Chapter 3
Theory of the Fluctuating Electromagnetic Field

There are two approaches for studying the fluctuating electromagnetic field. In the first approach, proposed by Rytov [5–7], it is assumed that the fluctuating electromagnetic field is created by the thermal and quantum fluctuations of current density $\mathbf{j}^f$ inside the medium. The average $\langle \mathbf{j}^f \rangle = 0$, and the correlation function $\langle \mathbf{j}^f \mathbf{j}^f \rangle \neq 0$ is expressed through the dielectric properties of medium on the basis of fluctuation-dissipative theorem. The electromagnetic field can be calculated from Maxwell's equations with the fluctuating current density as the source. Knowing the fluctuating electromagnetic field, it is possible to calculate the Poynting's vector, stress tensor, and so on, and to determine the heat transfer between the bodies [13, 93, 94, 115], the van der Waals–Casimir interaction [42, 43] and the Casimir friction [11]. Among these problems, the calculation of Casimir friction is the most complex, because it requires a complex electrodynamic problem with moving boundaries to be solved [99, 100, 121, 128]. In the second approach the electromagnetic field is described by Green's functions [43], which can be calculated using quantum electrodynamics [183]. For equilibrium problems, such as the Casimir interaction, both approaches give the same result [43], although the Green's functions method is more general. For non-equilibrium problems, Rytov's approach is simpler; therefore, correct results for the radiative heat transfer [93] and Casimir friction between two parallel planes [10, 11, 100, 121] were for the first time obtained using this approach.

3.1 Electromagnetic Fluctuations at Thermodynamical Equilibrium

3.1.1 Electromagnetic Fluctuations and Linear Response Theory

In this section, the key formulas of linear response theory are given, which then are used for the description of the fluctuations of electromagnetic fields. For a more

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detailed presentation of linear response theory and its application in the theory of the electromagnetic fluctuations, see [8, 107, 184, 185]. Consider a quantum-mechanical system characterized by a Hamiltonian H_0 and the equilibrium density matrix

$$\rho = \frac{e^{-\beta H_0}}{\mathrm{Sp}(e^{-\beta H_0})}, \quad \beta = \frac{1}{k_B T}, \tag{3.1}$$

where k_B is the Boltzmann constant and T is temperature. Let us perturb this system by an external perturbation of the form

$$H_{int} = -\int d^3r \sum_j \hat{A}_j(\mathbf{r}, t) f_j(\mathbf{r}, t), \tag{3.2}$$

where $f_j(\mathbf{r}, t)$ are the external forces and $\hat{A}_j(\mathbf{r}, t)$ are the dynamical variables of the system under consideration. A straightforward perturbation theory shows that the linear response of the variable A_j to f_j is given by

$$A_i(\mathbf{r}, t) = \sum_j \int d^3r' \int dt' \alpha_{ij}(\mathbf{r}, \mathbf{r}', t - t') f_j(\mathbf{r}', t'), \tag{3.3}$$

where $\alpha_{ij}(\mathbf{r}, \mathbf{r}', t - t')$ is the usual susceptibility tensor defined by

$$\alpha_{ij}(\mathbf{r}, \mathbf{r}', t - t') = \frac{i}{\hbar}\theta(t - t')\left\langle \hat{A}_i(\mathbf{r}, t)\hat{A}_j(\mathbf{r}', t') - \hat{A}_j(\mathbf{r}', t')\hat{A}_i(\mathbf{r}, t)\right\rangle, \tag{3.4}$$

where θ is the step function: $\theta(\tau) = 1$ if $\tau > 0$ and zero otherwise, and where $\langle \cdots \rangle$ denotes an average with respect to the equilibrium density matrix (3.1). It is clear from (3.3) that

$$\frac{\delta A_i(\mathbf{r}, \omega)}{\delta f_j(\mathbf{r}', \omega)} = \alpha_{ij}(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{\hbar}\int_0^\infty dt e^{i\omega t}\left\langle \hat{A}_i(\mathbf{r}, t)\hat{A}_j(\mathbf{r}', 0) - \hat{A}_j(\mathbf{r}', 0)\hat{A}_i(\mathbf{r}, t)\right\rangle, \tag{3.5}$$

where the Fourier-transformed quantities are defined by

$$\psi(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \psi(\omega) e^{-i\omega t}. \tag{3.6}$$

According to the fluctuation-dissipative theorem, the spectral function of fluctuations is expressed through the generalized susceptibility $\alpha_{ij}(\mathbf{r}, \mathbf{r}')$

$$\varphi_{ij}(\mathbf{r}, \mathbf{r}', \omega) = \langle A_i(\mathbf{r}) A_j(\mathbf{r}')\rangle_\omega = \frac{i\hbar}{2}(\alpha^*_{ji}(\mathbf{r}', \mathbf{r}, \omega) - \alpha_{ij}(\mathbf{r}, \mathbf{r}', \omega)) \coth\left(\frac{\beta\hbar\omega}{2}\right), \tag{3.7}$$

where $\langle A_i(\mathbf{r}) A_j(\mathbf{r})'\rangle_\omega$ is the Fourier-component of the symmetrized correlation function

$$\varphi_{ij}(\mathbf{r},\mathbf{r}',t-t') = \frac{1}{2}\langle \hat{A}_i(\mathbf{r},t)\hat{A}_j(\mathbf{r}',t') + \hat{A}_j(\mathbf{r}',t')\hat{A}_i(\mathbf{r},t)\rangle, \tag{3.8}$$

Equation (3.7) can be expressed through the fictitious random forces, whose action would give the result, equivalent to the spontaneous fluctuations of the values of $A_i(\mathbf{r},t)$. We write for this

$$A_i(\mathbf{r},\omega) = \sum_j \int d^3r'\alpha_{ij}(\mathbf{r},\mathbf{r}',\omega) f_j(\mathbf{r}',\omega), \tag{3.9}$$

$$f_i(\mathbf{r},\omega) = \sum_j \int d^3r'\alpha^{-1}_{ij}(\mathbf{r},\mathbf{r}',\omega) A_j(\mathbf{r}',\omega), \tag{3.10}$$

so that

$$\langle f_i(\mathbf{r}) f_j(\mathbf{r}')\rangle_\omega = \sum_l \int d^3r''\alpha^{-1}_{il}(\mathbf{r},\mathbf{r}'',\omega)\times$$

$$\times \sum_m \int d^3r'''\alpha^{-1*}_{jm}(\mathbf{r}',\mathbf{r}''',\omega)\,\langle A_l(\mathbf{r}'')A_m(\mathbf{r}''')\rangle_\omega. \tag{3.11}$$

Using (3.7) and taking into account that

$$\int d^3r''\alpha^{-1}_{il}(\mathbf{r},\mathbf{r}'',\omega)\alpha_{lj}(\mathbf{r}'',\mathbf{r}',\omega) = \delta_{ij}\delta(\mathbf{r}-\mathbf{r}'),$$

we get

$$\langle f_i(\mathbf{r}) f_j(\mathbf{r}')\rangle_\omega = \frac{i\hbar}{2}(\alpha^{-1}_{ij}(\mathbf{r},\mathbf{r}',\omega) - \alpha^{-1*}_{ji}(\mathbf{r}',\mathbf{r},\omega)) \coth\left(\frac{\beta\hbar\omega}{2}\right). \tag{3.12}$$

If the variables A_i and A_j have the same signature under time reversal, then $\alpha_{ij}(\mathbf{r},\mathbf{r}',\omega) = \alpha_{ji}(\mathbf{r}',\mathbf{r},\omega)$. In this case, (3.7) can be rewritten in the form

$$\langle A_i(\mathbf{r})A_j(\mathbf{r})'\rangle_\omega = \hbar \mathrm{Im}\alpha_{ij}(\mathbf{r},\mathbf{r}',\omega) \coth\left(\frac{\beta\hbar\omega}{2}\right). \tag{3.13}$$

