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Thermally induced resonances in a three-body system including a solid surface

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Dispersion energy of a system out of equilibrium containing two molecules and substrate in different thermostats is calculated taking into account nonlocal optical effects. A resonance increase of energy due to three-body interaction in a system out of equilibrium is shown. In particular, dispersion energy of a two-body subsystem of the three-body system out of equilibrium may be essentially larger than the energy of the same subsystem in equilibrium. A necessary condition of the resonance increase is a closeness of eigenfrequencies of the subsystems composing the whole system. It is shown that different nonlocal reflectivities of surface corresponding to different additional boundary conditions lead to similar results in resonance magnification of dispersion interaction of subsystems in a system out of equilibrium.

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I. INTRODUCTION

Properties of many-body systems may be found using Green's functions or density matrices. But, starting with a two-body problem, conventional direct methods of solution of many-body problems allow to determine conditions of appearance of new principal phenomena due to adding a particle to the system of interest. An exact solution of a two-body problem is very well known. History of searching for a three-body problem includes a few hundreds years and connected with outstanding scientists. For instance, five exact solutions of a classical problem of celestial mechanics were found by Euler and Lagrange in case of fixed distance ratios between bodies. Asymptotes and periodicity of a general solution were investigated by Poincare. Related references can be found in encyclopedias and textbooks.

An exact solution of quantum three-body problem was derived in the twenty century at the condition $R/a \to 0$, where R is the hyperspherical radius determining a deviation of each particle from the center of mass of the whole system, a is the two-body scattering length. This condition may be satisfied in case when $R \to 0$ and a is the finite value, and in another case when $a \to \infty$ and R is the finite value. A solution for the first case was obtained by Thomas in 30s years of the last century. The second one as corresponding to the physical reality was discovered by Efimov in 70th [1,2]. So-called Efimov states were found experimentally [3] in a system of Cs atoms at very low temperatures ($T=10-250$ nK). Now, the Efimov state of a three-body system is regarded as by right as a new type of material bond side by side with a covalent, ionic, metallic or dispersion bond. That is why an enormous interests in new many-body systems to be observed in modern physics.

It should be emphasized that above described states manifest itself at low relative energies of particles. Moreover, corresponding resonances disappear with a temperature increase. But, however, there are three-body resonances connecting with a specific character of thermodynamic conditions. Namely, if separate subsystems of many-body system are situated in thermostats kept at different temperatures, then it is possible a resonance increase of the dispersion energy of "cold" subsystems due to an interaction with "hot" subsystems. The resonance amplification occurs at coinciding of eigenfrequencies of these subsystems. A physical reason of this phenomenon is that the most effective energy exchange among the subsystems occurs at the closeness of their eigenfrequencies [4,5].

The van der Waals interaction of bodies in thermodynamic equilibrium has been studied in details. The fluctuational and many-body nature of such an interaction were convincingly demonstrated in past. Various theoretical methods to calculate the dispersion forces acting between microscopic or macroscopic bodies were developed by different authors. A lot of monographs and reviews are known in this field, see, for example [6–9]. Theoretical predictions were verified experimentally on the basis of diverse experimental techniques including the novel subtle probe proximal tools. But, very often the dispersion interaction occurs in conditions out of equilibrium. These conditions may be found in the molecular-beam experiments, in the gas-phase deposition onto substrates, in the photochemical reactions, in the probe microscopy and so on. General expressions for the van der Waals interaction between two molecules having different temperatures were found by Linder and co-workers [10–12]. It was shown that the dispersion potential become repulsive when the temperature difference is large enough. A change of the adsorption potential between a molecule and a nonequilibrium semiconductor has been demonstrated by Bass and Lozovski [13]. Dispersion forces between two molecules that are in relative motion were calculated by Cohen and Mukamel [14]. They found that the nonequilibrium forces may be attractive or repulsive and may be nonconservative. It should be noticed that the works [10–14] were devoted to the equilibrium two- and three-particle and nonequilibrium two-particle systems. The dispersion interaction of two macroscopic bodies kept at different temperatures was considered in [15,16]. The problem was solved for materials described by arbitrary dielectric functions and magnetic permeabilities.

Recently, some important nonlocal effects are discussed in relation to the van der Waals forces and radiative heat transfer in Refs. [17–21]. Optical properties of systems are

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determined in general by the spatial and temporal dispersions. Spatial dispersion or nonlocality manifests itself as a dependence of the response function on the wave vector side by side with the dependence on the frequency. Importance of nonlocal effects for semiconductors or poor conductors was discussed for the equilibrium case in [22–24].

In this paper we show that a substantial increase of the dispersion interaction occurs between two particles near a hot surface compare with a case when these particles in a free space. In other words, energy of interaction between two molecules near a heating surface $U_{12}(T_G,T_S)$ may be much larger than the energy of interaction $U_{12}(T_G)$ of the same molecules in free space, where T_G,T_S are the temperatures of two thermostats containing molecules and a substrate, correspondingly. A magnitude of the resonance depends on temperatures of the subsystems, mutual geometry and properties of molecules and a substrate. Besides, we demonstrate that the three-body interactions in a system out of equilibrium may be larger than the two-body interactions in equilibrium system at some conditions. The necessary condition of this effect is a closeness of their eigenfrequencies $\omega_{1,2}$ with eigenfrequency of surface ω_{QP}. An eigenfrequency of the third body is the frequency ω_{QP} (QP-quasistatic polariton) of the surface Coulomb polariton. This frequency is a solution of equation $\mathrm{Re}\{\varepsilon(\omega)\}+1=0$, where $\varepsilon(\omega)$ is the dielectric function of substrate. In other words, the Coulomb polariton is the quasistatic limit of the surface plasmon- or phonon-polariton (which are eigenmodes of a flat surface). Besides, we demonstrate the resonance amplification of dispersion interaction of subsystems in a system out of equilibrium taking into account the nonlocal response function.

The paper is organized as follows. In Sec. II we provide theoretical basis to calculate the dispersion energy of a system out of equilibrium containing two molecules and substrate in different thermostats. Analytical formulas for the energy are given in Secs. II A and II B, both in general and local cases. Numerical results demonstrating the resonance energy increase and discussion are presented in Sec. III. Our conclusions are given in Sec. IV.

II. FORMALISM

Side by side with a three-body system involving, for instance, three molecules, it is possible to consider two molecules with eigenfrequencies ω_1 and ω_2 near a surface of solids, characterized by eigenfrequency ω_{QP}. We consider a situation when two molecules are placed in thermostat at the temperature T_G and a solid sample is placed in thermostat at $T_S \neq T_G$. The geometry of the problem is depicted in Fig. 1.

The selected particle 1 is located at the distance d nearby a substrate and the second particle 2 is situated at some distance R from the first one and at the distance z from the substrate. The image of the first particle is shown beneath of a surface at the distance d.

Consider two particles nearby a half-space in the system of coordinates depicted in Fig. 1 where the first particle at point $\vec{r}_1=\{0,0,d\}$ and the second particle at point $\vec{r}_2=\{r_\parallel,0,z\}$. The energy of interaction in the dipole approach may be found in the usual way [7,8]

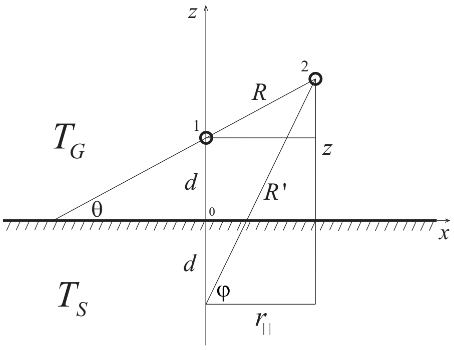

FIG. 1. Geometry of the problem and related notations for the coordinates of molecules located in the near surface region of substrate.

$$U=-\frac{1}{4}\langle\vec{\mu}_\Sigma(\vec{r}_1,t)\cdot\vec{E}_\Sigma(\vec{r}_1,t)+\vec{E}_\Sigma(\vec{r}_1,t)\cdot\vec{\mu}_\Sigma(\vec{r}_1,t)\rangle$$

$$\equiv-\frac{1}{2}\langle\vec{\mu}_\Sigma(\vec{r}_1,t)\cdot\vec{E}_\Sigma(\vec{r}_1,t)\rangle_S, \qquad (1)$$

where $\vec{\mu}_\Sigma$ is the total fluctuating moment of the selected particle and $\vec{E}_\Sigma$ is the total fluctuating field induced by the surroundings at point $\vec{r}_1$ where the selected particle is situated, the subscript s indicates the symmetrized value. The calculations are restricted to the nonretarded regime. The total moment and field may be written down as follows taking into account the two- and three-particle terms in the expression for energy

$$\vec{\mu}_\Sigma(\vec{r}_1,t)=\vec{\mu}_1^{sp}(\vec{r}_1,t)+\hat{\alpha}_1\vec{E}^{sp}(\vec{r}_1,t)+\hat{\alpha}_1\hat{T}\vec{\mu}_2^{sp}(\vec{r}_2,t)$$
$$+\hat{\alpha}_1\hat{\beta}_1(\vec{r}_1,\vec{r}_1)\vec{\mu}_1^{sp}(\vec{r}_1,t)+\hat{\alpha}_1\hat{\beta}_2(\vec{r}_1,\vec{r}_2)\vec{\mu}_2^{sp}(\vec{r}_2,t)$$
$$+\hat{\alpha}_1\hat{T}\hat{\alpha}_2\vec{E}^{sp}(\vec{r}_2,t)+\hat{\alpha}_1\hat{\beta}_2(\vec{r}_1,\vec{r}_2)\hat{\alpha}_2\vec{E}^{sp}(\vec{r}_2,t), \qquad (2)$$

