Kinetic fluctuations in a partially ionized plasma and in chemically reacting gases

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A kinetic theory is developed of the fluctuations in a partially ionized plasma and in chemically reacting gas systems. It is a generalization of the previously developed kinetic theory of fluctuations in simple gases and in a fully ionized plasma. The obtained general relations are used to calculate the intensities of the Langevin sources in the equations for the concentrations of the electrons, ions, and atoms in a partially ionized plasma with a uniform distribution of the particles.

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A large series of recent papers[1-6] is devoted to fluctuations in chemically reacting systems. So great an interest is brought about by a large number of problems: light scattering,[7,8] analogy with phase transitions,[9,10] study of the kinetic properties of chemically reacting systems,[11] and noise in semiconductors.[12]

The irreversible-thermodynamics method, the method of the master equation for the distribution function of the particle-number density, and the Langevin description of hydrodynamic fluctuations, which are used in[1-10], are phenomenological to one degree or another.

In this paper we develop a kinetic theory of fluctuations in a partially ionized plasma and in chemically reacting gas systems. The results are a generalization of the previously developed kinetic theory of fluctuations in a simple gas in a fully ionized plasma.[13,15-18]

Just as in the construction of a kinetic theory of gases in a fully ionized plasma ([13], Chaps, 4 and 11), we introduce for the partially ionized plasma an operator particle-pair density matrix $\tilde{\rho}_{\alpha\beta}(\mathrm{P},\mathrm{P}',t)$ smoothed out over a physically infinitesimally small volume. We confine ourselves here to fluctuations with characteristic order times and a relaxation time defined by collision integrals. In this approximation the matrix $\tilde{\rho}_{\alpha\beta}(\mathrm{P},\mathrm{P}',t)$ can be regarded as diagonal:

$$\tilde{\rho}_{\alpha\beta}(\mathbf{P},\mathbf{P}',t)=\delta_{\alpha\beta}\delta(\mathbf{P}-\mathbf{P}')\frac{(2\pi\hbar)^3}{V}\tilde{f}_\alpha(\mathbf{P},t).$$

For a partially ionized plasma, the discrete values of the parameter α correspond to bound states of the particle pairs, namely atoms, while the continuous values correspond to free states, namely pairs of electrons and ions; for example, for a diatomic gas discrete values of α correspond to bound states of the atoms (diatomic molecules), while continuous values correspond to free states of the atom pair (dissociated molecules).

In the polarization approximation, in a partially ionized plasma ([13], § 80), the Born approximation for atom interactions, supplemented by allowance for the plasma polarization—the equation for $\tilde{f}_\alpha(\mathrm{P},t)$ takes the form

$$\begin{aligned}\frac{\partial}{\partial t}\tilde{f}_\alpha(\mathbf{P},t)&=\frac{4nV}{(2\pi\hbar)^3}\sum_{\beta\gamma\eta}\int d\omega\,d\mathbf{k}\,d\mathbf{P}'d\mathbf{P}_1d\mathbf{P}_1'\\&\times\frac{|\Pi_{\alpha\beta}(\mathbf{k})|^2|\Pi_{\gamma\eta}(\mathbf{k})|^2}{k^4|\varepsilon(\omega,\mathbf{k})|^2}\cdot\delta(\hbar\mathbf{k}-(\mathbf{P}-\mathbf{P}'))\delta(\hbar\mathbf{k}-(\mathbf{P}_1-\mathbf{P}_1'))\\&\times\delta(\hbar\omega-(E_\alpha+E_{\mathbf{P}}-E_\beta-E_{\mathbf{P}'}))\cdot\delta(\hbar\omega-(E_\gamma+E_{\mathbf{P}_1}-E_\eta-E_{\mathbf{P}_1'}))\\&\times(\tilde{f}_\beta(\mathbf{P}',t)\tilde{f}_\gamma(\mathbf{P}_1,t)-\tilde{f}_\alpha(\mathbf{P},t)\tilde{f}_\eta(\mathbf{P}_1',t))\equiv\hat{I}_\alpha(\mathbf{P})\tilde{f}_\alpha(\mathbf{P},t).\end{aligned}\tag{1}$$

We have used here the following notation for the matrix element

$$\Pi_{\alpha\beta}(\mathbf{k})=\int\Big[e_e\exp\Big(i\frac{m_i}{m_e+m_i}\mathbf{kr}\Big)+e_i\exp\Big(-i\frac{m_e}{m_e+m_i}\mathbf{kr}\Big)\Big]\psi_\alpha(\mathbf{r})\psi_\beta^*(\mathbf{r})\,d\mathbf{r}$$