If variables A_i and A_j have opposite parity, then $\alpha_{ij}(\mathbf{r},\mathbf{r}',\omega) = -\alpha_{ji}(\mathbf{r}',\mathbf{r},\omega)$. In this case, (3.7) can be rewritten in the form

$$\langle A_i(\mathbf{r})A_j(\mathbf{r})'\rangle_\omega = -i\hbar \mathrm{Re}\alpha_{ij}(\mathbf{r},\mathbf{r}',\omega) \coth\left(\frac{\beta\hbar\omega}{2}\right). \tag{3.14}$$

For the problem of electromagnetic fluctuations, the external probes will be taken to be external polarization $\mathbf{P}_{ext}(\mathbf{r}, t)$ and external magnetization $\mathbf{M}_{ext}(\mathbf{r}, t)$. The Hamiltonian H_{ext}, in the present case is

$$H_{int} = -\int d^3r \left[\mathbf{P}^{ext}(\mathbf{r}, t) \cdot \hat{\mathbf{E}}(\mathbf{r}, t) + \mathbf{M}^{ext}(\mathbf{r}, t) \cdot \hat{\mathbf{H}}(\mathbf{r}, t)\right], \tag{3.15}$$

where $\hat{\mathbf{E}}(\mathbf{r}, t)$ and $\hat{\mathbf{H}}(\mathbf{r}, t)$ are the second-quantized operators corresponding to the electric and magnetic field, respectively. We now introduce four types of response functions:

$$D_{ij}^{EE}(\mathbf{r}, \mathbf{r}', \omega) = \frac{\delta E_i(\mathbf{r}, \omega)}{\delta P_j^{ext}(\mathbf{r}', \omega)}, \tag{3.16}$$

$$D_{ij}^{HE}(\mathbf{r}, \mathbf{r}', \omega) = \frac{\delta H_i(\mathbf{r}, \omega)}{\delta P_j^{ext}(\mathbf{r}', \omega)}, \tag{3.17}$$

$$D_{ij}^{EH}(\mathbf{r}, \mathbf{r}', \omega) = \frac{\delta E_i(\mathbf{r}, \omega)}{\delta M_j^{ext}(\mathbf{r}', \omega)}, \tag{3.18}$$

$$D_{ij}^{HH}(\mathbf{r}, \mathbf{r}', \omega) = \frac{\delta H_i(\mathbf{r}, \omega)}{\delta M_j^{ext}(\mathbf{r}', \omega)}. \tag{3.19}$$

and we introduce the corresponding symmetrized correlation functions

$$S_{ij}^{EE}(\mathbf{r}, \mathbf{r}', t - t') = \frac{1}{2}\left\langle \hat{E}_i(\mathbf{r}, t)\hat{E}_j(\mathbf{r}', t') + \hat{E}_j(\mathbf{r}', t')\hat{E}_i(\mathbf{r}, t)\right\rangle, \tag{3.20}$$

$$S_{ij}^{HE}(\mathbf{r}, \mathbf{r}', t - t') = \frac{1}{2}\left\langle \hat{H}_i(\mathbf{r}, t)\hat{E}_j(\mathbf{r}', t') + \hat{E}_j(\mathbf{r}', t')\hat{H}_i(\mathbf{r}, t)\right\rangle, \tag{3.21}$$

$$S_{ij}^{EH}(\mathbf{r}, \mathbf{r}', t - t') = \frac{1}{2}\left\langle \hat{E}_i(\mathbf{r}, t)\hat{H}_j(\mathbf{r}', t') + \hat{H}_j(\mathbf{r}', t')\hat{E}_i(\mathbf{r}, t)\right\rangle, \tag{3.22}$$

$$S_{ij}^{HH}(\mathbf{r}, \mathbf{r}', t - t') = \frac{1}{2}\left\langle \hat{H}_i(\mathbf{r}, t)\hat{H}_j(\mathbf{r}', t') + \hat{H}_j(\mathbf{r}', t')\hat{H}_i(\mathbf{r}, t)\right\rangle. \tag{3.23}$$

Taking into account that $\mathbf{E}(\mathbf{H})$ is an even (odd) variable under time reversal, from the fluctuation-dissipation theorem we get

$$\langle E_i(\mathbf{r})E_j(\mathbf{r}')\rangle_\omega = \hbar \mathrm{Im} D_{ij}^{EE}(\mathbf{r}, \mathbf{r}', \omega) \coth\left(\frac{\beta\hbar\omega}{2}\right), \tag{3.24}$$

$$\langle H_i(\mathbf{r})H_j(\mathbf{r}')\rangle_\omega = \hbar \mathrm{Im} D_{ij}^{HH}(\mathbf{r}, \mathbf{r}', \omega) \coth\left(\frac{\beta\hbar\omega}{2}\right), \tag{3.25}$$

$$\langle H_i(\mathbf{r})E_j(\mathbf{r}')\rangle_\omega = -i\hbar \mathrm{Re} D_{ij}^{HE}(\mathbf{r},\mathbf{r}',\omega)\coth\left(\frac{\beta\hbar\omega}{2}\right), \tag{3.26}$$

$$\langle E_i(\mathbf{r})H_j(\mathbf{r}')\rangle_\omega = -i\hbar \mathrm{Re} D_{ij}^{EH}(\mathbf{r},\mathbf{r}',\omega)\coth\left(\frac{\beta\hbar\omega}{2}\right). \tag{3.27}$$

Thus, the four response functions defined by (3.16)–(3.19) completely determine the correlation functions. Note that the expressions (3.24) and (3.25) are real, and expression (3.26) and (3.27) imaginary. This means that the time correlation functions of the components of **E** (and the components of **H**) are even functions of the time $t = t_1 - t_2$ (as must be for the correlation between two functions, both of which are even or odd with respect to the time reversal). However, the time correlation function of the components **E** with the components of **H** is odd on the time (as must be for two functions, one of which is even, and another is odd relative to time reversal). Hence, it follows that the correlation functions between **E** and **H** at identical time are not correlated with each other (odd function t becomes zero at $t = 0$). Thus the average values of any bilinear product of **E** and **H** (at identical of time), for example the Poynting's vectors will vanish. The latter fact is, however, obvious: in a medium that is in the thermal equilibrium and invariant relative to time reversal, internal macroscopic energy flows cannot prevail.

Equation (3.24) can be expressed through the fictitious random components of polarization, whose action would give the result, equivalent to the spontaneous fluctuations of the values of $E_i(\mathbf{r}, t)$. We write for this

$$E_i(\mathbf{r},\omega) = \sum_j \int d^3r' D_{ij}(\mathbf{r},\mathbf{r}',\omega)P_j(\mathbf{r}',\omega), \tag{3.28}$$

$$P_i(\mathbf{r},\omega) = \sum_j \int d^3r' D_{ij}^{-1}(\mathbf{r},\mathbf{r}',\omega)E_j(\mathbf{r}',\omega), \tag{3.29}$$

where $D_{ij}(\mathbf{r},\mathbf{r}',\omega) = D_{ij}^{EE}(\mathbf{r},\mathbf{r}',\omega)$. For a non-magnetic medium, $\mathbf{B} = \mathbf{H}$ (Gaussian's system of units is used) and

$$\mathbf{D}(\mathbf{r}) = \int d^3\mathbf{r}' \overleftrightarrow{\varepsilon}(\mathbf{r},\mathbf{r}',\omega)\mathbf{E}(\mathbf{r}'), \tag{3.30}$$

where $\overleftrightarrow{\varepsilon}(\mathbf{r},\mathbf{r}',\omega)$ is the dielectric diadic of surrounding media. In this case, from the Maxwell's equations:

$$\nabla \times \mathbf{E} = i\frac{\omega}{c}\left(\mathbf{B} + 4\pi\mathbf{M}^{ext}\right), \tag{3.31}$$

$$\nabla \times \mathbf{H} = -i\frac{\omega}{c}\left(\mathbf{D} + 4\pi\mathbf{P}^{ext}\right), \tag{3.32}$$

it follows that the generalized susceptibility $D_{ij}(\mathbf{r}, \mathbf{r}', \omega)$ obeys

$$\left(\nabla_i \nabla_k - \delta_{ik} \nabla^2\right) D_{kj}(\mathbf{r}, \mathbf{r}', \omega) - \left(\frac{\omega}{c}\right)^2 \int d^3x'' \varepsilon_{ik}(\mathbf{r}, \mathbf{r}'', \omega) D_{kj}(\mathbf{r}'', \mathbf{r}', \omega) = = \left(\frac{4\pi\omega^2}{c^2}\right) \delta_{ij} \delta(\mathbf{r} - \mathbf{r}'), \tag{3.33}$$

$$\left(\nabla'_j \nabla'_k - \delta_{jk} \nabla'^2\right) D_{ik}(\mathbf{r}, \mathbf{r}', \omega) - \left(\frac{\omega}{c}\right)^2 \int d^3x'' \varepsilon_{kj}(\mathbf{r}'', \mathbf{r}', \omega) D_{ik}(\mathbf{r}, \mathbf{r}'', \omega) = = \left(\frac{4\pi\omega^2}{c^2}\right) \delta_{ij} \delta(\mathbf{r} - \mathbf{r}'). \tag{3.34}$$