$$\vec{E}_\Sigma(\vec{r}_1,t)=\vec{E}^{sp}(\vec{r}_1,t)+\hat{\beta}_1(\vec{r}_1,\vec{r}_1)\vec{\mu}_1^{sp}(\vec{r}_1,t)+\hat{\beta}_2(\vec{r}_1,\vec{r}_2)\mu_2^{sp}(\vec{r}_2,t)$$
$$+\hat{T}\vec{\mu}_2^{sp}(\vec{r}_2,t)+\hat{T}\hat{\alpha}_2\vec{E}^{sp}(\vec{r}_2,t)+\hat{\beta}_1(\vec{r}_1,\vec{r}_1)\hat{\alpha}_1\vec{E}^{sp}(\vec{r}_1,t)$$
$$+\hat{\beta}_2(\vec{r}_1,\vec{r}_2)\hat{\alpha}_2\vec{E}^{sp}(\vec{r}_2,t)+\hat{T}\hat{\alpha}_2\hat{T}\vec{\mu}_1^{sp}(\vec{r}_1,t)$$
$$+\hat{T}\hat{\alpha}_2\hat{\beta}_1(\vec{r}_2,\vec{r}_1)\vec{\mu}_1^{sp}(\vec{r}_1,t)+\hat{\beta}_2(\vec{r}_1,\vec{r}_2)\hat{\alpha}_2\hat{T}\vec{\mu}_1^{sp}(\vec{r}_1,t), \qquad (3)$$

where $\vec{\mu}^{sp}(\vec{r}_i,t)$ is the proper spontaneous dipole moment of the particle, situated at point "i," $\vec{E}^{sp}(\vec{r}_i,t)$ is the fluctuating electric field at the same point created by a half-space, $\hat{T}=T_{ij}=(3n_in_j-\delta_{ij})/R^3$, $\vec{n}=\vec{R}/|\vec{R}|$, δ_{ij} is the Kronecker symbol, $R=\sqrt{r_\parallel^2+(z-d)^2}$ is defined in Fig. 1.

Each term in Eqs. (2) and (3) has a clear physical meaning, for instance

$$\hat{\alpha}\vec{E}^{sp}(\vec{r}_1,t)=\int_{-\infty}^{t}\hat{\alpha}(t-t')\vec{E}^{sp}(\vec{r}_1,t')dt'=\vec{\mu}^{ind}(\vec{r}_1,t), \qquad (4)$$

$$\hat{\beta}_2(\vec{r}_1,\vec{r}_2)\vec{\mu}^{sp}(\vec{r}_2,t) = \int_{-\infty}^{t} \hat{\beta}_2(\vec{r}_1,\vec{r}_2;t-t')\vec{\mu}^{sp}(\vec{r}_2,t')dt' = \vec{E}^{ind}(\vec{r}_1,t), \tag{5}$$

$$\hat{\beta}_1(\vec{r}_2,\vec{r}_1)\vec{\mu}^{sp}(\vec{r}_1,t) = \int_{-\infty}^{t} \hat{\beta}_1(\vec{r}_2,\vec{r}_1;t-t')\vec{\mu}^{sp}(\vec{r}_1,t')dt' = \vec{E}^{ind}(\vec{r}_2,t), \tag{6}$$

the operator $\hat{\beta}$ is taking into account the nonlocal response of a half-space in a general case.

Such operator, for example, $\hat{\beta}_2$ creates the field at point $\vec{r}_1$ followed by inducing the dipole moment at the same point under the action of the operator $\hat{\alpha}_1$

$$\hat{\alpha}_1\hat{\beta}_2(\vec{r}_1,\vec{r}_2)\vec{\mu}^{sp}(\vec{r}_2,t) = \int_{-\infty}^{t} \hat{\alpha}_1(t-t')\int_{-\infty}^{t'} \hat{\beta}_2(\vec{r}_1,\vec{r}_2;t' - t'')\vec{\mu}^{sp}(\vec{r}_2,t'')dt'dt''. \tag{7}$$

The Fourier transforms follow from Eqs. (4) and (5),

$$\mu_i^{ind}(\vec{r}_1,\omega) = \alpha_{ik}(\omega)E_k^{sp}(\vec{r}_1,\omega), \tag{8}$$

$$E_i^{ind}(\vec{r}_1,\omega) = \beta_{ik}(\vec{r}_1,\vec{r}_2;\omega)\mu_k^{sp}(\vec{r}_2,\omega). \tag{9}$$

The number of terms in Eqs. (2) and (3) corresponds to the following terms in the expression for energy [Eq. (1)] $U \sim \alpha_1\alpha_2+\alpha_1\beta+\alpha_2\beta+\alpha_1\alpha_2\beta+\alpha_1\alpha_2\beta^2$, where the first term describes the pair interaction between molecules, the second and third terms describe an interaction of molecules with a substrate separately and the last two terms take into account of the triple interaction.

States of microparticles nearby solids depend on various factors including electromagnetic properties of the solids. A matter of great concern is the case of nonlocal description of the properties. In thermal equilibrium the van der Waals energy of a system constituted by two microparticles and a solid characterized by a local response was calculated in [25]. The same problem, but in the nonlocal approach was studied in [26]. Here, a similar problem will be considered, but in a system out of thermal equilibrium, when the temperature of a substrate T_S differs from the temperature of a gas T_G. This approach is the same as one accepted in the papers [15,16].

A. General case

Substituting of Eqs. (2) and (3) to Eq. (1) and taking into account that molecules in environment at T_G and the sample is held at T_S, we have

$$\begin{aligned} U_{\mathrm{neq}}(z,r_\parallel,d,T_G,T_S) = {} & U_{12}(z,r_\parallel,d,T_G) + U_{1S}(z,r_\parallel,d,T_G,T_S) \\ & + U_{12S}^{(1)}(z,r_\parallel,d,T_G,T_S) \\ & + U_{12S}^{(2)}(z,r_\parallel,d,T_G,T_S), \end{aligned} \tag{10}$$

where

$$U_{12}(z,r_\parallel,d,T_G) = -\frac{6T_G}{R^6}\sum_{n=0'}^{\infty} \alpha_1(i\omega_n)\alpha_2(i\omega_n), \tag{11}$$

$$U_{1S}(z,r_\parallel,d,T_G,T_S) = -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\left[\frac{2\Theta_G}{\omega}A_1(\omega) + \frac{2\Theta_S}{\omega}A_2(\omega)\right], \tag{12}$$

$$U_{12S}^{(1)}(z,r_\parallel,d,T_G,T_S) = -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\left[\frac{2\Theta_G}{\omega}B_1(\omega) + \frac{2\Theta_S}{\omega}B_2(\omega)\right], \tag{13}$$

$$U_{12S}^{(2)}(z,r_\parallel,d,T_G,T_S) = -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\left[\frac{2\Theta_G}{\omega}C_1(\omega) + \frac{2\Theta_S}{\omega}C_2(\omega)\right], \tag{14}$$

where $\Theta_{G,S}=(\hbar\omega/2)\coth(\hbar\omega/2T_{G,S})$,

$$A_1(\omega) = \alpha_1''(\omega)\beta^*(\omega), \quad A_2(\omega) = \beta''(\omega)\alpha_1^*(\omega),$$

$$\begin{aligned} B_1(\omega) = {} & 2\alpha_1''(\omega)[\alpha_2'(\omega)B'(\omega) - \alpha_2''(\omega)B''(\omega)] \\ & + 2\alpha_2''(\omega)\alpha_1'(\omega)B'(\omega), \end{aligned} \tag{15}$$

$$B_2(\omega) = B''(\omega)\alpha_1'(\omega)\alpha_2'(\omega), \quad B(\omega) = \mathrm{Tr}\{T_{ik}\beta_{kj}\}, \tag{16}$$

$$\begin{aligned} C_1(\omega) = {} & \alpha_1''(\omega)\mathrm{Re}\{\alpha_2^*(\omega)\mathrm{Tr}[\beta_{ik}^*\tilde{\beta}_{kj}^*]\} \\ & + \alpha_2''(\omega)\mathrm{Re}\{\alpha_1'(\omega)\mathrm{Tr}[\beta_{ik}\tilde{\beta}_{kj}^*]\}, \end{aligned}$$

$$\begin{aligned} C_2(\omega) = {} & \mathrm{Re}\{\alpha_1(\omega)\alpha_2^*(\omega)\mathrm{Tr}[\beta_{ik}''\tilde{\beta}_{kj}^*]\} \\ & + \mathrm{Re}\{\alpha_1(\omega)\alpha_2(\omega)\mathrm{Tr}[\beta_{ik}''\tilde{\beta}_{kj}]\}, \end{aligned} \tag{17}$$