($\psi_\alpha(r)$ is an eigenfunction of the Hamiltonian operator of the particle pair) and the following definition of the dielectric constant

$$\varepsilon(\omega,\mathbf{k})=1+\frac{4nV}{(2\pi\hbar)^3k^2}\sum_{\gamma\beta}\int d\mathbf{P}'d\mathbf{P}''\delta(\hbar\mathbf{k}-(\mathbf{P}'-\mathbf{P}''))\times|\Pi_{\gamma\beta}(\mathbf{k})|^2\frac{\tilde{f}_\beta(\mathbf{P}',t)-\tilde{f}_\gamma(\mathbf{P}'',t)}{\hbar(\omega+i\Delta)-(E_\beta+E_{\mathbf{P}'}-E_\gamma-E_{\mathbf{P}''})}\tag{2}$$

($n=N/V$, where N is the total number of atoms at zero degree of ionization). The summation with respect to the indices β,γ,η in (1) and (2) is carried out both over the discrete parts of the spectrum (for the bound states) and over the continuous ones (for free charged particles), with

$$\sum_\beta\to\sum_m+\int\frac{V}{(2\pi\hbar)^3}d\mathbf{p}'.$$

The collision integrals in (1) takes into account the dynamic polarization. This leads to an additional dependence on the distribution function. Just as before ([13], § 47), we confine ourselves to the contribution of the averaged dynamic polarization, replacing $1/|\epsilon(\omega,k)|^2$ with the value averaged over ω.

Equation (1) describes the large-scale fluctuations, since the contribution of the small-scale correlations has already been taken into account in the derivation of Eq. (1) itself.

On the basis of basis of (1), just as before (see [13], §§ 22 and 62), we can obtain equations for the moments

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of the random functions $\delta\tilde{f}_\alpha(\mathbf{P}, t)$:

$$\left(\frac{\partial}{\partial t}+\delta\hat{I}_\alpha(\mathbf{P})\right)\langle\delta\tilde{f}_\alpha(\mathbf{P},t)\delta\tilde{f}_\beta(\mathbf{P}',t')\rangle=0, \tag{3}$$

$$\left(\frac{\partial}{\partial t}+\delta\hat{I}_\alpha(\mathbf{P})+\delta\hat{I}_\beta(\mathbf{P}')\right)\langle\delta\tilde{f}_\alpha(\mathbf{P},t)\delta\tilde{f}_\beta(\mathbf{P}',t)\rangle=A_{\alpha\beta}(\mathbf{P},\mathbf{P}',t)$$

$$=\frac{(2\pi\hbar)^3}{NV}[\delta_{\alpha\beta}\delta(\mathbf{P}-\mathbf{P}')\hat{I}_\alpha(\mathbf{P})f_\alpha(\mathbf{P},t)+I_{\alpha\beta}(\mathbf{P},\mathbf{P}',t)$$

$$+(\delta\hat{I}_\alpha(\mathbf{P})+\delta\hat{I}_\beta(\mathbf{P}'))\delta_{\alpha\beta}\delta(\mathbf{P}-\mathbf{P}')f_\alpha(\mathbf{P},t)]. \tag{4}$$

In (3) and (4) $\langle\cdots\rangle$ stands for the operation of averaging over the ensemble, $\delta\hat{I}_\alpha(\mathbf{P})$ is the linearized collision operator

$$\delta\hat{I}_\alpha(\mathbf{P})\delta f_\alpha(\mathbf{P},t)=-\frac{4nV}{(2\pi\hbar)^3}\sum_{\beta\gamma\eta}\int d\omega\, d\mathbf{k}\, d\mathbf{P}'d\mathbf{P}_1d\mathbf{P}_1'$$

$$\times\frac{|\Pi_{\alpha\beta}(\mathbf{k})|^2|\Pi_{\gamma\eta}(\mathbf{k})|^2}{k^4|\varepsilon(\omega,\mathbf{k})|^2}\delta(\hbar k-(\mathbf{P}-\mathbf{P}'))\delta(\hbar k-(\mathbf{P}_1-\mathbf{P}_1'))$$

$$\times\delta(\hbar\omega-(E_\alpha+E_\mathbf{P}-E_\beta-E_{\mathbf{P}'}))\delta(\hbar\omega-(E_\gamma+E_{\mathbf{P}_1}-E_\eta-E_{\mathbf{P}_1'}))$$