From (3.33) and (3.34) we get

$$D_{ij}^{-1}(\mathbf{r}, \mathbf{r}', \omega) = \left(\frac{c^2}{4\pi\omega^2}\right) \left[\left(\nabla_i \nabla_j - \delta_{ik} \nabla^2\right) \delta(\mathbf{r} - \mathbf{r}') - \left(\frac{\omega}{c}\right)^2 \varepsilon_{ij}(\mathbf{r}, \mathbf{r}', \omega) \right]. \tag{3.35}$$

Taking into account (3.12) and (3.24), we get

$$\langle P_i(\mathbf{r}) P_j(\mathbf{r}') \rangle_\omega = \frac{\hbar}{4\pi} \mathrm{Im} \varepsilon_{ij}(\mathbf{r}, \mathbf{r}', \omega) \coth\left(\frac{\beta\hbar\omega}{2}\right). \tag{3.36}$$

Since the current density $j_i(\mathbf{r}, \omega) = -i\omega P_i(\mathbf{r}, \omega)$, from (3.36) we get

$$\langle j_i(\mathbf{r}) j_j(\mathbf{r}') \rangle_\omega = \frac{\hbar\omega^2}{4\pi} \mathrm{Im} \varepsilon_{ij}(\mathbf{r}, \mathbf{r}', \omega) \coth\left(\frac{\beta\hbar\omega}{2}\right). \tag{3.37}$$

3.1.2 Electromagnetic Fluctuations in a Homogeneous Medium

For a spatially homogeneous medium the functions D_{ij} and ε_{ij} in (3.33) depend only on difference $\mathbf{r} - \mathbf{r}'$. Using the Fourier-transformation the differential equation (3.33) can be transformed to the system of algebraic equations

$$\left(k_i k_k - \delta_{ik} k^2\right) D_{kj}(\mathbf{k}, \omega) + \left(\frac{\omega}{c}\right)^2 \varepsilon_{ik}(\mathbf{k}, \omega) D_{kj}(\mathbf{k}, \omega) = = -\left(\frac{4\pi\omega^2}{c^2}\right) \delta_{ij}. \tag{3.38}$$

For the long-wave fluctuations, for which the wavelength is considerably larger than interatomic distance (e.g., at room temperatures the characteristic wavelength of thermal radiation $\lambda_T = c\hbar/k_B T \approx 10^{-5}$m), it is possible to neglect the dependence of ε_{ij} on $\mathbf{k}$. In this case, for a spatially homogeneous medium, it is possible to assume $\varepsilon_{ij}(\mathbf{k}, \omega) = \delta_{ij} \varepsilon(\omega)$. In this case, the solution of equations (3.38) has the form

$$D_{ik}(\omega, \mathbf{k}) = -\frac{4\pi\omega^2/c^2}{\omega^2\varepsilon(\omega)/c^2 - k^2}\left[\delta_{ik} - \frac{c^2 k_i k_k}{\omega^2\varepsilon(\omega)}\right]. \tag{3.39}$$

In the vacuum $\varepsilon(\omega) = 1$. But since in every material medium the sign of $\mathrm{Im}\varepsilon(\omega)$ coincides with the sign of ω, then the vacuum corresponds to $\varepsilon \to 1 + i0 \cdot \mathrm{sign}\,\omega$. In this case, we get

$$D_{ik}(\omega, \mathbf{k}) = -\frac{4\pi\omega^2/c^2}{\omega^2/c^2 - k^2 + i0 \cdot \mathrm{sign}\,\omega}\left[\delta_{ik} - \frac{c^2 k_i k_k}{\omega^2}\right]. \tag{3.40}$$

For spatially homogeneous unrestricted medium, the functions of D_{ik} depend only on the difference $\mathbf{r} - \mathbf{r}'$, and they are even function of this variable ((3.33) and (3.34) contain only second order derivatives, and therefore $D_{ik}(\omega, \mathbf{r})$ and $D_{ik}(\omega, -\mathbf{r})$ satisfy identical equations). Using the Fourier-transformation on $\mathbf{r}$ on both sides of (3.24), we get

$$\left\langle E_i(\mathbf{r})E_k(\mathbf{r}')\right\rangle_{\omega\mathbf{k}} = \hbar \mathrm{Im} D_{ij}(\mathbf{k}, \omega)\coth\left(\frac{\beta\hbar\omega}{2}\right). \tag{3.41}$$

For an isotropic nonmagnetic medium ($\mu = 1$), the function $D_{ik}(\mathbf{k}, \omega)$ is determined by (3.39). The problem of finding the spatial correlation function of fluctuations is reduced to the calculation of the integral

$$D_{ik}(\mathbf{r}, \omega) = \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{r}} D_{ik}(\mathbf{k}, \omega). \tag{3.42}$$

The integration is performed using formulas

$$\int \frac{d^3k}{(2\pi)^3}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{k^2 + \kappa^2} = \frac{e^{-\kappa r}}{4\pi r}, \tag{3.43}$$

$$\int \frac{d^3k}{(2\pi)^3}\frac{k_i k_k e^{i\mathbf{k}\cdot\mathbf{r}}}{k^2 + \kappa^2} = -\frac{\partial^2}{\partial_i \partial_k}\frac{e^{-\kappa r}}{4\pi r}. \tag{3.44}$$

The first of which is obtained by taking the Fourier-transformation of both side of the known equality

$$(\nabla^2 - \kappa^2)\frac{e^{-\kappa r}}{r} = -4\pi\delta(\mathbf{r}), \tag{3.45}$$

and the second is obtained by the differentiation of the first. As a result, we get

$$D_{ik}(\mathbf{r}, \omega) = \left[\frac{\omega^2}{c^2}\delta_{ik} + \frac{\partial^2}{\varepsilon\partial_i \partial_k}\right]\frac{1}{r}\exp\left(-\frac{\omega}{c}\sqrt{-\varepsilon}r\right), \tag{3.46}$$

where $r = |\mathbf{r} - \mathbf{r}'|$, and square-root must be taken with such sigh that $\mathrm{Re}\sqrt{-\varepsilon} > 0$. For vacuum $\varepsilon = 1$, and $\sqrt{-\varepsilon} = -i$. Hence according to (3.24)

$$\left\langle E_i(\mathbf{r})E_k(\mathbf{r}')\right\rangle_\omega = \hbar\coth(\beta\hbar)\,\mathrm{Im}\left\{\frac{1}{\varepsilon}\left[\frac{\omega^2}{c^2}\delta_{ik} + \frac{\partial^2}{\partial_i\partial_k}\right]\frac{1}{r}\exp\left(-\frac{\omega}{c}\sqrt{-\varepsilon}r\right)\right\}. \tag{3.47}$$

After contraction over indexes $i,\ k$ (and using (3.45)), we get

$$\left\langle \mathbf{E}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r}')\right\rangle_\omega = 2\hbar\coth\left(\frac{\beta\hbar\omega}{2}\right)\mathrm{Im}\left\{\frac{1}{\varepsilon}\left[\frac{\varepsilon\omega^2}{c^2 r}\exp\left(-\frac{\omega}{c}\sqrt{-\varepsilon}r\right) - 2\pi\delta(\mathbf{r})\right]\right\}. \tag{3.48}$$