$\alpha_{1,2}(\omega)$ are the polarizabilities of the molecules, $\beta_{ik}(\vec{r}_1,\vec{r}_2;\omega)$ is the 3×3 matrix [26] with components

$$\begin{aligned} \beta_{xx}(\vec{r}_1,\vec{r}_2;\omega) = {} & \frac{1}{2}\int_0^\infty p^2dp[J_0(pr_\parallel) \\ & - J_2(pr_\parallel)]r_{12}^p(p,\omega)\exp[-p(z+d)], \end{aligned}$$

$$\begin{aligned} \beta_{yy}(\vec{r}_1,\vec{r}_2;\omega) = {} & \frac{1}{2}\int_0^\infty p^2dp[J_0(pr_\parallel) \\ & + J_2(pr_\parallel)]r_{12}^p(p,\omega)\exp[-p(z+d)], \end{aligned}$$

$$\beta_{zz}(\vec{r}_1,\vec{r}_2;\omega) = \int_0^\infty p^2dpJ_0(pr_\parallel)r_{12}^p(p,\omega)\exp[-p(z+d)],$$

$$\begin{aligned} \beta_{xz}(\vec{r}_1,\vec{r}_2;\omega) & = -\beta_{zx}(\vec{r}_1,\vec{r}_2;\omega) \\ & = \int_0^\infty p^2dpJ_1(pr_\parallel)r_{12}^p(p,\omega)\exp[-p(z+d)], \end{aligned} \tag{18}$$

other components of the matrix are equal to zero, $r_{12}^{p}(p,\omega)$ is the Fresnel coefficient taking into account the nonlocal peculiarities of the optical response of the substrate in a general case, $J_{0,1,2}$ are the Bessel functions. In a special case $r_{\|}=0$, $z=d$, the matrix $\beta_{ik}(\vec{r}_1,\vec{r}_2;\omega)$ is reduced to $\beta(\omega)=\beta_{zz}(\vec{r}_1,\vec{r}_1;\omega)=2\beta_{xx}(\vec{r}_1,\vec{r}_1;\omega)=2\beta_{yy}(\vec{r}_1,\vec{r}_1;\omega)$.

In the quasistatic local approach, $r_{12}^{p}(p,\omega)=r_{12}^{p}(\omega)=\chi(\omega)=[\varepsilon(\omega)-1]/[\varepsilon(\omega)+1]$ and $\beta(\omega)=\chi(\omega)/4d^3$. It is seen from the structure of formulas (18) that $\hat{\beta}_2(\vec{r}_1,\vec{r}_2)=\hat{\beta}_1(\vec{r}_2,\vec{r}_1)$ in formulas (2) and (3).

The force acting between the selected first particle and substrate under an influence of the second particle is $f_{1S}^{\mathrm{neq}}=-\partial U_{\mathrm{neq}}(z,r_{\|},d,T_G,T_S)/\partial d$.

The Eqs. (12)–(14) may be transformed, explicitly extracting the equilibrium terms, as follows:

$$U_{1S}(d,T_G,T_S)=U_{1S}^{\mathrm{eq}}(d,T_G)+U_{1S}(d,T_G,T_S), \tag{19}$$

$$U_{12S}^{(1,2)}(z,r_{\|},d,T_G,T_S)=U_{12S}^{(1,2)\mathrm{eq}}(z,r_{\|},d,T_G)+U_{12S}^{(1,2)}(z,r_{\|},d,T_G,T_S), \tag{20}$$

where

$$U_{1S}(d,T_G,T_S)=-\hbar\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\Omega(\omega;T_S,T_G)A_2(\omega), \tag{21}$$

$$U_{12S}^{(1)}(z,r_{\|},d,T_G,T_S)=-\hbar\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\Omega(\omega;T_S,T_G)B_2(\omega), \tag{22}$$

$$U_{12S}^{(2)}(z,r_{\|},d,T_G,T_S)=-\hbar\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\Omega(\omega;T_S,T_G)C_2(\omega), \tag{23}$$

where $\Omega(\omega;T_S,T_G)=\coth(\hbar\omega/2T_S)-\coth(\hbar\omega/2T_G)$.

Explicit expressions for the terms $U_{1S}^{\mathrm{eq}}(d,T_G)$ and $U_{12S}^{(1,2)\mathrm{eq}}(z,r_{\|},d,T_G)$ in Eqs. (19) and (20) are given in [26].

B. Local limit

First of all we put our special attention to a local description of matter because a first goal of this work is to study the resonance effects in a system out of equilibrium. It should be noticed that the case for thermal equilibrium [25,26] follows directly from the formulas (10)–(17). In a local approach for a system out of equilibrium we have from Eqs. (10)–(17) of the same expression (11) for the energy of interaction between two molecules in free space $U_{12}(z,r_{\|},d,T_G)$ and for other terms

$$U_{1S}(d,T_S,T_G)=-\frac{T_G}{2d^3}\sum_{n=0'}^{\infty}\alpha_1(i\omega_n)\chi(i\omega_n)-\frac{\hbar}{4\pi d^3}\int_0^{\infty}d\omega\,\alpha_1'(\omega)\chi''(\omega)\Omega(\omega;T_S,T_G), \tag{24}$$

$$U_{12S}^{(1)}(z,r_{\|},d,T_S,T_G)=\frac{T_G(2+3\,\mathrm{Cos}\,2\theta+3\,\mathrm{Cos}\,2\varphi)}{(RR')^3}\sum_{n=0'}^{\infty}\alpha_1(i\omega_n)\alpha_2(i\omega_n)\chi(i\omega_n)+\frac{\hbar(2+3\,\mathrm{Cos}\,2\theta+3\,\mathrm{Cos}\,2\varphi)}{4\pi(RR')^3}\int_0^{\infty}d\omega\,\chi''(\omega)\times\{\mathrm{Re}[\alpha_1^{*}(\omega)\alpha_2(\omega)]+\mathrm{Re}[\alpha_1(\omega)\alpha_2(\omega)]\}\Omega(\omega;T_S,T_G), \tag{25}$$

$$U_{12S}^{(2)}(z,r_{\|},d,T_S,T_G)=-\frac{6T_G}{(R')^6}\sum_{n=0'}^{\infty}\alpha_1(i\omega_n)\alpha_2(i\omega_n)\chi^2(i\omega_n)+-\frac{3\hbar}{\pi(R')^6}\int_0^{\infty}d\omega\,\chi''(\omega)\{\mathrm{Re}[\alpha_1(\omega)\alpha_2^{*}(\omega)\chi^{*}(\omega)]+\mathrm{Re}[\alpha_1(\omega)\alpha_2(\omega)\chi(\omega)]\}\Omega(\omega;T_S,T_G), \tag{26}$$

where $R'=\sqrt{R^2+4zd}$, $\mathrm{Cos}(2\theta)=1-2(z-d)^2/R^2$, $\mathrm{Cos}(2\varphi)=1-2(z+d)^2/(R^2+4zd)$.

The formulas for R', $\mathrm{Cos}(2\theta)$, $\mathrm{Cos}(2\varphi)$ can be regarded as the functions of "d" at fixed distance "R" between of the two molecules, or as the functions of "R" between of the two molecules at fixed distance "d."

Thus, the quite complex expression for energy depends on the geometrical configuration, electrodynamical properties of particles and substrate and difference of the temperatures between them. In the case $T_S=T_G$ we clearly have the known result obtained by McLachlan [25] for the first time.

Here, it should be noted that every term of energy in Eqs. (24)–(26) is the sum of "equilibrium" and additional "nonequilibrium" terms. The equilibrium terms may be represented via imaginary frequencies using the Cauchy theorem. Response functions have no singularities along the imaginary axis. This is a mathematical consequence of the absence of any energy flows (in average) in such the systems. Spectral density of energy of systems out of thermal equilibrium contains parts which are not analytical functions, see formulas (24)–(26). The additional nonanalytical functions are combinations of the pure real and pure imaginary parts of different susceptibilities. Therefore, due to their non analyticity, the additional parts of energy could not be expressed via imaginary frequencies. That is why the additional energy in this case can be expressed only via real frequencies on the complex plane of a frequency. But, at the real axis the density of energy has some singularities of the different susceptibilities of subsystems composing the whole system. We will find further below that an immediate proximity of the resonances yields the resonance magnification of the dispersion energy in our case.

III. RESULTS AND DISCUSSION

Numerical calculations in local approach for dielectric substrate were performed for the GaAS case characterized by dielectric function in the frame of oscillatory model

$$\varepsilon(\omega)=\varepsilon_{\infty}\left(1+\frac{\omega_L^2-\omega_T^2}{\omega_T^2-\omega^2-i\gamma\omega}\right), \tag{27}$$

where $\varepsilon_{\infty}=11$, $\omega_T=268.7\ \mathrm{cm}^{-1}$, $\omega_L=292.1\ \mathrm{cm}^{-1}$, and $\gamma=2.4\ \mathrm{cm}^{-1}$. The symbols ω_T, ω_L, γ designate the transverse and longitudinal frequencies and the damping constant due to an anharmonicity. The frequency of the Coulomb polariton is $\omega_{QP}\approx 290\ \mathrm{cm}^{-1}$ for this material.

The polarizabilities $\alpha_i(\omega)$ $(i=1,2)$ of molecules are modeled by the Lorentzian profile

$$\alpha_{1,2}(\omega)=\frac{e^2f/m_e}{\omega_{1,2}^2-\omega^2-i\Gamma\omega}, \tag{28}$$

where e and m_e are the charge and mass of an electron, f is the oscillator strength.

The eigenfrequencies $\omega_1=\omega_2=\omega_{QP}\cdot\mu$, where μ is the mismatch parameter (dimensionless) and Γ is the width of the transition line due to relaxation processes in a gas (damping).