$$\times(f_\beta(\mathbf{P}',t)\delta f_\gamma(\mathbf{P}_1,t)+\delta f_\beta(\mathbf{P}',t)f_\gamma(\mathbf{P}_1t)$$

$$-f_\alpha(\mathbf{P},t)\delta f_\eta(\mathbf{P}_1',t)-\delta f_\alpha(\mathbf{P},t)f_\eta(\mathbf{P}_1',t)), \tag{5}$$

and $I_{\alpha\beta}(\mathbf{P}, \mathbf{P}', t)$ is defined as

$$I_{\alpha\beta}(\mathbf{P},\mathbf{P}',t)=\frac{4nV}{(2\pi\hbar)^3}\sum_{\gamma\eta}\int d\omega\, d\mathbf{k}\, d\mathbf{P}_1d\mathbf{P}_1'\frac{|\Pi_{\alpha\gamma}(\mathbf{k})|^2|\Pi_{\eta\beta}(\mathbf{k})|^2}{k^4|\varepsilon(\omega,\mathbf{k})|^2}$$

$$\times\delta(\hbar\mathbf{k}-(\mathbf{P}-\mathbf{P}_1))\delta(\hbar\mathbf{k}-(\mathbf{P}_1'-\mathbf{P}'))\delta(\hbar\omega-(E_\alpha+E_\mathbf{P}-E_\gamma-E_{\mathbf{P}_1}))$$

$$\times\delta(\hbar\omega-(E_\eta+E_{\mathbf{P}_1'}-E_\beta-E_{\mathbf{P}'}))(f_\gamma(\mathbf{P}_1,t)f_\eta(\mathbf{P}_1',t)-f_\alpha(\mathbf{P},t)f_\beta(\mathbf{P}',t)). \tag{6}$$

An analogous expression for a simple gas was dubbed[18] "unintegrated collision integral."

Equations (3) and (4) must be supplemented with the equation for the particle-pair distribution function $\langle\tilde{f}_\alpha(\mathbf{P}, t)\rangle = f_\alpha(\mathbf{P}, t)$:

$$\frac{\partial}{\partial t}f_\alpha(\mathbf{P},t)=\hat{I}_\alpha(\mathbf{P})f_\alpha(\mathbf{P},t). \tag{7}$$

Instead of the system of equations (3) and (4) we can use for the single-time and two-time correlations the corresponding Langevin equation for the fluctuations $\delta\tilde{f}_\alpha(\mathbf{P}, t)$:

$$\left(\frac{\partial}{\partial t}+\delta\hat{I}_\alpha(\mathbf{P})\right)\delta f_\alpha(\mathbf{P},t)=y_\alpha(\mathbf{P},t), \tag{8}$$

in which $y_\alpha(\mathbf{P}, t)$ is a Langevin δ-correlated source whose intensity is determined by the right-hand side of Eq. (3):

$$\langle y_\alpha(\mathbf{P},\ t)y_\beta(\mathbf{P}',\ t')\rangle=\delta(t-t')A_{\alpha\beta}(\mathbf{P},\ \mathbf{P}',\ t). \tag{9}$$

Substituting (1), (5), and (6) in (4) and (9), we write down the intensity of the Langevin source in general form

$$\langle y_\alpha(\mathbf{P},t)y_\beta(\mathbf{P}',t')\rangle=\frac{4}{V}\delta(t-t')\sum_{\gamma\eta}\int\frac{d\omega\, d\mathbf{k}\, d\mathbf{P}_1d\mathbf{P}_1'}{k^4|\varepsilon(\omega,\mathbf{k})|^2}\Big\{\delta_{\alpha\beta}\delta(\mathbf{P}-\mathbf{P}')$$

$$\times\sum_\xi d\mathbf{P}''|\Pi_{\alpha\gamma}(\mathbf{k})|^2|\Pi_{\eta\xi}(\mathbf{k})|^2\delta(\hbar\mathbf{k}-(\mathbf{P}-\mathbf{P}''))\delta(\hbar\mathbf{k}-(\mathbf{P}_1-\mathbf{P}_1'))$$

$$\times\delta(\hbar\omega-(E_\alpha+E_\mathbf{P}-E_\gamma-E_{\mathbf{P}''}))\delta(\hbar\omega-(E_\eta+E_{\mathbf{P}_1}-E_\xi-E_{\mathbf{P}_1'}))$$