Spectral correlation function for fluctuations of the magnetic field can be calculated from (3.47) taking into account the equality

$$\left\langle B_i(\mathbf{r})B_j(\mathbf{r}')\right\rangle_\omega = \frac{c^2}{\omega^2}e_{iml}e_{jnk}\nabla_m\nabla'_n\left\langle E_l(\mathbf{r})E_k(\mathbf{r}')\right\rangle_\omega, \tag{3.49}$$

where e_{iml} and e_{ink} are the unit fully antisymmetric tensors. Using (3.49) leads to correlation functions of the magnetic field, which differ from (3.47) and (3.48) by the absence of the coefficient $1/\varepsilon$ before the square bracket. In this case, the δ-function term under the sign Im in (3.48) becomes real and drops out. The appearance of the imaginary part of ε in (3.47) and (3.48) shows the connection between the electromagnetic fluctuations and the energy dissipation in the medium. Note that even in the limit $\mathrm{Im}\varepsilon \to 0$ (3.47) and (3.48) give non-vanishing expressions. This is connected with order of transition to two limits—to the infinite size of medium and vanishing $\mathrm{Im}\varepsilon$. Since in the infinite medium, even infinitesimally small $\mathrm{Im}\varepsilon$ leads eventually to energy absorption, then the used order of transitions to the limits concerns to physically transparent environment, in which, as in any real medium, non-vanishing absorption still exists.

Let us make, for example, the specified transition in the formula (3.48). For this purpose we notice, that at small positive $\mathrm{Im}\varepsilon$ (at $\omega > 0$)

$$\sqrt{-\varepsilon} \approx -i\sqrt{\mathrm{Re}\varepsilon}\left(1 + i\frac{\mathrm{Im}\varepsilon}{2\mathrm{Re}\varepsilon}\right)$$

(taking into account requirement $\mathrm{Re}\sqrt{-\varepsilon} > 0$). Therefore, in the limit $\mathrm{Im}\varepsilon \to 0$ we get

$$\left\langle \mathbf{E}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r}')\right\rangle_\omega = \frac{1}{n^2}\left\langle \mathbf{H}(\mathbf{r})\cdot\mathbf{H}(\mathbf{r}')\right\rangle_\omega = \frac{2\omega^2\hbar}{c^2 r}\sin\frac{\omega n r}{c}\coth\left(\frac{\beta\hbar\omega}{2}\right), \tag{3.50}$$

where $n = \sqrt{\varepsilon}$ is a real refraction index. Due to absence of term with δ-function this expression remains finite at $\mathbf{r} = \mathbf{r}'$:

$$\left\langle \mathbf{E}^2 \right\rangle_\omega = \frac{1}{n^2} \left\langle \mathbf{H}^2 \right\rangle_\omega = \frac{2\omega^3 \hbar n}{c^3} \coth\left(\frac{\beta\hbar\omega}{2}\right). \tag{3.51}$$

Limiting transition to a case of the transparent medium can be performed at earlier stage of calculations. Taking into account that the sign of Im$\varepsilon(\omega)$ coincides with the sign of ω, in the limit of transparent medium (3.39) takes the form

$$D_{ik}(\omega, \mathbf{k}) = -\frac{4\pi\omega^2/c^2}{\omega^2 n^2/c^2 - k^2 + i0 \cdot \operatorname{sign}\omega} \left[\delta_{ik} - \frac{c^2 k_i k_k}{\omega^2 n^2}\right]. \tag{3.52}$$

The imaginary part of this function is can be obtained using the formula

$$-\mathrm{Im}\frac{1}{\omega^2 n^2/c^2 - k^2 + i0 \cdot \operatorname{sign}\omega} = \pi \cdot \operatorname{sign}\omega\, \delta\left(\frac{\omega^2 n^2}{c^2} - k^2\right) =$$

$$= \frac{\pi}{2k}\left\{\delta\left(\frac{n\omega}{c} - k\right) - \delta\left(\frac{n\omega}{c} + k\right)\right\},$$

As a result we get

$$\langle E_i(\mathbf{r}) E_k(\mathbf{r}')\rangle_{\omega\mathbf{k}} =$$

$$= \frac{2\pi^2\hbar}{k}\left(\frac{\omega^2}{c^2}\delta_{ik} - \frac{k_i k_k}{n^2}\right)\left\{\delta\left(\frac{\omega n}{c} - k\right) - \delta\left(\frac{\omega n}{c} + k\right)\right\} \coth\left(\frac{\beta\hbar\omega}{2}\right). \tag{3.53}$$

The arguments of the δ-functions in this expression have simple physical meaning: they show that the fluctuation of field with the given value $\mathbf{k}$ are propagated in the space with the velocity c/n, i.e. with the velocity of propagation of electromagnetic waves in the medium. Using the inverse Fourier-transformation, it is possible from (3.53) to get again (3.47).

The energy density of the fluctuating electromagnetic field in the transparent medium (with $\mu = 1$), in spectral interval $d\omega$ is given by [191]

$$u(\omega)d\omega = \frac{1}{8\pi}\left[2\left\langle \mathbf{E}^2\right\rangle_\omega \frac{d(\omega\varepsilon)}{d\omega} + 2\left\langle \mathbf{H}^2\right\rangle_\omega\right]\frac{d\omega}{2\pi}. \tag{3.54}$$

The factor 2 in the square brackets is connected with fact that in the calculation of the energy density of the electromagnetic field, the integration is assumed only over positive values of ω. At the same time, in calculating energy with the use of spectral correlation function, the ω integration is assumed from $-\infty$ to ∞. The transformation of integration over infinite interval to semi-infinite interval gives an additional factor 2. Using (3.52) in (3.54), we get

$$u(\omega)d\omega = \left[\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\right]\frac{\omega^2 n^2}{\pi^2 c^3}\frac{d(n\omega)}{d\omega}d\omega. \tag{3.55}$$

The first term in the brackets is connected with the zero-point energy of the field. The second term gives energy density of the thermodynamically equilibrium electromagnetic radiation in the transparent medium, i.e., the energy of *black-body radiation*. This part of the formula could be also obtained without consideration of fluctuations, by the corresponding generalization of the Planck formula for the black-body radiation in vacuum. According to the latter, the energy density of black-body radiation in the of the wave-vectors volume d^3k is given by the formula

$$\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\frac{2d^3k}{(2\pi)^3}$$

where the factor 2 takes into account two directions of polarization. To obtain the spectral density of energy it is necessary to replace d^3k on $4\pi k^2 dk$ and to substitute $k = n\omega/c$, i.e.:

$$k^2dk = k^2\frac{dk}{d\omega}d\omega = \frac{\omega^2 n^2}{c^3}\frac{d(n\omega)}{d\omega}d\omega,$$

what gives the required result.