The relaxation of molecules is determined by a gas pressure and may be estimated as follows $\Gamma\sim\sigma v n_B\approx(10^{-9}-10^{-10})n_B$, where $\sigma\sim 10^{-14}\ \mathrm{cm}^2$ is the molecular cross-section of scattering, $v=\sqrt{2T_G/m}\approx 10^4-10^5\ \mathrm{cm/s}$, m is the mass of molecule, n_B is the buffer gas concentration. For a wide range of $n_B=10^{18}-10^{20}\ \mathrm{cm}^{-3}$ the damping is $\Gamma=10^8-10^{11}\ \mathrm{s}^{-1}$. For definiteness we consider the damping $\Gamma\approx 10^{-2}\omega_{1,2}$ at $\mu=1$ for vibration transitions or it will be indicated in figure captions. Run a few steps forward we can say that the chosen molecular damping is the worst value for the resonance effect of our interest, because the smaller width of the molecular line, the larger is the resonance magnification of the dispersion energy.

The resonance increase of the van der Waals energy of molecules near surface was found in our calculations as well as in the case of multiparticle interactions in a gaseous media [4,5]. Such an enhancement occurs in the closeness $(\mu\approx 1)$ of eigenmodes of the subsystems kept at different temperatures. At fixed geometrical locations of the interacting particles and substrate the value of enhancement depends on a characteristic frequency range of eigenmodes of whole system, on dampings and difference of temperatures.

The most prominent resonance effect manifests itself in range of frequencies of the rovibrational molecular transitions and corresponding spectral range of excitation of the surface polaritons due to the temperature factor $\Omega(T_S,T_G)=\coth(\hbar\omega/2T_S)-\coth(\hbar\omega/2T_G)$ in formulas (24)–(26) at reasonable temperatures. From these formulas it follows that the energy of the selected first molecule in the system may be represented as follows:

$$U_{1S}(d,T_S,T_G)=U_{1S}(\mathrm{eq})+U_{1S}(\mathrm{neq}), \tag{29}$$

$$U_{12S}^{(1,2)}(z,r_{\parallel},d,T_S,T_G)=U_{12S}^{(1,2)}(\mathrm{eq})+U_{12S}^{(1,2)}(\mathrm{neq}), \tag{30}$$

where $U_{1S}(\mathrm{eq})$ is the dispersion energy of interaction of the first molecule with a substrate in equilibrium at T_G, $U_{12S}^{(1,2)}(\mathrm{eq})$ are the three-body corrections [25,26] taking into account an influence of the second molecule in equilibrium at T_G. The additional terms $U_{1S}(\mathrm{neq})$ and $U_{12S}^{(1,2)}(\mathrm{neq})$ which are present-due to the difference of the subsystem temperatures $T_G\neq T_S$.

It is clear from Eqs. (24)–(26) and Eqs. (29) and (30) that the corresponding ratios $U_{1S}(\mathrm{neq})/U_{1S}(\mathrm{eq})$ and $U_{12S}^{(1,2)}(\mathrm{neq})/U_{12S}^{(1,2)}(\mathrm{eq})$ are not depend on the geometrical factors in local approach. These are universal functions determined by the temperatures of subsystems and their electrodynamic properties.

Figure 2 shows the universal ratios $U_{1S}(\mathrm{neq})/U_{1S}(\mathrm{eq})$ and $U_{12S}^{(1,2)}(\mathrm{neq})/U_{12S}^{(1,2)}(\mathrm{eq})$ as the functions of the mismatch parameter μ at $T_G=300$ K and $T_S=800$ K for two different relaxation molecular parameters $\Gamma=0.01\omega_{1,2}$ and $\Gamma=0.005\omega_{1,2}$. It is clearly seen that accounting of the temperature difference and the three-particle interaction may crucially change the value and sign of interaction. It should be noted, that it is possible to analyze the case when the temperatures of gaseous subsystems are different. Such a situation can be met in experiments for several crossed molecular beams nearby a surface of solids. In this case, a manifestation of the dispersion interactions in multiparticle nonequilibrium system is wider compare with an equilibrium one.

The graphic (a) of the figure demonstrates the modification of the dispersion interaction in a system "one particle-sample" when a temperature of gas is not equal to the temperature of a substrate. The graphics (b) and (c) correspond to the case when an influence of the third particle is taken into account: both the particles are kept at the same temperatures of the gaseous thermal bath T_G, but the temperature of a substrate is $T_S\neq T_G$. It should bear in mind that in equilibrium $U_{1S}(\mathrm{eq})\gg U_{12S}^{(1)}(\mathrm{eq})\gg U_{12S}^{(2)}(\mathrm{eq})$.

A. Resonance energy increase in a "molecule-substrate" subsystem

Here we consider modification of the dispersion energy in a "molecule-substrate" subsystem due to the additional molecule near the selected subsystem, see Fig. 1. We define the dimensionless parameters $r_1=R/d$ and $z_1=z/d$ so that $R'=d\sqrt{r_1^2+4z_1}$. Thus, the geometric factor in Eq. (25) is

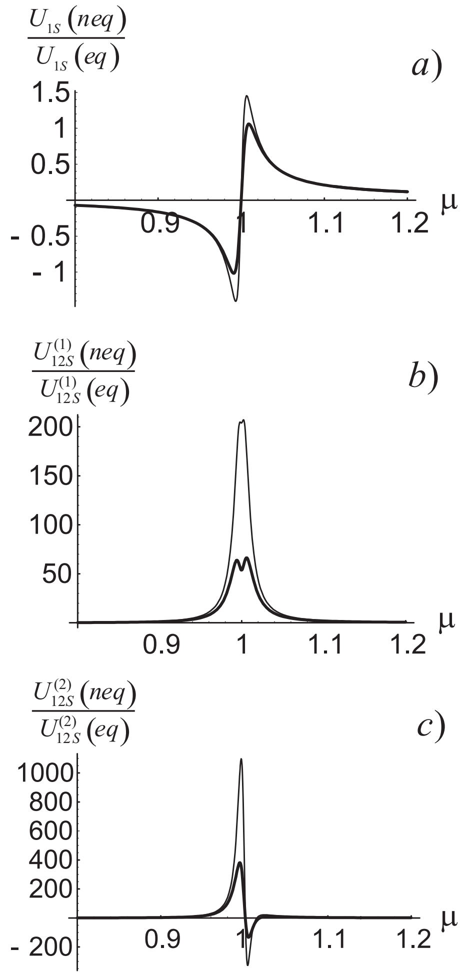

FIG. 2. Universal ratios $U_{1S}(\text{neq})/U_{1S}(\text{eq})$-a), $U_{12S}^{(1)}(\text{neq})/U_{12S}^{(1)}(\text{eq})$-b) and $U_{12S}^{(2)}(\text{neq})/U_{12S}^{(2)}(\text{eq})$-c) as the functions of the mismatch parameter μ at $T_G=300$ K and $T_S=800$ K for two different relaxation molecular parameters $\Gamma=0.01\omega_{1,2}$ (thick line) and $\Gamma=0.005\omega_{1,2}$ (thin line).

$$\frac{(2+3\,\text{Cos}\,2\theta+3\,\text{Cos}\,2\varphi)}{(RR')^3} = \frac{8-6[(z_1-1)^2/r_1^2+(z_1+1)^2/(r_1^2+4z_1)]}{d^6(r_1\sqrt{r_1^2+4z_1})^3}, \quad (31)$$

where we have taken into account that $\sin\varphi=(z+d)/R'$, $\cos\varphi=r_{\parallel}/R'$, $\sin\theta=(z-d)/R$, $\cos\theta=r_{\parallel}/R$, so that

$$2+3\,\text{Cos}\,2\theta+3\,\text{Cos}\,2\varphi = 8-6[(z-d)^2/R^2+(z+d)^2/(R^2+4zd)]. \quad (32)$$

Because in Eq. (26) the geometric factor $(R')^6=d^6(r_1^2+4z_1)^3$ we have different "d"-dependence in Eqs. (24)–(26). We consider the total energy in this case

$$U_{1S}(d,r_1,z_1,T_S,T_G) = U_{1S}(\text{eq}) + U_{12S}^{(1)}(\text{eq}) + U_{12S}^{(2)}(\text{eq}) + U_{1S}(\text{neq}) + U_{12S}^{(1)}(\text{neq}) + U_{12S}^{(2)}(\text{neq}). \quad (33)$$

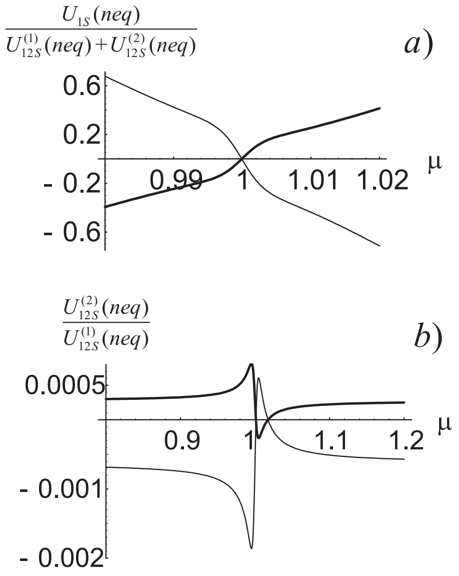

FIG. 3. Relative contribution of the nonequilibrium terms $U_{1S}(\text{neq})/[U_{12S}^{(1)}(\text{neq})+U_{12S}^{(2)}(\text{neq})]$-a) and $U_{12S}^{(2)}(\text{neq})/U_{12S}^{(1)}(\text{neq})$-b) in the expression for total energy, Eq. (30), as the functions of the mismatch parameter μ. The temperatures are $T_G=300$ K and $T_S=1000$ K. The geometry is set by $d=10^{-6}$ cm, $r_1=0.1$, $z_1=1.1$-thick line and $d=10^{-6}$ cm, $r_1=0.1$, $z_1=1$-thin line.