$$\times(f_\gamma(\mathbf{P}'',t)f_\eta(\mathbf{P}_1,t)+f_\alpha(\mathbf{P},t)f_\xi(\mathbf{P}_1',t))-[|\Pi_{\alpha\beta}(\mathbf{k})|^2|\Pi_{\gamma\eta}(\mathbf{k})|^2$$

$$\times\delta(\hbar\mathbf{k}-(\mathbf{P}-\mathbf{P}'))\delta(\hbar\mathbf{k}-(\mathbf{P}_1-\mathbf{P}_1'))\delta(\hbar\omega-(E_\alpha+E_\mathbf{P}-E_\beta-E_{\mathbf{P}'}))$$

$$\times\delta(\hbar\omega-(E_\gamma+E_{\mathbf{P}_1}-E_\xi-E_{\mathbf{P}_1'}))(f_\beta(\mathbf{P}',t)f_\gamma(\mathbf{P}_1,t)+f_\alpha(\mathbf{P},t)f_\eta(\mathbf{P}_1',t))$$

$$+|\Pi_{\alpha\gamma}(\mathbf{k})|^2|\Pi_{\beta\eta}(\mathbf{k})|^2\delta(\hbar\mathbf{k}-(\mathbf{P}-\mathbf{P}_1))\delta(\hbar\omega-(E_\alpha+E_\mathbf{P}-E_\gamma-E_{\mathbf{P}_1}))$$

$$\times(\delta(\hbar\mathbf{k}-(\mathbf{P}'-\mathbf{P}_1'))\delta(\hbar\omega-(E_\beta+E_{\mathbf{P}'}-E_\eta-E_{\mathbf{P}_1'}))$$

$$\times(f_\beta(\mathbf{P}',t)f_\gamma(\mathbf{P}_1,t)+f_\alpha(\mathbf{P},t)f_\eta(\mathbf{P}_1',t))-\delta(\hbar\mathbf{k}+(\mathbf{P}'-\mathbf{P}_1'))$$

$$\times\delta(\hbar\omega+(E_\beta+E_{\mathbf{P}'}-E_\eta-E_{\mathbf{P}_1'}))(f_\alpha(\mathbf{P},t)f_\beta(\mathbf{P}',t)+f_\gamma(\mathbf{P}_1,t)f_\eta(\mathbf{P}_1',t)))]\Big\} \tag{10}$$

This expression takes into account contributions from both the discrete and the continuous spectra. It is possible to separate from it, in particular, the correlations, obtained in[12], of the electron-electron fluctuations with allowance for the scattering of the electrons by impurities in semiconductors. We multiply expression (10) by $\varphi_\alpha(\mathbf{P})\psi_\beta(\mathbf{P}')$, integrate with respect to $\mathbf{P}$ and $\mathbf{P}'$, and sum over α and β. After symmetrization we obtain

$$\left(\frac{V}{2\pi\hbar}\right)^6\sum_{\alpha\beta}\int\langle y_\alpha(\mathbf{P},t)y_\beta(\mathbf{P}',t')\rangle\varphi_\alpha(\mathbf{P})\psi_\beta(\mathbf{P}')d\mathbf{P}\,d\mathbf{P}'$$

$$=\frac{2}{V}\delta(t-t')\sum_{\alpha\beta\gamma\eta}\int\frac{|\Pi_{\alpha\eta}(\mathbf{k})|^2|\Pi_{\beta\gamma}(\mathbf{k})|^2}{k^4|\varepsilon(\omega,\mathbf{k})|^2}\delta(\hbar\mathbf{k}-(\mathbf{P}-\mathbf{P}_1))$$

$$\times\delta(\mathbf{P}+\mathbf{P}'-\mathbf{P}_1-\mathbf{P}_1')\delta(\hbar\omega-(E_\alpha+E_\mathbf{P}-E_\eta-E_{\mathbf{P}_1'}))$$

$$\times\delta(E_\alpha+E_\beta+E_\mathbf{P}+E_{\mathbf{P}'}-E_\gamma-E_\eta-E_{\mathbf{P}_1}-E_{\mathbf{P}_1'})f_\alpha(\mathbf{P},t)f_\beta(\mathbf{P}',t)$$

$$\times[\varphi_\alpha(\mathbf{P})+\varphi_\beta(\mathbf{P}')-\varphi_\gamma(\mathbf{P}_1)-\varphi_\eta(\mathbf{P}_1')][\psi_\alpha(\mathbf{P})+\psi_\beta(\mathbf{P}')-\psi_\gamma(\mathbf{P}_1)$$

$$-\psi_\eta(\mathbf{P}_1')]\left(\frac{V}{2\pi\hbar}\right)^6d\mathbf{P}\,d\mathbf{P}_1d\mathbf{P}'d\mathbf{P}_1'd\mathbf{k}\,d\omega. \tag{11}$$