3.2 Electromagnetic Fluctuations for Nonequilibrium Systems

In Sect. 3.1 the theory of electromagnetic fluctuations was presented for systems in thermodynamic equilibrium. However, it is possible to develop the theory of electromagnetic fluctuations for nonequilibrium systems. This theory is based on the fluctuation-dissipation theorem for the current density. Assuming local thermal equilibrium, it is possible to determine the statistical properties of the currents. This approach composes the content of the Rytov's theory [5–7], which is based on the introduction of "random" current density into the Maxwell's equations (similar to the "random force in the theory of Brownian motion of particle). For the monochromatic field (time factor $\exp(-i\omega t)$) in a dielectric, nonmagnetic medium, these equations are:

$$\nabla \times \mathbf{E} = i\frac{\omega}{c}\mathbf{B}, \tag{3.56}$$

$$\nabla \times \mathbf{B} = -i\frac{\omega}{c}\mathbf{D}+\frac{4\pi}{c}\mathbf{j}^f, \tag{3.57}$$

where **E**, **D**, **B** are the electric and electric displacement field, and the magnetic induction field, respectively. In Rytov's theory the fluctuating current density has statistical properties determined by the fluctuation-dissipative theorem. According to fluctuation-dissipative theorem the average value of the product of components $\mathbf{j}^f$ is determined by the formula (3.37), which we rewrite in the form

$$\left\langle j_i^f(\mathbf{r},\omega) j_k^{f*}(\mathbf{r}',\omega')\right\rangle = \left\langle j_i^f(\mathbf{r}) j_k^{f*}(\mathbf{r}')\right\rangle_\omega \delta(\omega-\omega'), \tag{3.58}$$

$$\left\langle j_i^f(\mathbf{r}) j_k^{f*}(\mathbf{r}')\right\rangle_\omega = \frac{\hbar}{(2\pi)^2}\left(\frac{1}{2}+n(\omega)\right)\omega^2 \mathrm{Im}\varepsilon_{ik}(\mathbf{r},\mathbf{r}',\omega), \tag{3.59}$$

$$n(\omega) = \frac{1}{e^{\hbar\omega/k_BT}-1}. \tag{3.60}$$

In Rytov's theory, which will be used in the following for the nonequilibrium systems, the Fourier-transformation of the correlation functions is defined by

$$\psi(t) = \int_{-\infty}^{\infty} d\omega \psi(\omega) e^{-i\omega t}. \tag{3.61}$$

For this reason in (3.59) in comparison with (3.37) appears the additional factor $1/2\pi$. From Maxwell's equations it follows that the component of the electric field, created by the random current density $\mathbf{j}^f$, is given by

$$E_i(\mathbf{r}) = \frac{i}{\omega}\int \mathrm{d}^3\mathbf{r}' D_{ik}(\mathbf{r},\mathbf{r}',\omega) j_k^f(\mathbf{r}'), \tag{3.62}$$

where summation over repeated indexes is assumed. The Green's functions of the electromagnetic field, $D_{ij}(\mathbf{r},\mathbf{r}',\omega)$, obey (3.33) and (3.34).

Using (3.33), (3.34) and (3.59), we can calculate the spectral correlation function of the electric field, created by a body at a temperature of T by the fluctuations of current density inside the body [13] (see Appendix A):

$$\begin{aligned}\left\langle E_i(\mathbf{r}) E_j^*(\mathbf{r}')\right\rangle_\omega &= \frac{\hbar}{8\pi^2}\coth\left(\frac{\hbar\omega}{2k_BT}\right)\int \mathrm{d}\mathbf{r}''\int \mathrm{d}\mathbf{r}'''\mathrm{Im}\varepsilon_{kl}(\mathbf{r}'',\mathbf{r}''') D_{ik}(\mathbf{r},\mathbf{r}'') D_{jl}^*(\mathbf{r}',\mathbf{r}''') \\ &= \frac{\hbar c^2}{16\pi^2 i\omega^2}\coth\left(\frac{\hbar\omega}{2k_BT}\right)\int \mathrm{d}S_{1l}''\big(D_{ik}(\mathbf{r},\mathbf{r}'')\nabla_l'' D_{jk}^*(\mathbf{r}',\mathbf{r}'') - \\ &\quad - D_{jk}^*(\mathbf{r}',\mathbf{r}'')\nabla_l'' D_{ik}(\mathbf{r},\mathbf{r}'')\big),\end{aligned} \tag{3.63}$$

where the points $\mathbf{r}$ and $\mathbf{r}'$ are outside the body. Here we have transformed an integral over the volume of the body into an integral over the surface of the body. For the evanescent waves the surface of integration can be moved to infinity. Thus, using (3.33) and (3.34), and taking into account that the surface integral vanishes in this case, we get

$$\langle E_i(\mathbf{r}) E_j(\mathbf{r}')\rangle_\omega^{evan} = \frac{\hbar}{2\pi}\coth\left(\frac{\hbar\omega}{2k_BT}\right)\mathrm{Im} D_{ij}(\mathbf{r},\mathbf{r}'). \tag{3.64}$$

In the non-retarded limit the formalism can be simplified. In this case the electric field can be written as the gradient of an electrostatic potential, $\mathbf{E}(\mathbf{r}) = -\nabla\phi(\mathbf{r})$. Thus the total Poynting's vector becomes

$$(S_{total})_\omega = \frac{c}{8\pi}\int d\mathbf{S}\cdot\left\{\left\langle[\mathbf{E}\times\mathbf{B}^*]\right\rangle_\omega + c.c.\right\} =$$

$$= \frac{c}{8\pi}\int d\mathbf{S}\cdot\left\{-\left\langle[\nabla\times(\phi\mathbf{B}^*)] + \phi\left[\nabla\times\mathbf{B}^*\right]\right\rangle_\omega + c.c.\right\} =$$

$$= \frac{i\omega}{8\pi}\int d\mathbf{S}\cdot\nabla'\left(\left\langle\phi(\mathbf{r})\phi^*(\mathbf{r}')\right\rangle_\omega - c.c.\right)_{\mathbf{r}=\mathbf{r}'} \tag{3.65}$$

In the same approximation we can write

$$D_{ik}(\mathbf{r},\mathbf{r}') = -\frac{i}{\omega}\nabla_i\nabla'_k D(\mathbf{r},\mathbf{r}'),$$

where the function $D(\mathbf{r},\mathbf{r}')$ obeys the Poisson's equation

$$\Delta D(\mathbf{r},\mathbf{r}') = -4\pi\delta(\mathbf{r}-\mathbf{r}'). \tag{3.66}$$

Using the identities

$$D_{ik}(\mathbf{r},\mathbf{r}'')\left(\nabla''_l D^*_{jk}(\mathbf{r}',\mathbf{r}'') - \nabla''_k D^*_{jl}(\mathbf{r}',\mathbf{r}'')\right) =$$

$$= -\frac{i}{\omega}\nabla_i\nabla''_k\left[D(\mathbf{r},\mathbf{r}'')\left(\nabla''_l D^*_{jk}(\mathbf{r}',\mathbf{r}'') - \nabla''_k D^*_{jl}(\mathbf{r}',\mathbf{r}'')\right)\right] -$$

$$-\frac{1}{c^2}\nabla_i\nabla'_j D(\mathbf{r},\mathbf{r}'')\nabla''_l D^*(\mathbf{r}',\mathbf{r}''). \tag{3.67}$$

Equation (A.1) from Appendix A gives

$$\left\langle E_i(\mathbf{r})E_j(\mathbf{r}')\right\rangle_\omega = \nabla_i\nabla'_j\left\langle\phi(\mathbf{r})\phi^*(\mathbf{r}')\right\rangle_\omega, \tag{3.68}$$

$$\left\langle\phi(\mathbf{r})\phi^*(\mathbf{r}')\right\rangle_\omega = \frac{\hbar}{16\pi^2 i\omega^2}\coth\left(\frac{\hbar\omega}{2k_BT}\right)\int d\mathbf{S}''_1\Big\{D^*(\mathbf{r}',\mathbf{r}'')\nabla'' D(\mathbf{r},\mathbf{r}'') -$$

$$-D(\mathbf{r},\mathbf{r}'')\nabla'' D^*(\mathbf{r}',\mathbf{r}'')\Big\}. \tag{3.69}$$

3.3 Fluctuating Field in the Non-retarded Limit

In this section we present some applications where retardation effects can be neglected, and where the full formalism developed above is not necessary. We consider the interaction between an external charged or neutral particle (e.g., an electron, ion or an atom) and a solid with a flat surface. If the separation between the particle and the surface is small enough retardation effects can be neglected and the electric field can be described by a scalar potential.