The force acting on the first molecule is $f=-\partial U_{1S}(d,r_1,z_1,T_S,T_G)/\partial d$.

In order to study relative contribution of the nonequilibrium terms in Eq. (33) we calculate the ratios $U_{1S}(\text{neq})/[U_{12S}^{(1)}(\text{neq})+U_{12S}^{(2)}(\text{neq})]$ and $U_{12S}^{(2)}(\text{neq})/U_{12S}^{(1)}(\text{neq})$. Figure 3 demonstrates these ratios as the functions of the mismatch parameter μ at two different fixed mutual locations of molecules. Figure 3(a) clearly shows that the three-body term may be larger than the two-body term of the noneqiulibrium energy in case of the resonance condition $\omega_1\approx\omega_2\approx\omega_{QP}$ when $\mu\approx1$. The relative contribution of the three-body terms $U_{12S}^{(1)}(\text{neq})$ and $U_{12S}^{(2)}(\text{neq})$ is characterized by Fig. 3(b). The ratio $U_{12S}^{(2)}(\text{neq})/U_{12S}^{(1)}(\text{neq})$ is not depends on the distance d between the first molecule and sample as it follows from Eqs. (25), (26), and (31).

From Fig. 3 it is directly follows that the three-body terms of energy may be larger than the two-body term in a system out of equilibrium. To compare the terms describing the nonequilibrium part in total energy [Eq. (33)] with the energy in equilibrium we introduce the following ratio:

$$\tilde{U}_{1S} = \frac{U_{1S}(\text{neq}) + U_{12S}^{(1)}(\text{neq}) + U_{12S}^{(2)}(\text{neq})}{U_{1S}(\text{eq})}. \quad (34)$$

This relative value of energy is a function on the distance d due to different dependence of the related terms of energy in Eqs. (24)–(26). The total sum of terms in numerator of Eq. (34) corresponding to the nonequilibrium interaction can be normalized to the total sum of equilibrium energy $U_{1S}(\text{eq})+U_{12S}^{(1)}(\text{eq})+U_{12S}^{(2)}(\text{eq})$, but the sum of terms related to the three-body interaction $U_{12S}^{(1)}(\text{eq})+U_{12S}^{(2)}(\text{eq})$ accounts for negligible value (about 1%) from the value of the two-body term $U_{1S}(\text{eq})$. Figure 4 exemplifies the relative total energy $\tilde{U}_{1S}$ at

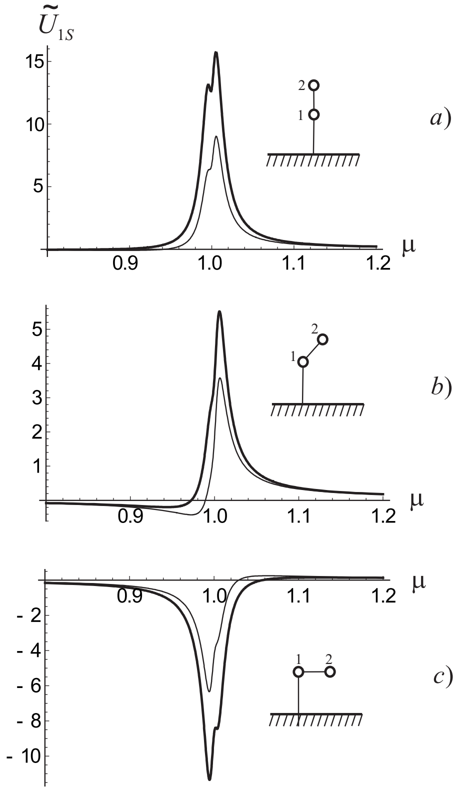

FIG. 4. Relative energy $\tilde{U}_{1S}$ at different distance d ($d=10^{-6}$ cm—thin line, $d=8\times10^{-7}$ cm—thick line) of the first molecule from surface at various spatial locations of the second molecule as the function of the mismatch parameter μ. The mutual geometry of the molecules and sample surface are clarified in the inserts in figures (a) at $r_1=0.1$, $z_1=1.1$, (b) at $r_1=0.1$, $z_1=1.071$, and (c) at $r_1=0.1$, $z_1=1$. The temperatures are $T_G=300$ K and $T_S=1000$ K.

different distance d of the first molecule from surface at various spatial locations of the second molecule.

The mutual geometry of the molecules and sample surface are clarified in the inserts in Figs. (a)–(c). A resonance increase of the dispersion interaction in a system out of equilibrium is obviously seen from the pictures. The force acting on the first molecule can change from attractive to repulsive in dependence on the geometry of interaction. A distance between two molecules is fixed in Figs. (a)–(c). Proximity of the subsystem eigenfrequencies is the necessary condition of the resonance under our consideration.

A possible range for the energy increase $\tilde{U}_{1S}$ at various distances from the surface and fixed temperatures $T_G=300$ K, $T_S=1000$ K is demonstrated in Fig. 5(a). Figure 5(b) shows a possible range for the energy at various temperatures T_S.

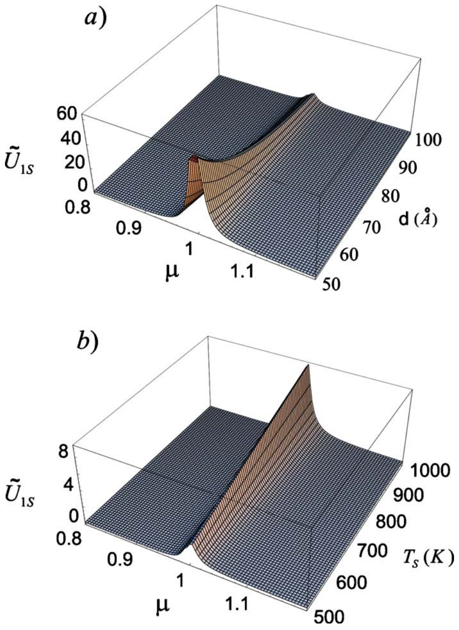

FIG. 5. (Color online) Possible range for the energy $\tilde{U}_{1S}$ at various distances d of the first molecule from the surface and fixed temperatures $T_G=300$ K, $T_S=1000$ K (a) at $r_1=0.1$, $z_1=1.1$. Figure 5(b) shows a possible range for the energy at different temperature T_S of substrate at fixed distance $d=10^{-6}$ cm, $r_1=0.1$, $z_1=1.1$ and $T_G=300$ K.

B. Resonance energy increase in a subsystem of two molecules near a substrate

It is clear, see Fig. 1, we may consider various two-body subsystems under the action of the third body. Here we consider modification of the previous results considering a subsystem “molecule-molecule” in the presence of a substrate. It is useful to define other dimensionless parameters $d_2=d/R$ and $z_2=z/R$ so that $R'=R\sqrt{1+4z_2d_2}$. Thus, the geometrical factor in Eq. (25)

$$\frac{(2+3\,\mathrm{Cos}\,2\theta+3\,\mathrm{Cos}\,2\varphi)}{(RR')^3} = \frac{8-6[(z_2-d_2)^2+(z_2+d_2)^2/(1+4z_2d_2)]}{R^6(\sqrt{1+4z_2d_2})^3}. \qquad (35)$$

Because in Eq. (26) the geometrical factor $(R')^6=R^6(1+4z_2d_2)^3$ we have the same “R” dependence in Eqs. (25) and (26). We consider the total energy in this case

$$U_{12}(R,d_2,z_2,T_S,T_G) = U_{12}(\mathrm{eq}) + U_{12S}^{(1)}(\mathrm{eq}) + U_{12S}^{(2)}(\mathrm{eq}) + U_{12S}^{(1)}(\mathrm{neq}) + U_{12S}^{(2)}(\mathrm{neq}). \qquad (36)$$

The force acting on the first molecule is $f=-\partial U_{12}(R,d_2,z_2,T_S,T_G)/\partial R$.

We introduce the following ratio:

$$\tilde{U}_{12} = \frac{U_{12S}^{(1)}(\mathrm{neq}) + U_{12S}^{(2)}(\mathrm{neq})}{U_{12}(\mathrm{eq})}. \qquad (37)$$

It should be noted that the relative energy $\tilde{U}_{12}$ is not function on the distance R between two molecules. Figure 6 exemplifies the resonance energy $\tilde{U}_{12}$ increase in case of various mutual locations of two molecules near surface at different temperature T_S. The mutual geometry of the molecules and sample surface is clarified in the corresponding inserts in this figure.