This leads to a property analogous to the laws of conservation of the total number of particle pairs, of the momentum, and of the energy, at $\varphi_\alpha(\mathbf{P}), \psi_\alpha(\mathbf{P}) = 1, \mathbf{P}, E_\alpha + E_\mathbf{P}$

$$\left(\frac{V}{2\pi\hbar}\right)^6\sum_{\alpha\beta}\int\varphi_\alpha(\mathbf{P})\psi_\beta(\mathbf{P}')\langle y_\alpha(\mathbf{P},t)y_\beta(\mathbf{P}',t')\rangle d\mathbf{P}\,d\mathbf{P}'=0. \tag{12}$$

We use the obtained general formulas to calculate the fluctuations of the concentrations in a spatially homogeneous partially ionized plasma. In the derivation of the equations for the particle concentrations and calculations of the Langevin sources in them, we assume that Maxwell-Boltzmann distributions have already been established for the electrons, ions, and atoms, but no chemical equilibrium has set in as yet, and consequently the concentrations n_e, n_i and n_{ei} do not satisfy the ionization-equilibrium condition

$$\frac{n_en_i}{n_{ei}}=\left(\frac{\mu\varkappa T}{2\pi\hbar^2}\right)^{3/2}\frac{1}{Z}$$

where Z is the partition function and μ is the reduced mass. To obtain, for example, an equation for the concentration n_a $(a=e, i)$ of the charged particles, we multiply (1) by $(nV/(2\pi\hbar))^3$ and, putting $\alpha=\mathbf{p}$, integrate with respect to $\mathbf{p}$ and $\mathbf{P}$. It is more convenient here to change over in the distribution functions of the free-particle pairs from the variables $\mathbf{p}$ and $\mathbf{P}$ to the variables $\mathbf{p}_e$ and $\mathbf{p}_i$:

$$\mathbf{P}=\mathbf{p}_e+\mathbf{p}_i, \quad \mathbf{p}=\frac{m_i\mathbf{p}_e-m_e\mathbf{p}_i}{M}$$

$$\mathbf{p}_e=\frac{\mu}{m_i}\mathbf{P}+\mathbf{p}, \quad \mathbf{p}_i=\frac{\mu}{m_e}\mathbf{P}-\mathbf{p},$$

where

$$M=m_e+m_i, \quad \mu=m_e m_i/(m_e+m_i).$$

With this change of variables, the distribution function $f_\mathbf{P}(\mathbf{P},t)\to f(\mathbf{P}_e,\mathbf{P}_i,t)$ determines the number of particle pairs in which the particles are separated by distances large enough to regard them as free. In these cases, where necessary, we use the additional correlation-weakening condition

$$Nf(\mathbf{p}_e,\mathbf{p}_i,t)=Nf(\mathbf{p}_e,t)Nf(\mathbf{p}_i,t),$$

i.e., the number of pairs in which the particles with momenta $\mathbf{p}_e$ and $\mathbf{p}_i$ are so far apart that they can be regarded as free is replaced by the product of the average numbers of the free particles having the same momentum values. Thus,

