} v_{\alpha i}(\mathbf{r}(v) - \mathbf{R}_i) \right. \right. \quad (4.2)$$

$$\left. \left. + \sum_{j=1}^{N_2} v_{\alpha j}(\mathbf{r}_{\alpha}(v) - \mathbf{R}_j) + \frac{1}{2} \sum_{\alpha'=1}^{N_2} v_{\alpha \alpha'}(\mathbf{r}_{\alpha}(v) - \mathbf{r}_{\alpha'}(v)) \right] \right\}.$$

Here H_{12} is the kinetic and potential energy of the classical components of the mixture; $v_{\alpha\beta}$ is the potential energy of interaction of particles of types α and β ; the trajectories of the electrons in (4.2) are closed, i.e., $\mathbf{r}(0) = \mathbf{r}(\beta) = \mathbf{r}$. In the expansion in Mayer diagrams in (4.2) we can use the usual diagrammatic formalism, but the coordinates of the particles in the Mayer functions f for the electrons will depend on the choice of propagation trajectory, and, therefore, in the final expression for the virial coefficients, we must integrate over all possible trajectories, with the appropriate weighting function. For example,

$$B_{ea} = -\langle f_{1e} \rangle, \quad (4.3)$$

$$B_{eaa} = \frac{1}{2} B_{ea}^2 - \frac{1}{2\tau} \int d\mathbf{R}_1 d\mathbf{R}_2 \left\langle f_{12} f_{1e} f_{2e} + f_{1e} f_{2e} \right\rangle,$$

and so on.

The equation of state has the form^[18]

$$p = p_0 + n_e n_a T (B_{ea} + B_{aa}) + n_a^2 T B_{aaa} + 2n_e n_a^2 T (B_{eaa} + B_{aaa}) + \dots \quad (4.4)$$

For the practical derivation of the virial expansions we must express the virial coefficients in terms of the partial phase shifts for scattering at N centers^[4]. From the integral representation

$$\text{Sp}(e^{-\beta\hat{K} - \beta\hat{V}} - e^{-\beta\hat{K}}) = \frac{1}{4\pi i} \int d\epsilon e^{-\beta\epsilon} \text{Sp} \left[\hat{S}^{-1}(\epsilon) \frac{\partial}{\partial \epsilon} \hat{S}(\epsilon) - \left(\frac{\partial}{\partial \epsilon} \hat{S}^{-1}(\epsilon) \right) \hat{S}(\epsilon) \right], \quad (4.5)$$

(cf., e.g.,^[17]; the integration is taken over a contour enclosing all the singularities of the resolvent $(\hat{H} - \epsilon)^{-1}$, going over directly to the eigen-amplitudes $A_\gamma(n)$ and eigenvalues $\exp(2i\eta_\gamma)$ of the collision operator $\hat{S}(\epsilon)$ and using the completeness of the system of eigenfunctions on the surface of a unit sphere^[20]

$$\sum_\gamma A_\gamma^*(n) A_\gamma(n') = \delta(n - n'), \quad \int dn A_\gamma^*(n) A_\gamma(n) = \delta_{\gamma\gamma'}, \quad (4.6)$$

we obtain

$$\text{Sp}(e^{-\beta\hat{K} - \beta\hat{V}} - e^{-\beta\hat{K}}) = \frac{1}{4\pi i} \sum_\gamma \int dn dn' d\epsilon e^{-\beta\epsilon} \left[A_\gamma^*(n) \right.$$

$$\times \exp(-2i\eta_\gamma) A_\gamma(n') \frac{\partial}{\partial \epsilon} (A_\gamma^*(n') \exp(2i\eta_{\gamma'}) A_\gamma(n))$$

$$\left. - \frac{\partial}{\partial \epsilon} (A_\gamma^*(n) \exp(-2i\eta_\gamma) A_\gamma(n')) A_\gamma^*(n') \exp(2i\eta_{\gamma'}) A_\gamma(n) \right]$$

$$= \frac{1}{\pi} \sum_\gamma \int d\epsilon e^{-\beta\epsilon} \frac{\partial}{\partial \epsilon} \eta_\gamma(\epsilon, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N).$$

In the presence of bound states the singularities in (4.5) lead to additional terms, forming a sum over the discrete spectrum.