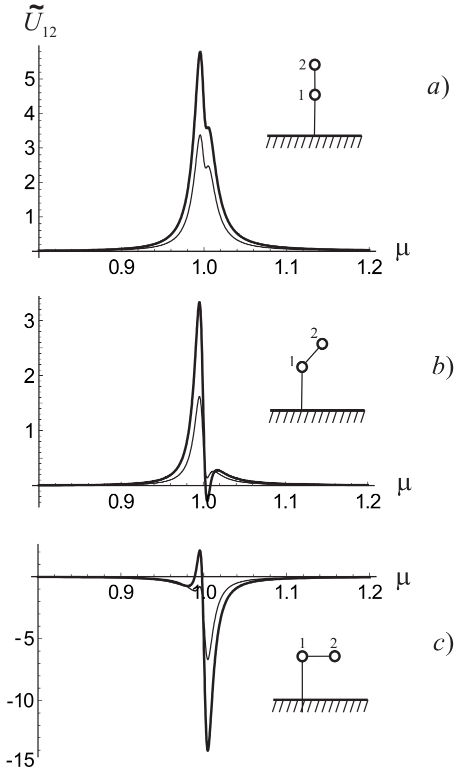

FIG. 6. Resonance energy $\tilde{U}_{12}$ increase as the function of the mismatch parameter μ in case of various locations of two molecules near surface at fixed temperatures $T_G=300$ K, $T_S=1000$ K. The mutual geometry of the molecules and sample surface is clarified in the corresponding inserts. In figure (a) at $d_2=1$, $z_2=2$ (thin line), $d_2=0.8$, $z_2=1.8$ (thick line), (b) at $d_2=1$, $z_2=1.71$ (thin line), $d_2=0.8$, $z_2=1.51$ (thick line), (c) at $d_2=z_2=1$ (thin line), $d_2=z_2=0.8$ (thick line).

Figure 7 shows the resonance energy $\tilde{U}_{12}$ increase in case of different damping of molecules and at various mutual locations of two molecules near surface. We recall that the dimensionless parameters d_2, z_2 determine geometry of the problem in this case.

A possible range for the energy $\tilde{U}_{12}$ at various normalized distances d_2 from the surface and fixed location of the second molecule z_2 at the temperatures $T_G=300$ K, $T_S=1000$ K is demonstrated in Fig. 8(a). Figure 8(b) shows a possible range for the energy at various temperature T_S and fixed geometry and $T_G=300$ K.

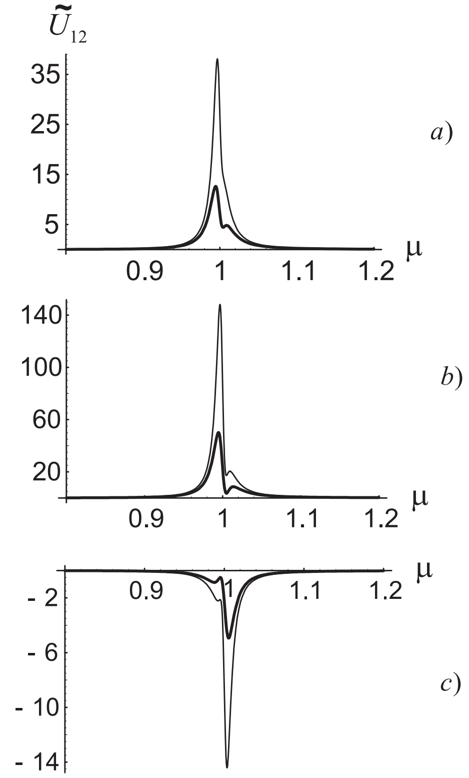

FIG. 7. Resonance energy $\tilde{U}_{12}$ increase as the function of the mismatch parameter μ in case of different damping of molecules $\Gamma=0.01$ s^{-1} (thick line) and $\Gamma=0.005$ s^{-1} (thin line) at various mutual locations of two molecules near surface and at fixed temperatures $T_G=300$ K, $T_S=1000$ K. In figure (a) at $d_2=0.5$, $z_2=1.5$, (b) at $d_2=1.25$, $z_2=0.25$, (c) at $d_2=z_2=1$.

C. Nonlocal corrections

It should be emphasized that an accounting of nonlocal material response leads to new interesting results. Some important nonlocal effects in relation to the van der Waals forces and radiative heat transfer are discussed, for example, in Ref. [17–24]. In particular, for a case of good conductors the dispersion force saturates at the short distances characterizing by the Thomas-Fermi screening length and deviates from the local curve at the distances compare with the mean free length of electrons in metals [26]. The reason of that is a saturation of the spectral power density of fluctuating electromagnetic fields generated by matter described by a nonlocal response. A nonlocal description of matter allows calculate the van der Waals potential at all distances among microparticles and a substrate. Because the potential is fully determined by the fluctuating electromagnetic fields, a related knowledge of the properties of the fields is a key element in the theory. One of the most essential characteristics of fluctuating electromagnetic fields is the density of states (or spectral power density) near the surface of solids generating such fields. Various ways to calculate the spectral properties of thermally stimulated fields of solids are described, for instance, in review [27].

A simplest way to describe nonlocality may be found in literature, see, for instance [28]. In a quasistatic approach $c\to\infty$ the Fresnel coefficients in Eq. (18) are expressed as follows

$$r_{12}^{p}(p,\omega)=\frac{1-Z^{p}(p,\omega)}{1+Z^{p}(p,\omega)},\qquad Z^{p}(p,\omega)=\frac{2p}{\pi}\int_{0}^{\infty}\frac{dq}{k^{2}\varepsilon_{\ell}(\omega,k)}, \tag{38}$$

where $Z^{p}(p,\omega)$ is the impedance, $\varepsilon_{\ell}(\omega,k)$ is the longitudinal dielectric function, $k^2=p^2+q^2$ is the wave number within a material domain.

For good conductors in semiclassical limit $k\ll 2k_F$ the Lindhard-Mermin dielectric function is

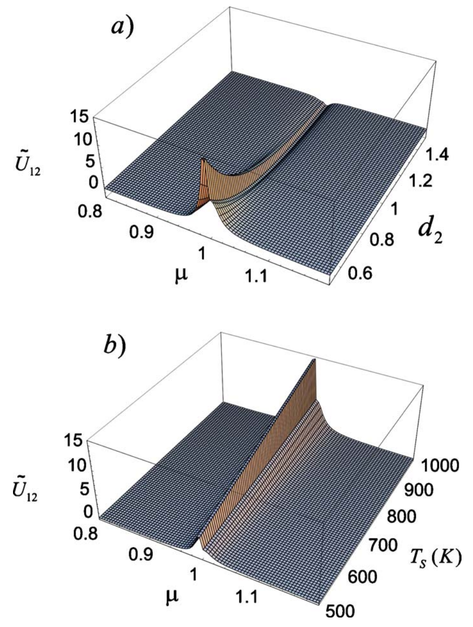

FIG. 8. (Color online) Possible range for the energy $\tilde{U}_{12}$ at various normalized distances d_2 from the surface and at various mismatch parameter μ at fixed location of the second molecule $z_2=1.5$ and at the fixed temperatures $T_G=300$ K, $T_S=1000$ K (a). Figure 8(b) shows a possible range for the energy at various T_S and μ at fixed geometry ($z_2=1.5$, $d_2=0.5$) and $T_G=300$ K.

$$\varepsilon_\ell(k,\omega)=\varepsilon_b(\omega)+\frac{3\omega_P^2}{\omega+i\nu}\frac{u^2 f_\ell(0,u)}{\omega+i\nu f_\ell(0,u)},$$

$$f_\ell(0,u)\approx 1-\frac{1}{2}u\ln\frac{u+1}{u-1}, \qquad (39)$$

where $\varepsilon_b(\omega)$ is the background dielectric constant associated with the bound electrons, ν is the electron-phonon collision frequency, ω_p is the plasma frequency, $u=(\omega+i\nu)/kv_F=1/k\ell$, $\ell=v_F/(\omega+i\nu)$, k_F, v_F are the Fermi wave number and velocity.

Importance of the space dispersion for both longitudinal and transverse components of the dielectric function at low temperatures were indicated in Ref. [18,19].

Besides, it is easy to find models for dielectrics functions in case of plasma, see, for instance [29,30]. For weakly ionized plasma in classical approach when $k_BT_\alpha \gg E_{F\alpha}$, where $E_{F\alpha}=(3\pi^2N_\alpha)^{2/3}\hbar^2/2m_\alpha$ is the Fermi energy at $\omega \gg k\mathrm{v}_{T\alpha}$ we have

$$\varepsilon_\ell(\omega,k)=1-\sum_\alpha \frac{\omega_{P\alpha}^2}{\omega^2}\left(1+3\frac{k^2\mathrm{v}_{T\alpha}^2}{\omega^2}\right)+i\left[\sqrt{\frac{\pi}{2}}\frac{\omega\omega_{P\alpha}^2}{k^3\mathrm{v}_{T\alpha}^3}\exp\left(-\frac{\omega^2}{2k^2\mathrm{v}_{T\alpha}^2}\right)+\frac{\omega_{P\alpha}^2\nu_{\alpha n}}{\omega^3}\right], \qquad (40)$$

where α means a sort of particle, $\omega_{P\alpha}=\sqrt{4\pi e^2N_\alpha/m_\alpha}$ is the plasma frequency of the αth particle, N_α is the concentration, $\mathrm{v}_{T\alpha}=\sqrt{3k_BT_\alpha/m_\alpha}$ is the thermal velocity of the αth particle, $\nu_{\alpha n}$ is the frequency of collisions of αth particle with neutral atoms.