$$\begin{aligned}
\frac{\partial}{\partial t}n_a=&\frac{(2nV)^2}{(2\pi\hbar)^9}V\sum_n\int d\omega\,d\mathbf{k}\,d\mathbf{p}\,d\mathbf{P}\,d\mathbf{P}'\frac{|\Pi_{\mathbf{p}n}(\mathbf{k})|^2}{k^4|\varepsilon(\omega,\mathbf{k})|^2}\\
&\times\delta(\hbar\mathbf{k}-(\mathbf{P}-\mathbf{P}'))\delta\left(\hbar\omega-\left(\frac{p^2}{2\mu}+\frac{P^2}{2M}-E_n-E_{\mathbf{P}'}\right)\right)\\
&\times\Big\{\sum_{ml}\int d\mathbf{P}_1 d\mathbf{P}_1'|\Pi_{ml}(\mathbf{k})|^2\delta(\hbar\mathbf{k}-(\mathbf{P}_1-\mathbf{P}_1'))\\
&\times\delta(\hbar\omega-(E_m+E_{\mathbf{P}_1}-E_l-E_{\mathbf{P}_1'}))(f_n(\mathbf{P}',t)f_m(\mathbf{P}_1,t)\\
&-f_l(\mathbf{P}_1',t)f(\mathbf{p}_e,\mathbf{p}_i,t))+\frac{V}{(2\pi\hbar)^3}\sum_m\int d\mathbf{P}_1 d\mathbf{P}_1' d\mathbf{p}_1'|\Pi_{m\mathbf{p}_1'}(\mathbf{k})|^2\\
&\times\delta(\hbar\mathbf{k}-(\mathbf{P}_1-\mathbf{P}_1'))\delta\left(\hbar\omega-\left(E_m+E_{\mathbf{P}_1}-\frac{p_1'^2}{2\mu}-\frac{P_1'^2}{2M}\right)\right)\\
&\times(f_n(\mathbf{P}',t)f_m(\mathbf{P}_1,t)-f(\mathbf{p}_e,\mathbf{p}_i,t)f(\mathbf{p}_{1e}',\mathbf{p}_{1i}',t))+\\
&+\frac{V}{(2\pi\hbar)^3}\sum_l\int d\mathbf{P}_1' d\mathbf{P}_1 d\mathbf{p}_1|\Pi_{\mathbf{p}_1 l}(\mathbf{k})|^2\delta(\hbar k-(\mathbf{P}_1-\mathbf{P}_1'))\\
&\times\delta\left(\hbar\omega-\left(\frac{p_1^2}{2\mu}+\frac{P_1^2}{2M}-E_l-E_{\mathbf{P}_1'}\right)\right)(f_n(\mathbf{P}',t)f(\mathbf{p}_{1e},\mathbf{p}_{1i},t)\\
&-f_l(\mathbf{P}_1',t)f(\mathbf{p}_e,\mathbf{p}_i,t))+\frac{V^2}{(2\pi\hbar)^6}\int d\mathbf{P}_1 d\mathbf{P}_1' d\mathbf{p}_1 d\mathbf{p}_1'|\Pi_{\mathbf{p}_1\mathbf{p}_1'}(\mathbf{k})|^2\\
&\times\delta(\hbar\mathbf{k}-(\mathbf{P}_1-\mathbf{P}_1'))\delta\left(\hbar\omega-\left(\frac{p_1^2}{2\mu}+\frac{P_1^2}{2M}-\frac{p_1'^2}{2\mu}-\frac{P_1'^2}{2M}\right)\right)\\
&\times(f_n(\mathbf{P}',t)f(\mathbf{p}_{1e},\mathbf{p}_{1i},t)-f(\mathbf{p}_{1e}',\mathbf{p}_{1i}',t)f(\mathbf{p}_e,\mathbf{p}_i,t))\Big\}.
\end{aligned}\tag{13}$$

We assume that the distribution functions in (13) are at equilibrium and take into account the equality of the electron and ion densities: $n_e=n_i$. In this case we can represent (13) in the form

$$\begin{aligned}
\frac{\partial}{\partial t}n_a=&(\alpha n_a n_{ei}-\beta n_a^3)+(\alpha_1 n_{ei}^2-\beta_1 n_a^2 n_{ei})\\
&+(\alpha_2 n_{ei}^2-\beta_2 n_a^4)+(\alpha_3 n_{ei}n_a^2-\beta_3 n_{ei}n_a^2),
\end{aligned}\tag{14}$$

where α is the impact-ionization coefficient, β is the triple recombination coefficient, α_1 is the ionization coefficient for collision of two atoms, β_1 is the recombination coefficient for the triple collision of an electron, ion, and atom, β_2 is the recombination coefficient of four charged particles, α_2 is the corresponding ionization coefficient, and α_3 and β_3 are the coefficients of the exchange processes.