Consider first a classical point charge moving along a prescribed path $\mathbf{x}(t)$ outside a body with a flat surface. The electric potential from the charge can be written as a sum of evanescent plane waves of the form

$$\phi_{\text{ext}} = e^{qz} e^{i(\mathbf{q}\cdot\mathbf{x}-\omega t)},$$

where $\mathbf{q} = (q_x, q_y)$ is a two-dimensional wavevector, and where the xy is in the surface, while the positive z direction point outwards from the solid. The external potential ϕ_{ext} polarizes the solid, and the induced polarization charges give rise to a potential which for $z > 0$ must take the form

$$\phi_{\text{ind}} = -g(q,\omega) e^{-qz} e^{i(\mathbf{q}\cdot\mathbf{x}-\omega t)}.$$

The linear response function $g(q,\omega)$ determines the response of the solid to any external space and time-varying potential. If the solid can be described by a local scalar dielectric function $\epsilon(\omega)$, then

$$g = \frac{\epsilon - 1}{\epsilon + 1}. \tag{3.70}$$

Since $\epsilon(\omega)$ has been measured for many materials, this expression for g is very useful. One can show that (3.70) is exact in the limit $q \to 0$ but holds only approximately for finite q. Indeed, much effort has been devoted to calculating $g(q,\omega)$ for simple metals using the jellium model and various mean-field approximations to account for the interaction between the electrons. Furthermore, the structure of $g(q,\omega)$ is constrained by exact sum rules.

So far, our discussion has assumed that ϕ_{ext} arises from an external (classical) time-varying charge distribution. In the problems which interest us here it is crusial to treat the particle and substrate quantum mechanically. The quantum degrees of freedom of the polarizable solid can be included by assuming that the induced potential ϕ_{ind} arises from a set of quantized boson excitations (e.g., surface plasmons or low-energy electron-hole pairs). The total Hamiltonin is then given by

$$H = \frac{\mathbf{p}^2}{2m} + U(\mathbf{x}) + \sum_{\mathbf{q}\alpha} \hbar\omega_{\mathbf{q}\alpha} b^+_{\mathbf{q}\alpha} b_{\mathbf{q}\alpha} + \sum_{\mathbf{q}\alpha} C_{\mathbf{q}\alpha} e^{-qz} \left(b_{\mathbf{q}\alpha} e^{i\mathbf{q}\cdot\mathbf{x}} + H.c. \right). \tag{3.71}$$

Here, $\mathbf{x}$ and $\mathbf{p}$ are the position and momentum operators of the external electron with mass m, treated as a distinguishable particle, $\omega_{\mathbf{q}\alpha}$, $b^+_{\mathbf{q}\alpha}$ and $b_{\mathbf{q}\alpha}$ are the angular frequency and the creation and anhilation operators for the boson with the quantum number $(\mathbf{q}, \alpha)$, and $C_{\mathbf{q}\alpha}$ is an energy parameter which determines its coupling to the external electron. The parameters $\omega_{\mathbf{q}\alpha}$ and $C_{\mathbf{q}\alpha}$ can be related to $g(q,\omega)$ in the following way. Assume that we constrain the electron to move (classically) along a prescribed path $\mathbf{x}(t)$. We assume that the particle starts far away at $t = 0$, then moves close to the surface of the solid, and then far away again so that $z(0) \approx z(t_0) \sim \infty$.

From (3.71), we obtain the equation of motion for the boson operator $b_{\mathbf{q}\alpha}$ (in the Heisenberg picture),

$$i\dot{b}_{\mathbf{q}\alpha} = \omega_{\mathbf{q}\alpha} b_{\mathbf{q}\alpha} + \frac{C_{\mathbf{q}\alpha}}{\hbar} e^{-qz(t)} e^{i\mathbf{q}\cdot\mathbf{x}(t)}$$

and the solution

$$b_{\mathbf{q}\alpha}(t_0) = e^{-i\omega_{\mathbf{q}\alpha} t_0} b_{\mathbf{q}\alpha}(0) - i\frac{C_{\mathbf{q}\alpha}}{\hbar}\int_0^{t_0} dt\; e^{-i\omega_{\mathbf{q}\alpha}(t_0-t)} e^{-qz(t)+i\mathbf{q}\cdot\mathbf{x}(t)} \tag{3.72}$$

Using (3.71) and (3.72), we obtain the net energy transfer from the particle to the substrate

$$\Delta E = \langle\Psi|[H(t_0) - H(0)]|\Psi\rangle = \sum_{\mathbf{q}} \int d\omega\; \omega \sum_{\alpha} |C_{\mathbf{q}\alpha}|^2 \delta(\omega - \omega_{\mathbf{q}\alpha}) |F_{\mathbf{q}}(\omega)|^2/\hbar, \tag{3.73}$$

where

$$F_{\mathbf{q}}(\omega) = \int_0^{t_0} dt\; e^{-qz(t)} e^{i[\omega t - \mathbf{q}\cdot\mathbf{x}(t)]}, \tag{3.74}$$

and where we have used the fact that the interaction energy term in H is zero at $t = 0$ and $t = t_0$ as a result of our assumptions. Note that (3.73) is independent of the state $|\Psi\rangle$ of the boson system at $t = 0$.

On the other hand, the energy transfer ΔE can also be expressed in terms of $g(q, \omega)$ as follows. By solving Poisson's equation

$$\nabla^2 \phi_{\text{ext}} = -4\pi e \delta(\mathbf{x} - \mathbf{x}(t)),$$

one obtains [for $z < z(t)$] the external potential

$$\phi_{\text{ext}} = \int d^2q d\omega\; \tilde{\phi}_{\text{ext}}(\mathbf{q}, \omega) e^{i(\mathbf{q}\cdot\mathbf{x} - \omega t) + qz},$$

where

$$\tilde{\phi}_{\text{ext}} = -\frac{e}{4\pi^2 q} F_{\text{q}}(\omega). \tag{3.75}$$

The energy transfer from the external particle is obtained by integrating the Poynting vector over the surface $z = 0$ and over time. This gives:

$$\Delta E = \frac{1}{4\pi} \int dt\; d^2x \left[\phi \frac{\partial}{\partial t} \frac{\partial}{\partial z} \phi\right], \tag{3.76}$$

where the total potential $\phi = \phi_{\text{ext}} + \phi_{\text{ind}}$ is given by [for $0 \le z < z(t)$]

$$\phi = \int d^2q d\omega\, \tilde{\phi}_{\text{ext}}(\mathbf{q}, \omega) \left[e^{qz} - g(q, \omega)e^{-qz}\right] e^{i(\mathbf{q}\cdot\mathbf{x}-\omega t)}, \tag{3.77}$$

Substituting (3.75) and (3.77) in (3.76) gives

$$\Delta E = \frac{e^2}{2\pi^2} \int d^2q \int_0^\infty d\omega\, \frac{\omega}{q} |F_{\mathbf{q}}(\omega)|^2 \text{Im} g(q, \omega). \tag{3.78}$$

Comparing (3.73) with (3.78), and replacing

$$\sum_{\text{q}} \to \frac{A}{(2\pi)^2} \int d^2q, \tag{3.79}$$

where A is the surface area, gives

$$\sum_\alpha |C_{\mathbf{q}\alpha}|^2 \delta(\omega - \omega_{\mathbf{q}\alpha}) = \frac{2e^2\hbar}{Aq} \text{Im} g(q, \omega) \tag{3.80}$$

which is our *fundamental result*.

As a simple example, assume that g is given by (3.70) with $\epsilon = 1 - \omega_p^2/\omega^2$ as is valid for simple metals. Then

$$g = \frac{\epsilon - 1}{\epsilon + 1} = \frac{1}{1 - \left(\frac{\omega}{\omega_\text{s}}\right)^2},$$

where $\omega_\text{s} = \omega_\text{p}/\sqrt{2}$ is the surface plasmon frequency. Letting $\omega \to \omega + i0$, we obtain

$$\text{Im} g = \pi\omega_\text{s}\delta(\omega - \omega_\text{s})/2,$$

and from (3.80), $\omega_\text{q} = \omega_\text{s}$ and

$$|C_{\mathbf{q}\alpha}|^2 = \pi e^2 \hbar\omega_\text{s}/Aq.$$

We will now give some important applications, which all involves the interaction between an external charged or neutral particle (e.g., an ion or an atom) with the fluctuating electromagnetic field of a nearby solid with a flat surface. When the separation between the external particle is small enough so that retardation effects can be neglected, but still large enough that there is negligible overlap between the wavefunction of the particle and the wavefunction of the atoms of the solid, these problems can be studied using the Hamiltonian Equation (3.71) with (3.80).