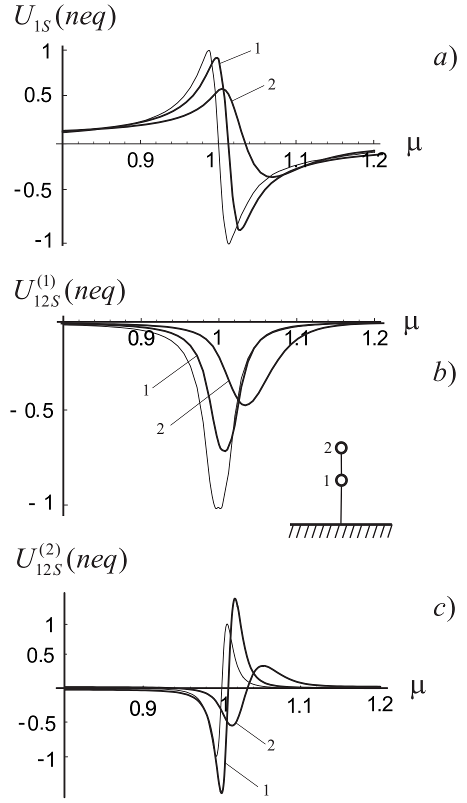

FIG. 9. Normalized energies $U_{1S}(\mathrm{neq})$ (a) and $U_{12S}^{(1,2)}(\mathrm{neq})$ (b,c) from Eqs. (21)–(23) as the functions of the mismatch parameter μ for two identical atoms with a polarizabilities [Eq. (28)] $(\omega_{1,2}=(\omega_P/\sqrt{2})\cdot\mu)$ near a plasma halfspace characterized by reflectivity [Eq. (38)] and dielectric function [Eq. (40)] with $\omega_P=10^{15}$ rad/s, $\nu_{en}=0.01\omega_P$, $\mathrm{v}_{Te}=3\times10^7$ cm/s at $T_G=300$ K and $T_S=2000$ K. The arrows correspond to different distances of the first atom from plasma surface ($d=5\times10^{-6}$ cm^{-1} and $d=10^{-6}$ cm^{-2}). Geometry is depicted in the insert. A distance between two atoms $R=0.1d$. Corresponding energies $U_{1S}(\mathrm{neq})$, $U_{12S}^{(1,2)}(\mathrm{neq})$ in local approach are shown by thin curves. Normalization is done to a maximum value in each graphic.

The first term of the imaginary part in Eq. (40) is stipulated by Cherenkov's absorption of electromagnetic waves in plasma and the second one describes the energy dissipation due to collisions of electrons and ions with atoms.

Figure 9 shows the normalized energies $U_{1S}(\mathrm{neq})$-(a) and $U_{12S}^{(1,2)}(\mathrm{neq})$-(b,c) from Eqs. (21)–(23) as the functions of the mismatch parameter μ for two identical atoms with polarizabilities [Eq. (28)] $[\omega_{1,2}=(\omega_P/\sqrt{2})\cdot\mu]$ near a plasma halfspace characterized by the reflectivity [Eq. (38)] and by the dielectric function [Eq. (40)]. We take into account only electron response ($\alpha=e$) in Eq. (40) with $\omega_P=5305$ cm^{-1} ($\sim10^{15}$ rad/s), $\nu_{en}=0.01\omega_P$, $\mathrm{v}_{Te}=3\times10^7$ cm/s. The arrows correspond to two distances of the first atom from plasma surface $d=5\times10^{-6}$ cm^{-1}) and $d=1\times10^{-6}$ cm^{-2}). Geometry is depicted in the insert. A fixed distance between two atoms $R=0.1d$. The energies $U_{1S}(\mathrm{neq})$, $U_{12S}^{(1,2)}(\mathrm{neq})$ in a local approach are shown in this figure by thin curves.

It is seen the shift of the curves in nonlocal approach to the higher frequency range. The smaller the distance d the larger is the displacement. The matter is that the Fresnel coefficient [Eq. (38)] is expressed via the longitudinal dielectric function determining tensors $\beta_{ik}(\omega)$ in [Eq. (18)]. From the expression (18) it follows that the principal contributions to the integral give the lateral wave numbers $p \sim 1/2d$ due to the exponential factor. From the dispersion relation for the quasistatic surface waves [31] $Z_P(p,\omega)=-1$ it is easy to find that the larger p the larger is the frequency ω of the corresponding Coulomb surface mode. Thus, in accordance with Fig. 9, the smaller d the larger are p giving principal contribution to $\beta_{ik}(\omega)$ and the larger is the frequency of the quasistatic Coulomb resonance and, as a consequence, the larger are the eigenfrequencies $\omega_{1,2}=\omega_{QP}\cdot\mu$ used in our calculations.

In the presence of spatial dispersion in case of dielectrics and semiconductors [32–35,38] for frequency range $\Delta\omega$ near the excitation frequency ω_{ex}, the dielectric function may be approximated by the form

$$\varepsilon(\omega,k) = \varepsilon_B + \frac{\omega_P^2}{\omega_{ex}^2 - \omega^2 + Dk^2 - i\gamma\omega}, \tag{41}$$

where ε_B is the background dielectric constant, ω_{ex} is the transverse resonance frequency of TO phonon or the resonance frequency of an exciton, ω_P is a measure of the oscillator strength, γ is the damping constant, $D=\hbar\omega_{ex}/m^*$, where m^* is the exciton mass. The longitudinal excitation occurs at $\omega_L^2=\omega_T^2+Dk^2+\omega_P^2/\varepsilon_B$, $k^2=p^2+q^2$.

At given frequency ω there exist two transverse and one longitudinal modes. They are follows from the dispersion relations $c^2k^2/\omega^2=\varepsilon(\omega,k)$ and $\varepsilon(\omega,k)=0$, correspondingly. The three roots are given by

$$\begin{aligned} q_{1,2}^2 &= (1/2)[(\Gamma_B^2 + \varepsilon_B k_0^2 - p^2) \\ &\quad \pm \sqrt{(\Gamma_B^2 - \varepsilon_B k_0^2 + p^2)^2 + 4\omega_P^2\omega^2/c^2D}], \\ q_3^2 &= \Gamma_B^2 - \omega_P^2/\varepsilon_B D, \end{aligned} \tag{42}$$

where $\Gamma_B^2=(\omega^2-\omega_{ex}^2-Dp^2+i\gamma\omega)/D$, $k_0=\omega/c$.

Expressions for the Fresnel coefficients may be found in [32–37]. For instance, the Fresnel coefficient for p-polarized waves is given by

$$r_{12}^P(\omega,p) = \frac{\sqrt{k_0^2 - p^2} + k_0/Q}{\sqrt{k_0^2 - p^2} - k_0/Q}, \tag{43}$$

where

$$Q = \Gamma_B - \frac{p^4 + p^2(q_1^2 + q_1q_2 + q_2^2) + (q_1 + q_2)q_1q_2q_3}{p^2(q_1 + q_1q_2 - q_3) + q_1q_2q_3}. \tag{44}$$

It should be noted that the reflectivity [Eq. (43)] has been derived with the help of the additional boundary condition (ABC) $\vec{P}|_{z=0}+i\Gamma_B\partial\vec{P}/\partial z|_{z=0}=0$. Another form for the Fresnel coefficients was obtained in [35] using the ABC for the density of nonlocal polarization $\vec{P}|_{z=0}=0$. The p-polarized reflection amplitude is

$$r_{12}^P(\omega,p) = -r_{12}^S(\omega,p)\left[\frac{n_1^2(w_0 + w_2)(w_2w_3 + p^2) - n_2^2(w_0 + w_1)(w_1w_3 + p^2)}{n_1^2(w_0 - w_2)(w_2w_3 + p^2) - n_2^2(w_0 - w_1)(w_1w_3 + p^2)}\right], \tag{45}$$

where in case of the dielectric function [Eq. (41)] $w_3=q_3$ from [Eq. (42)] for the longitudinal wave, $w_i=\sqrt{n_i^2(\omega/c)^2-p^2}$, $(i=1,2)$ for the transverse waves, $w_0=\sqrt{(\omega/c)^2-p^2}$,

$$r_{12}^S(\omega,p) = [(w_0 - w_1)(w_2 - w_0)]/[(w_1 + w_0)(w_2 + w_0)], \tag{46}$$

$$n_{1,2}^2 = \frac{1}{2}\left[\frac{(\omega^2 - \omega_{ex}^2 + \varepsilon_B Dk_0^2 + i\gamma\omega)}{Dk_0^2} \pm \sqrt{\left(\frac{(\omega^2 - \omega_{ex}^2 + \varepsilon_B Dk_0^2 + i\gamma\omega)}{Dk_0^2}\right)^2 + \frac{4[\omega_P^2 + \varepsilon_B(\omega_{ex}^2 - \omega^2 - i\gamma\omega)]}{Dk_0^2}}\right] \tag{47}$$

for two different transverse waves inside the spatially dispersive matter.

In local approach $(D=0)$ we used the parameters corresponding to *ZnSe* $\omega_{ex}=\omega_{TO}=200$ cm^{-1}, $\varepsilon_B=\varepsilon_\infty=5.8$, $\omega_P^2=(\varepsilon_0-\varepsilon_\infty)\omega_{TO}^2$, $\varepsilon_0=9.06$, $\gamma=0.02\omega_{TO}$. Nonlocality was taken into account by the parameter $D=\hbar\omega_{TO}/m_e$ in Eq. (41). In this case the eigenfrequencies of molecules were chosen as $\omega_{1,2}=\omega_{QP}\cdot\mu$, where $\omega_{QP}\approx 243$ cm^{-1} is the root of the dispersion equation $\mathrm{Re}[\varepsilon(\omega)]+1=0$.