We present by way of example the expressions for the coefficients α and β[14]:

$$\begin{aligned}
\alpha=&\frac{4V}{(2\pi\hbar)^3}\sum_c e_c^2\sum_m\int d\mathbf{p}'d\mathbf{P}'d\mathbf{P}''d\mathbf{p}_c'd\mathbf{p}_c''d\omega\,d\mathbf{k}\\
&\times\frac{|\Pi_{p'm}(\mathbf{k})|^2}{k^4|\varepsilon(\omega,\mathbf{k})|^2}\delta(\hbar\mathbf{k}-(\mathbf{P}'-\mathbf{P}''))\delta(\mathbf{P}'+\mathbf{p}_c''-\mathbf{P}''-\mathbf{p}_c')\\
&\times\delta\left(\hbar\omega-\left(\frac{p'^2}{2\mu}+\frac{P'^2}{2M}-E_m-\frac{P''^2}{2M}\right)\right)\\
&\times\frac{\delta(p'^2/2\mu+P'^2/2M+p_c''^2/2m_c-E_m-P''^2/2M-p_c'^2/2m_c)}{[2\pi(m_cM)^{1/2}\varkappa T]^3 Z}\\
&\times\exp\left[-\left(E_m+\frac{P''^2}{2M}+\frac{p_c^2}{2m_c}\right)\Big/\varkappa T\right],
\end{aligned}\tag{15}$$

$$\beta=(2\pi\hbar^2/\mu\varkappa T)^{3/2}Z\alpha.\tag{16}$$

Since $n_\alpha+n_{ei}=n=\text{const}$, we have $\partial n_{ei}/\partial t=-\partial n_\alpha/\partial t$.

Let us obtain, in the same approximation, an expression for the spectral density of a Langevin source in the equation for the fluctuations of the density of the number of charged particles:

$$\begin{aligned}
(\xi_a\xi_a)_\Omega=&\frac{n^2V^4}{(2\pi\hbar)^{12}}\int(y_\mathbf{p}(\mathbf{P})y_{\mathbf{p}'}(\mathbf{P}'))_\Omega d\mathbf{p}\,d\mathbf{P}\,d\mathbf{p}'d\mathbf{P}'\\
=&\frac{(2nV)^2}{(2\pi\hbar)^9}\sum_n\int d\omega\,d\mathbf{k}\,d\mathbf{p}\,d\mathbf{P}\,d\mathbf{P}'\frac{|\Pi_{n\mathbf{p}}(\mathbf{k})|^2}{k^4|\varepsilon(\omega,\mathbf{k})|^2}\\
&\times\delta(\hbar\mathbf{k}-(\mathbf{P}-\mathbf{P}'))\delta\left(\hbar\omega-\left(\frac{p^2}{2\mu}+\frac{P^2}{2M}-E_n-E_{\mathbf{P}'}\right)\right)\\
&\times\Big\{\sum_{ml}\int d\mathbf{P}'d\mathbf{P}_1'|\Pi_{ml}(\mathbf{k})|^2\delta(\hbar\mathbf{k}-(\mathbf{P}_1-\mathbf{P}_1'))\\
&\times\delta(\hbar\omega-(E_m+E_{\mathbf{P}_1}-E_l-E_{\mathbf{P}_1'}))(f_m(\mathbf{P}_1,t)f_n(\mathbf{P}',t)\\
&+f_l(\mathbf{P}_1',t)f(\mathbf{p}_e,\mathbf{p}_i,t))+\frac{2V}{(2\pi\hbar)^3}\sum_m\int d\mathbf{P}_1 d\mathbf{P}_1' d\mathbf{p}_1'|\Pi_{m\mathbf{p}_1'}(\mathbf{k})|^2\\
&\times\delta(\hbar\mathbf{k}-(\mathbf{P}_1-\mathbf{P}_1'))\delta\left(\hbar\omega-\left(E_m+E_{\mathbf{P}_1}-\frac{p_1'^2}{2\mu}-\frac{P_1'^2}{2M}\right)\right)\\
&\times(f_m(\mathbf{P}_1,t)f_n(\mathbf{P}',t)+f(\mathbf{p}_{1e}',\mathbf{p}_{1i}',t)f(\mathbf{p}_e,\mathbf{p}_i,t))+\frac{V^2}{(2\pi\hbar)^6}\int d\mathbf{P}_1 d\mathbf{P}_1' d\mathbf{p}_1 d\mathbf{p}_1'\\
&\times\Big[e_e^2\delta(\mathbf{p}_{1i}-\mathbf{p}_{1i}')\delta(\hbar\mathbf{k}-(\mathbf{p}_{1e}-\mathbf{p}_{1e}'))\delta\left(\hbar\omega-\left(\frac{p_{1e}^2}{2m_e}-\frac{p_{1e}'^2}{2m_e}\right)\right)\\
&+e_i^2\delta(\mathbf{p}_{1e}-\mathbf{p}_{1e}')\delta(\hbar\mathbf{k}-(\mathbf{p}_{1i}-\mathbf{p}_{1i}'))\delta\left(\hbar\omega-\left(\frac{p_{1i}^2}{2m_i}-\frac{p_{1i}'^2}{2m_i}\right)\right)\Big]\\
&\times(f_n(\mathbf{P}',t)f(\mathbf{p}_{1e},\mathbf{p}_{1i},t)+f(\mathbf{p}_e,\mathbf{p}_i,t)f(\mathbf{p}_{1e}',\mathbf{p}_{1i}',t)\\
=&\frac{1}{V}(\alpha n_a n_{ei}+\beta n_a^3+\alpha_1 n_{ei}^2+\beta_1 n_{ei}n_a^2+2\alpha_2 n_{ei}^2+2\beta_2 n_a^4).
\end{aligned}\tag{17}$$