3.3.1 Interaction Energy Between a Charged Particle and a Solid: Image Potential

Consider first an external charged point particle at rest at $\mathbf{x} = (0, 0, z)$. In this case, we obtain

$$\sum_{\mathbf{q}\alpha} \hbar\omega_{\mathbf{q}\alpha} b^+_{\mathbf{q}\alpha} b_{\mathbf{q}\alpha} + \sum_{\mathbf{q}\alpha} C_{\mathbf{q}\alpha} e^{-qz} \left(b_{\mathbf{q}\alpha} + b^+_{\mathbf{q}\alpha}\right) = \sum_{\mathbf{q}\alpha} \hbar\omega_{\mathbf{q}\alpha} B^+_{\mathbf{q}\alpha} B_{\mathbf{q}\alpha} - \sum_{\mathbf{q}\alpha} |C_{\mathbf{q}\alpha}|^2 \frac{e^{-2qz}}{\hbar\omega_{\mathbf{q}\alpha}}$$

where we have introduced shifted boson operators $B_{\mathbf{q}\alpha} = b_{\mathbf{q}\alpha} + C_{\mathbf{q}\alpha} e^{-qz}/\hbar\omega_{\mathbf{q}\alpha}$. Note that $B_{\mathbf{q}\alpha}$ and $B^+_{\mathbf{q}\alpha}$ satisfy the same commutation algebra as the original operators. The last term is the relaxation energy and can be identified as the generalized static image-potential energy,

$$U_{\mathrm{im}}(z) = -\sum_{\mathbf{q}\alpha} |C_{\mathbf{q}\alpha}|^2 \frac{e^{-2qz}}{\hbar\omega_{\mathbf{q}\alpha}}$$

Using (3.80), this can also be written as

$$U_{\mathrm{im}} = -\frac{e^2}{2\pi^2} \int d^2q \int_0^\infty d\omega \, \frac{\mathrm{Im} g(q,\omega)}{q\omega} e^{-2qz}.$$

However, according to the $\omega \to 0$ limit of the appropriate Kramers–Kronig relation,

$$\int_0^\infty d\omega \, \frac{\mathrm{Im} g(q,\omega)}{\omega} = \frac{\pi}{2} g(q,0),$$

so that

$$U_{\mathrm{im}} = -\frac{e^2}{2} \int_0^\infty dq \; g(q,0) e^{-2qz}.$$

Using the classical expression (3.70) for g gives $g(q,0) = 1$ and $U_{\mathrm{im}} = -e^2/4z$. A more accurate expression for g is given by

$$g(q,0) = e^{2qd_\perp(0)}$$

where $d_\perp(0)$ is the centroid of the induced charge density at the metal surface (at zero frequency). This formula gives

$$U_{\mathrm{im}} = -\frac{e^2}{4\left[z - d_\perp(0)\right]}.$$

The quantity $d_\perp(0)$ has been tabulated by Lang and Kohn for the jellium model at different values of the electron gas density parameter r_s.

3.3.2 *Interaction Energy Between a Neutral Particle and a Solid: van der Waals Interaction*

We consider now the interaction between a neutral particle; for example, an atom, and a solid with a flat surface. The atom has many electrons with coordinates $\mathbf{x}_i$ so now (3.71) takes the form

$$H = H_0 + V$$

where

$$H_0 = \sum_i \frac{\mathbf{p}_i^2}{2m} + U\left(\mathbf{x}_1, \mathbf{x}_2, ...\right) + \sum_{\mathbf{q}\alpha} \hbar\omega_{\mathbf{q}\alpha} b_{\mathbf{q}\alpha}^{+} b_{\mathbf{q}\alpha}$$

where U is the interaction energy between the electrons (and the ion) of the atom, and

$$V = \sum_{\mathbf{q}\alpha} C_{\mathbf{q}\alpha} \sum_i e^{-qz_i} \left(b_{\mathbf{q}\alpha} e^{i\mathbf{q}\cdot\mathbf{x_i}} + H.c.\right). \tag{3.81}$$

We now use second order pertubation theory to calculate the interaction energy between the particle and the solid. We can write

$$\Delta E = \langle A\Psi|V|A\Psi\rangle - \left\langle A\Psi|V \frac{1}{H_0 - E_0} V|A\Psi\right\rangle$$

where $|A\rangle$ is the ground state of the atom and $|\Psi\rangle$ the ground state of the solid. Using (3.81), the first term in ΔE clearly vanishes, and the second term gives the atom-solid van der Waals interaction energy:

$$U_{\text{VdW}} = -\left\langle A\Psi|V \frac{1}{H_0 - E_0} V|A\Psi\right\rangle$$

Substituting (3.81) in this expression gives

$$U_{\text{VdW}} = -\sum_{\mathbf{q}\alpha} |C_{\mathbf{q}\alpha}|^2 \sum_B \frac{\left|\langle A| \sum_i e^{i\mathbf{q}\cdot\mathbf{x_i}} |B\rangle\right|^2}{\hbar\omega_{\mathbf{q}\alpha} + E_B - E_A}$$

$$= -\int_0^\infty d\omega \sum_{\mathbf{q}} \sum_\alpha |C_{\mathbf{q}\alpha}|^2 \delta(\omega - \omega_{\mathbf{q}\alpha}) \sum_B \frac{|\langle A| \sum_i e^{-qz_i} e^{i\mathbf{q}\cdot\mathbf{x_i}} |B\rangle|^2}{\hbar\omega + E_B - E_A}$$

where $\sum_B$ is the sum over all states of the atom excluding the ground state A. Using (3.80), this equation can be written as

$$U_{\text{VdW}} = -\frac{2e^2\hbar}{A} \int_0^\infty d\omega \sum_{\mathbf{q}} \frac{1}{q} \text{Im} g(q, \omega) \sum_B \frac{|\langle A| \sum_i e^{-qz_i} e^{i\mathbf{q}\cdot\mathbf{x_i}} |B\rangle|^2}{\hbar\omega + E_B - E_A} \tag{3.82}$$

Next we write

$$(\mathbf{x}_i, z_i) = \hat{z}z + \mathbf{r}_i$$

where z is the distance between the center of mass of the atom and the surface ($z = 0$) of the solid. Since the relevant q in the sum in (3.82) are of the order $1/z$ or smaller, and if we assume the size of the atom is small compare to z we can expand

$$e^{-qz_i} e^{i\mathbf{q}\cdot\mathbf{x_i}} \approx e^{-qz} \left(1 + i\mathbf{r}_i \cdot \mathbf{Q}\right)$$

where $\mathbf{Q} = (\mathbf{q}, iq)$. Substitute this result in (3.82) gives

$$U_{\mathrm{VdW}} = -\frac{2\hbar}{A}\int_0^\infty d\omega \sum_{\mathbf{q}} \frac{1}{q}\mathrm{Im}g(q,\omega)e^{-2qz}\mathbf{Q}^* \cdot \sum_B \frac{\langle A|\sum_i e\mathbf{r}_i|B\rangle\langle B|\sum_i e\mathbf{r}_i|A\rangle}{\hbar\omega + E_B - E_A} \cdot \mathbf{Q}$$

For an atom the dyadic function

$$\bar{\Pi} = \sum_B \frac{\langle A|\sum_i e\mathbf{r}_i|B\rangle\langle B|\sum_i e\mathbf{r}_i|A\rangle}{\hbar\omega + E_B - E_A}$$

is proportional to the unit tensor $\bar{\Pi}_{\mu\nu}(\omega) = \Pi(\omega)\delta_{\mu\nu}$ where

$$\Pi(\omega) = \sum_B \frac{\langle A|\sum_i ex_i|B\rangle\langle B|\sum_i ex_i|A\rangle}{\hbar\omega + E_B - E_A}$$