Taking into account that the formulas (43) and (45) for the p-polarized reflection amplitudes were found for different ABC it is worth to compare their influence to the problem of our interest. Figure 10 exemplifiers the universal ratios $U_{1S}(\mathrm{neq})/U_{1S}(\mathrm{eq})$ and $U_{12S}^{(1,2)}(\mathrm{neq})/U_{12S}^{(1,2)}(\mathrm{eq})$ from Eqs. (19)–(23) as the functions of the mismatch parameter μ at $T_G=300$ K and $T_S=700$ K for two different models of the nonlocal reflectivities [Eqs. (43) and (45)]. The dashed lines represent the same ratios, but in local approach of the reflectivity. All graphics were calculated at the same distance $d=5\times10^{-6}$ cm of the first molecule from the surface of ZnSe substrate. Geometry is depicted in the insert. The distance between two molecules is $R=0.1d$.

It is seen from this figure and our study that both models of the reflectivities [Eqs. (43) and (45)] give similar results at

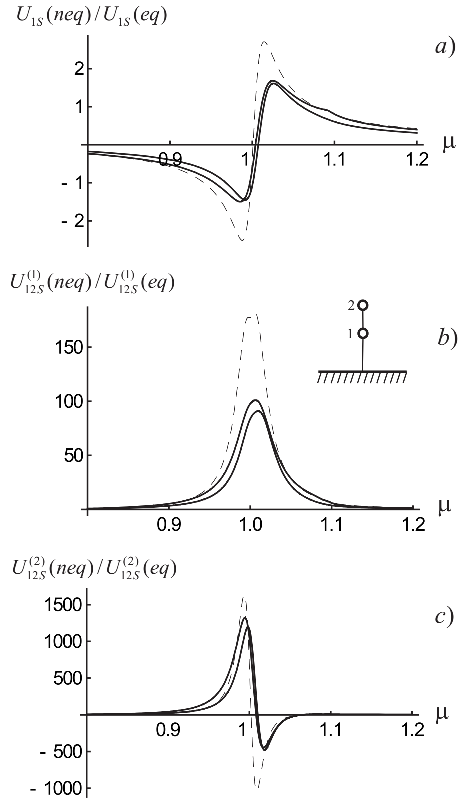

FIG. 10. Universal ratios $U_{1S}(\text{neq})/U_{1S}(\text{eq})$ (a) and $U^{(1,2)}_{12S}(\text{neq})/U^{(1,2)}_{12S}(\text{eq})$ (b, c) from Eqs. (19)–(23) as the functions of the mismatch parameter μ at $T_G=300$ K and $T_S=700$ K for two different models (thick curves) of the nonlocal reflectivities [Eqs. (43) and (45)] corresponding to different ABC. The dashed lines represent the same ratios, but in local approach of the reflectivity. All graphics were calculated at the same distance $d=5\times10^{-6}$ cm of the first atom from the surface of ZnSe substrate. Geometry is depicted in the insert. A distance between two atoms $R=0.1d$.

distances of molecules from surface substrate larger than $d=10^{-6}$ cm. At smaller distances the discrepancies are quite essential.

We note that it is possible to study the similar effects in case of excitonic transition in matter. For ZnSe corresponding parameters may be found in [32,33,35,37,38].

IV. CONCLUSIONS

A resonance enhancement of the van der Waals interaction was studied in the three-body systems out of thermal equilibrium. One of the bodies occupies a half-space. A material of the half-space may be characterized both by local or nonlocal optical reflectivities. An analytical expression for energy depends on the geometrical configuration, electrodynamical properties of particles and substrate and on a difference in temperature between thermostats. Formulas relating to the systems in equilibrium directly follow from the general expression. In particular, the known expression for the energy of three-body system obtained by McLachlan [25] for the first time. The resonance increase of the van der Waals energy of molecules near surface was found in our calculations as well as in the case of multiparticle interactions in a gaseous media [4,5]. Such an enhancement occurs in the closeness of eigenmodes of the subsystems kept at different temperatures. At fixed geometrical locations of the interacting particles nearby substrate the value of enhancement depends on a characteristic frequency range of eigenmodes of whole system, on dampings and on a difference in temperature. The most prominent resonance effect manifests itself in range of frequencies of the rovibrational molecular transitions and corresponding spectral range of excitation of the surface polaritons due to the temperature factor $\Omega(T_S,T_G)=\coth(\hbar\omega/2T_S)-\coth(\hbar\omega/2T_G)$ in formulas (24)–(26) at reasonable temperatures. We considered different two-body subsystems of the whole three-body system. For instance, the resonance energy increase was established in the "molecule-substrate" subsystem due to the additional molecule nearby and in the subsystem of two molecules near a substrate. Different constituents of whole system exchange by energy among itself most effectively via the frequency channels in closeness of eigenmodes of the subsystems An opportunity of the resonance increase of the dispersion interaction between molecule and substrate under the action of another molecule nearby was examine in case of nonlocal description of the substrate reflectivity. Despite of different ABC the resonance magnification occurs in the system of interest. The resonance enhancement of the dispersion energy in a three-body system depends on the geometrical configuration, electromagnetic properties of subsystems and on the temperature difference among subsystems.

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[1] V. Efimov, Phys. Lett. B **33**, 563 (1970).
[2] E. Braaten and H.-W. Hammer, Phys. Rep. **428**, 259 (2006).
[3] T. Kraemer, M. Mark, P. Waldburger *et al.*, Nature (London) **440**, 315 (2006).
[4] I. Dorofeyev, Phys. Lett. A **340**, 251 (2005).
[5] I. Dorofeyev, "Energy and momentum transfer between microparticles and solids," Les Houches Physics School on "Nanoscale thermal radiation: forces, heat transfer and coherence" (France, May 21–25, 2007) http://www.em2c.ecp.fr/TRN07/.
[6] Yu. S. Barash and V. L. Ginzburg, Sov. Phys. Usp. **18**, 305 (1975).
[7] Yu. S. Barash and V. L. Ginzburg, Sov. Phys. Usp. **27**, 467 (1984).
[8] Yu. S. Barash, *The van der Waals Forces* (Nauka, Moscow, 1988) (in Russian).
[9] J. N. Israelachvili, *Intermolecular and Surface Forces*

(Academic, London, 1991).
[10] B. Linder, J. Chem. Phys. **44**, 265 (1966).
[11] Bruno Linder, in *Intermolecular Forces*, edited by Joseph O. Hirschfelder (Interscience Publishers, New York, 1967).
[12] J. P. Rosenkrans, B. Linder, and R. A. Kromhout, J. Chem. Phys. **49**, 2927 (1968).
[13] F. G. Bass and V. Z. Lozovski, Phys. Rev. B **58**, 10721 (1998).
[14] A. E. Cohen and S. Mukamel, Phys. Rev. Lett. **91**, 233202 (2003).
[15] I. A. Dorofeyev, J. Phys. A **31**, 4369 (1998).
[16] M. Antezza, L. P. Pitaevskii, S. Stringari, and V. B. Svetovoy, Phys. Rev. Lett. **97**, 223203 (2006).
[17] R. Esquivel and V. B. Svetovoy, Phys. Rev. A **69**, 062102 (2004).
[18] B. E. Sernelius, Phys. Rev. B **71**, 235114 (2005).
[19] V. B. Svetovoy and R. Esquivel, Phys. Rev. E **72**, 036113 (2005).
[20] R. Esquivel-Sirvent, C. Villarreal, W. L. Mochán, A. M. Contreras-Reyes, and V. B. Svetovoy, J. Phys. A **39**, 6323 (2006).
[21] P.-O. Chapuis, S. Volz, C. Henkel, K. Joulain, and J.-J. Greffet, Phys. Rev. B **77**, 035431 (2008).
[22] L. P. Pitaevskii, Phys. Rev. Lett. **101**, 163202 (2008).
[23] V. B. Svetovoy, Phys. Rev. Lett. **101**, 163603 (2008).
[24] D. A. R. Dalvit and S. K. Lamoreaux, Phys. Rev. Lett. **101**, 163203 (2008).
[25] A. D. McLachlan, Mol. Phys. **6** 423 (1963); **7**, 381 (1964).
[26] I. Dorofeyev, Phys. Lett. A **363**, 251 (2007).
[27] E. A. Vinogradov and I. A. Dorofeyev, Phys. Usp. **52**, 425 (2009).
[28] G. W. Ford and W. H. Weber, Phys. Rep. **113**, 195 (1984).
[29] E. M. Lifshitz and L. P. Pitaevskii, *Physical Kinetics* (Pergamon, Oxford, 1981).
[30] A. F. Aleksandrov, L. S. Bogdankevich, and A. A. Rukhadze, *Principles of Plasma Electrodynamics* (Springer-Verlag, Berlin; New York, 1984).
[31] R. N. Ritchie and A. L. Marusak, Surf. Sci. **4**, 234 (1966).
[32] A. A. Maradudin and D. L. Mills, Phys. Rev. B **7**, 2787 (1973).
[33] G. S. Agarwal, D. N. Pattanayak, and E. Wolf, Phys. Rev. B **10**, 1447 (1974).
[34] J. T. Foley and A. J. Devaney, Phys. Rev. B **12**, 3104 (1975).
[35] M. R. Philpott, Phys. Rev. B **14**, 3471 (1976).
[36] P. J. Feibelman, Prog. Surf. Sci. **12**, 287 (1982).
[37] R. Ruppin, Phys. Rev. B **29**, 2232 (1984).
[38] E. A. Vinogradov, Phys. Usp. **45**, 1213 (2002).