Since $n_\alpha+n_{ei}=\text{const}$, a similar expression is obtained also for the source in the equation for the fluctuation of the density of the number of neutral particles:

$$(\xi_{ei}\xi_{ei})_\Omega=\frac{n^2V^2}{(2\pi\hbar)^6}\sum_{mn}\int(y_n(\mathbf{P})y_m(\mathbf{P}'))_\Omega d\mathbf{P}\,d\mathbf{P}',$$

and when taken with a minus sign this is also the result for the cross correlation. Thus,

$$(\xi_a\xi_{ei})_\Omega+(\xi_a\xi_a)_\Omega+(\xi_{ei}\xi_a)_\Omega+(\xi_{ei}\xi_{ei})_\Omega=0,$$

which corresponds to property (12) at $\varphi=1$ and $\psi=1$.

Let us calculate the variance of the fluctuation of the particle number in the state of chemical equilibrium. The equation for the fluctuation of the electron (ion) concentration is then

$$\frac{\partial}{\partial t}\delta n_a+\lambda_a\delta n_a=\xi_a,\quad \delta n_a=-\delta n_{ei}, \tag{18}$$

where

$$\lambda_a=\left(1+2\frac{n_{ei}}{n_a}\right)(\alpha n_a+\alpha_1 n_{ei}+2\alpha_2 n_{ei}). \tag{19}$$

It follows from (17)–(19) that the single-time moment $\langle\delta n_\alpha^2(t)\rangle$, which is equal to

$$\langle\delta n_a^2(t)\rangle=\frac{(\xi_a\xi_a)_\Omega}{2\lambda_a}=\frac{1}{V}\frac{n_{ei}n_a}{2n_{ei}+n_a}$$

and the variance of the particle-number fluctuation,

$$\langle\delta N_a^2\rangle=\langle\delta N_{ei}^2\rangle=N_a\frac{N-N_a}{2N-N_a}, \tag{20}$$

do not depend on the generation and recombination coefficients. It follows from this formula that in two limiting cases (fully ionized plasma, when $N_a=N$, and zero degree of ionization, i.e., $N_a=0$) there are no concentration fluctuations. This result is the consequence of the fact that we are considering a spatially homogeneous case under the additional condition $N_a+N_{ei}=N$ is given. As a result, formula (20) describes only fluctuations due to chemical reactions—the change of the number of particles in the components.

In the spatially inhomogeneous case it is necessary to take into account the diffusion of the particles in the equation for the concentration. This produces, naturally, additional terms in the Langevin sources. Since the intensity of this source is

$$2D\frac{\partial^2}{\partial \mathbf{r}\,\partial \mathbf{r}'}n(\mathbf{r},t)\delta(\mathbf{r}-\mathbf{r}'),$$

then, as previously shown,[5] the single-time correlation of the particle-number density is δ-correlated in the coordinates. The importance of taking diffusion processes into account when fluctuations of the concentrations are considered in chemically reacting systems has been pointed out, in particular, in a recent paper.[6]

We note, finally, that the reported results describe fluctuations due to the atomic structure of the considered systems. For states far from equilibrium, however, an additional term $\tilde{I}_\alpha(\mathbf{P})$ appears in the kinetic equation and is determined by the contribution of the large-scale fluctuations ([13], §§ 22 and 62). A corresponding additional term $A_{\alpha\beta}(\mathbf{P},\mathbf{P}',t)$ appears also in the right-hand side of (4). The analysis of examples of this kind is of independent interest.

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