Using this result and that $\mathbf{Q}^* \cdot \mathbf{Q} = 2q^2$ we get

$$U_{\mathrm{VdW}} = -\frac{2\hbar}{A}\int_0^\infty d\omega \sum_{\mathbf{q}} q\mathrm{Im}g(q,\omega)e^{-2qz}\Pi(\omega) = -\frac{\hbar}{2\pi^2}\int d^2q\; qe^{-2qz}\mathrm{Im}\int_0^\infty d\omega\; g(q,\omega)\Pi(\omega)$$

where we have used that $\Pi(\omega)$ is real, and where we have replaced the sum over $\mathbf{q}$ with the integral over $\mathbf{q}$ using (3.79). Since $g(q,\omega)$ is a causal response function, it has its poles in the lower complex ω-half space. Thus, we can close the integral over the upper half space and write the integral over the imaginary frequency axis. Thus, with $\omega = iu$ and using that $g(q, iu)$ is real we get:

$$U_{\mathrm{VdW}} = -\frac{\hbar}{2\pi^2}\int d^2q\; qe^{-2qz}\int_0^\infty du\; g(q,iu)\mathrm{Re}\;\Pi(iu)$$

Since

$$\mathrm{Re}\Pi(iu) = \sum_B (E_B - E_A)\frac{\langle A|\sum_i ex_i|B\rangle\langle B|\sum_i ex_i|A\rangle}{(\hbar u)^2 + (E_B - E_A)^2} = \alpha(iu)$$

where $\alpha(\omega)$ is the atomic polarizability, we get

$$U_{\mathrm{VdW}} = -\frac{\hbar}{\pi}\int_0^\infty dq\, q^2 e^{-2qz}\int_0^\infty du\, g(q, iu)\alpha(iu)$$

If we assume that $g(q,\omega)$ is given by (3.70) we get

$$U_{\mathrm{VdW}} = -\frac{\hbar}{4\pi z^3}\int_0^\infty d\omega \frac{\epsilon(iu)-1}{\epsilon(iu)+1}\alpha(iu)$$

3.3.3 Inelastic Electron Scattering from Surfaces

As a final application of (3.71) and (3.80) consider inelastic scattering of electrons from the fluctuating electromagnetic field of a solid with a flat surface. In this case, we assume that the potential $U(\mathbf{x})$ is an infinite potential step at the surface $z = 0$, so that the stationary states for an electron, in the absence of coupling to the boson system, are given by

$$\langle \mathbf{x}|\mathbf{k}\rangle = (2\pi)^{-3/2}\left(e^{-ik_z z} - e^{ik_z z}\right)e^{i\mathbf{k}_\parallel\cdot\mathbf{x}_\parallel}.$$

If the coupling to the substrate excitations is weak, one may use first-order pertubation theory (the golden rule) to calculate the rate w of inelastic scattering $\mathbf{k} \to \mathbf{k}'$ via excitation of a single boson,

$$w = \frac{2\pi}{\hbar}\int d^3k' \sum_{\mathbf{q}\alpha}\sum_{n_{\mathbf{q}\alpha}} P(n_{\mathbf{q}\alpha})\delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'} - \hbar\omega_{\mathbf{q}\alpha})|\langle \mathbf{k}', n_{\mathbf{q}\alpha}+1|C_{\mathbf{q}\alpha}e^{-qz-i\mathbf{q}\cdot\mathbf{x}}b^+_{\mathbf{q}\alpha}|\mathbf{k}, n_{\mathbf{q}\alpha}\rangle|^2,$$

where $P(n_{\mathbf{q}\alpha})$ is the probability that the boson mode $\mathbf{q}\alpha$ contains $n_{\mathbf{q}\alpha}$ quanta. An electron can also absorb a thermally excited boson, which is given by a similar expression to that above but with $n_{\mathbf{q}\alpha}+1$ replaced by $n_{\mathbf{q}\alpha}$ and $b^+_{\mathbf{q}\alpha}$ replaced by $b_{\mathbf{q}\alpha}$. Using (3.80) this expression for w can be rewritten as

$$w = \frac{4\pi e^2}{\hbar A}\int d^3k' \sum_{\mathbf{q}}(n_\omega + 1)\frac{1}{q}\mathrm{Im}g(q,\omega)|\langle \mathbf{k}'|e^{-qz-i\mathbf{q}\cdot\mathbf{x}}|\mathbf{k}\rangle|^2,$$

where $\hbar\omega = \epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}$. However,

$$\langle \mathbf{k}'|e^{-qz-i\mathbf{q}\cdot\mathbf{x}}|\mathbf{k}\rangle = \frac{1}{\pi}\delta(\mathbf{k}_\parallel - \mathbf{k}'_\parallel - \mathbf{q})\left[\frac{q}{q^2+(k_z+k'_z)^2} - \frac{q}{q^2+(k_z-k'_z)^2}\right],$$

so that

$$w = \frac{e^2}{\hbar\pi^3}\frac{A}{(2\pi)^2}\int d^3k'(n_\omega+1)\frac{q_\parallel}{(q_\parallel^2+q_\perp^2)^2}\mathrm{Im}g(q,\omega),$$

where $q_\parallel = |\mathbf{k}_\parallel - \mathbf{k}'_\parallel|$ and $q_\perp = k_z - k'_z$. Finally, since the number of electrons that hit the surface area A per unit time is given by

$$\dot{N} = \frac{\hbar k A}{(2\pi)^3 m} \cos\theta,$$

we obtain, using

$$\int d^3k' = \int d\Omega_{k'} d\hbar\omega \frac{mk'}{\hbar^2},$$

$$\frac{w}{\dot{N}} = \frac{2}{(\pi e a_0)^2} \frac{1}{\cos\theta} \int d\Omega_{k'} d\hbar\omega (n_\omega + 1) \frac{k'}{k} \frac{q_\parallel}{(q_\parallel^2 + q_\perp^2)^2} \mathrm{Im} g(q, \omega),$$

where a_0 is the Bohr radius. If one defines $P(\mathbf{k}, \mathbf{k}') d\Omega_{\mathbf{k}'} d\hbar\omega$ to be the relative probability that an incident electron is scattered into the range of energy losses between $\hbar\omega$ and $\hbar(\omega + d\omega)$ and into the solid angle $d\Omega_{\mathbf{k}'}$ around the direction $\mathbf{k}'$, then

$$P(\mathbf{k}, \mathbf{k}') = \frac{2}{(\pi e a_0)^2} \frac{1}{\cos\theta} (n_\omega + 1) \frac{k'}{k} \frac{q_\parallel}{(q_\parallel^2 + q_\perp^2)^2} \mathrm{Im} g(q, \omega),$$

This equation represents the most general formulation of so-called dipole scattering theory, which has been remarkably useful in analyzing electron energy-loss measurements [186]. As an application, consider electron scattering from the (collective) C–O stretch vibrational mode of an ordered layer of CO molecules adsorbed on a Cu(100) surface. The open circles in Fig. 3.1 shows the measured inelastic electron scattering intensity, as a function of the polar collection angle θ. The solid line is the

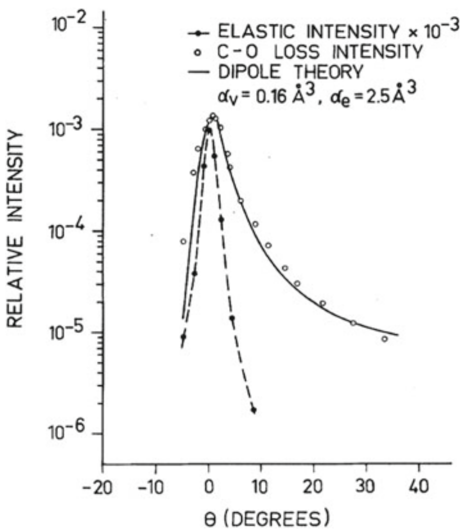

Fig. 3.1 Experimental elastic peak intensity (*solid circles*) and C–O loss peak intensity (*open circles*) versus collection angle θ. The *solid curve* is the dipole theory calculation

theory prediction using the expression for the $g(q, \omega)$ function for an ordered layer of point particles (polarizability α) on a perfect conducting substrate [187] (see (6.47)). Another important applications of the dipole scattering theory presented has been the study of non-local dielectric response of metal surfaces [188–190].