For the virial coefficients in (4.3), it follows from (4.7) that

$$-B_{ea} = \pi^{1/2} (2\beta)^{3/2} \int_0^\infty dk \exp\left(-\frac{\beta}{2} k^2\right) \frac{\partial}{\partial k} \sum_{l=0}^\infty (2l+1) \eta_l^{(1)}(k),$$

$$-B_{eaa} = (2\pi)^{1/2} \beta^{3/2} \int d\mathbf{R} \exp[-\beta v_{aa}(R)] \int_0^\infty dk \exp\left(-\frac{\beta}{2} k^2\right) \quad (4.8)$$

$$\times \frac{\partial}{\partial k} \left[\sum_\gamma \eta_\gamma^{(2)}(k, R) - 2 \sum_{l=0}^\infty (2l+1) \eta_l^{(1)}(k) \right] - \frac{1}{2} B_{ea}^2.$$

The second virial coefficients (the classical B_{ia} for the polarization interaction and the quantum B_{ea} for scattering by a center with a short-range potential) have been calculated by Likal'ter^[21]; the second and third classical virial coefficients were recently discussed in a paper by Vetchin et al.^[22]. For an arbitrary potential, the calculation of the phases η_γ is extremely laborious even in the simplest case of scattering at two centers. However, in the approximation of short-range stationary centers (s-scattering of slow electrons), the calculation of η_γ reduces to the solution of an algebraic equation of degree N ^[20]*

$$\left| \left(\frac{\sin kR_{ij}}{R_{ij}} + \text{tg } \eta \frac{\cos kR_{ij}}{R_{ij}} \right) (1 - \delta_{ij}) + \left(\frac{\text{tg } \eta}{a_i} + k \right) \delta_{ij} \right| = 0. \quad (4.9)$$

Here a_i is the scattering amplitude at the i -th center; R_{ij} is the distance between the scattering centers i and j . In particular, for scattering at one and two identical centers,

$$\eta_0^{(1)} = -\arctg ak, \quad \sum_{\gamma=1,2} \eta_\gamma^{(2)} - 2\eta_0^{(1)} \quad (4.10)$$

$$= \arctg \frac{(1 - a^2 k^2) \sin 2kR - 2ak \cos 2kR}{(1 + a^2 k^2)^2 R^2 / a^2 - 2ak \sin 2kR - (1 - a^2 k^2) \cos 2kR}.$$

An interesting feature of (4.9)–(4.10) is the presence of resonances arising as a consequence of interference of electron waves during simultaneous scattering at several centers, as in diffractive scattering at one

center. In a low-temperature plasma, therefore, the results of the classical and quantum calculations of the electron-atom virial coefficients can differ sharply. With allowance for the polarizability α of the scattering centers, we have for the partial phase shifts η_l [23]

$$k \operatorname{ctg} \eta_0 = -\frac{1}{a} + \frac{\pi \alpha k}{3a^2} + \frac{4}{3} \frac{\alpha k^2}{a} \ln(1.23k\sqrt{\alpha}) + \frac{1}{2} \left[r_0 + \frac{2\pi}{3} \sqrt{\alpha} - \frac{2\pi}{3} \frac{\alpha^2}{a^2} - \frac{2\pi^2}{9} \frac{\alpha^2}{a^3} \right] k^2 + \dots, \quad (4.11)$$

$$\operatorname{tg} \eta_l = \frac{\pi \alpha k^2}{(2l+1)(2l+3)(2l-1)}, \quad l \geq 1,$$

As an example, we shall consider the calculation of Be_a in a low-temperature mercury plasma⁵⁾. According to Füchtbauer and Gössler [24], $a = 1.73$; the effective range r_0 is unknown, but since the other terms in the square brackets in (4.11) are of the order of 10^2 , we have put $r_0 = 0$. At temperatures $T = (1.5-2) \times 10^3$ K, the principal contribution to the integral (4.8) is made by k for which the partial phase shifts from (4.11) do not exceed 0.15–0.20, and therefore the results of the work of O'Malley et al. [23] can apparently still be used. A semi-classical treatment of the scattering of an electron by a polarization potential is applicable (cf., e.g., [21]) when $T \geq 16 \text{ Ry}/\alpha \sim 10 \text{ eV}$, so that, as we should expect, the calculated virial coefficients $Be_a = 3.94 \times 10^{-22} \text{ cm}^3$ at $T = 1600 \text{ K}$ and $Be_a = 3.88 \times 10^{-22} \text{ cm}^3$ at $T = 1700 \text{ K}$ differ considerably from the classical coefficients [22]. In the calculation of Be_a , we assumed that there is no bound state of Hg^- [25].

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* $\operatorname{tg} = \tan$.

¹⁾An analogous result in the calculation of the correlation corrections to the Holtzmark distribution for micro-fields in a plasma was obtained by another method in [5] (cf. also [6]).

²⁾For a random distribution of centers ($g_{12} = 1$), the eikonal approximation (2.13)–(2.15) and the corresponding Green function have been obtained recently [7,8] by means of a diagram technique (cf. also [9]); some specific (unsubstantiated) models of eikonal scattering have been considered by Jones [10].

³⁾In a weakly ionized dense plasma the transition at the critical point of the system of neutral particles can be regarded as isomorphous with respect to perturbations due to the electrons.

⁴⁾In the case of spherically symmetric scattering at one center, the appropriate formula was first obtained by Beth and Uhlenbeck [19].

⁵⁾The author thanks M. Berlin for help in the calculations.

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