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# Electronic friction forces on molecules moving near metals

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It is well known that molecules feel a long-ranged attractive force to metals which arises from the interaction of various molecular charges with their metal-induced ''image charges.'' Here we calculate (in this image charge model) the friction force coefficients for molecules moving near a metal. We consider the cases of ions, polar molecules, and spherical atoms. [S0163-1829(97)01732-3]

## I. INTRODUCTION

Frictional forces on moving molecules neighboring a metallic conductor have been of considerable interest. The pioneering work on long-ranged static forces was done by Casimir,[1] Lifshitz and co-workers,[2,3] and later by Dzialoshinskii, Lifshitz, and Pitaevskii[4] who used quantum electrodynamic field theory propagator methods. Teodorovich and later Levitov[5] extended the propagator methods (virtual photon exchange) to shed new light on the sliding friction problem. Theoretical friction studies of physisorbed atoms on metallic substrates include both molecular dynamics (for the study of internal phonon friction)[6] and electronic friction (due to particle hole pair heating in the metal).[7,8] Experimental techniques (such as quality factor measurements on a quartz crystal microbalance) have measured the sliding friction forces in submonolayer adsorbed films.[9–11]

When a molecule is at a fixed position above a metal, the static forces on the molecule are due to the ''image charges'' within the metal, which describe the induced electric fields above the metal. If a molecule is moving with velocity $\mathbf{V}$, then the induced charges on the metal surface must also be moving. This motion of induced conductor charge must be accompanied by Ohm's law heating within the metal. Thus, as the molecule moves, there exists (in addition to the normal ''image'' attractive force) an induced friction force opposing the motion. To lowest order in the velocity, the friction force obeys $\mathbf{F}_{\rm friction}=-\mathbf{\Gamma}\cdot\mathbf{V}$. The friction tensor coefficients $\Gamma_{ij}$ depend on the properties of the molecule and on the conductivity properties of the metal. The friction is due to the conduction electrons in the metal. The ''image charges'' must follow the moving molecule. The situation is pictured in Fig. 1. This requires electronic currents which give rise to Ohmic heating in the metal. The heat generated inside the metal is the source of the friction force on the molecule outside the metal.

It is possible to determine the order of magnitude of static attractive forces and friction coefficients for *some cases* by using only the analysis of physical dimensions. For example, in the Gaussian c.g.s. units which will be employed in what follows, the height of a particle above the conductor $h\sim(\mathrm{cm})$; The charge $e\sim(\mathrm{gm}^{1/2}\,\mathrm{cm}^{3/2}\,\mathrm{sec}^{-1})$; The conductivity of the metal $\sigma\sim(\mathrm{sec}^{-1})$; The attractive potential $U\sim(\mathrm{gm\,cm}^2\,\mathrm{sec}^{-2})$, and the friction coefficient $\Gamma\sim(\mathrm{gm\,sec}^{-1})$.

Thus, merely by dimensional analysis for an Ohm's law heating model, if a particle with charge $e$ (say an ion) is at a height $h$ above the metal, then the attractive energy $U_e\sim(e^2h^{-1})$ does not depend on the conductivity $\sigma$ of the metal. The variation of the charged particle friction coefficient with the height $h$ above the metal and the conductivity $\sigma$ is given by $\Gamma_e\sim(e^2\sigma^{-1}h^{-3})$. For an uncharged polar molecule (say water $H_2O$) with a net dipole moment $p\sim(\mathrm{gm}^{1/2}\mathrm{cm}^{5/2}\mathrm{sec}^{-1})$, the attractive force does not depend on conductivity $U_p\sim(p^2h^{-3})$. The friction coefficient $\Gamma_p\sim(p^2\sigma^{-1}h^{-5})$. In what follows, these classical results will be computed in more detail, and the additional role of quantum fluctuations will be explored.

In Sec. II, the electric field fluctuation spectral functions will be computed employing the Coulomb Green's function solution to the point charge problem via the image charge. In imaginary time, these fluctuations can be used to compute a static attractive potential $U$. For real time, these fluctuations can be used to compute the friction coefficients. To illustrate the method, the attractive potential $U$ is calculated in Sec. III for the cases of a charged ion, a polar molecule, and a spherical atom. For the case of a charged ion, the friction coefficients are calculated in Sec. IV. For the case of a polar molecule the friction coefficients are calculated in Sec. V. The spherical atom friction coefficient is discussed in Sec. VI.

## II. ELECTRIC FIELD FLUCTUATIONS ABOVE A METAL

Neglecting electromagnetic radiation and other relativistic effects, we consider here only the nonrelativistic Coulomb

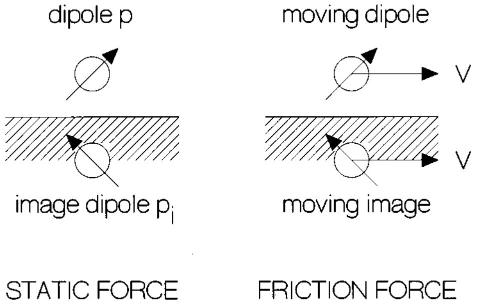

FIG. 1. Shown schematically is a stationary molecule with a permanent dipole moment $\mathbf{p}$ and its image dipole moment $\mathbf{p}_i$ in the metal. When the molecule (which could be of arbitrary shape) moves, the metallic surface charge (described by the image) flows with the velocity of the molecule. The resulting Ohm's law electronic current heats the metal, which yields a ''friction force'' on the atom.

interactions. Positions in space will be denoted by $\mathbf{r}=(x,y,z)$, and the half space $z<0$ will be presumed to be filled with a material described by a dielectric response function $\varepsilon(\zeta)$ at complex frequency $\zeta$; i.e., for retarded response functions $\mathrm{Im}(\zeta)>0$. For $z>0$ and $z'>0$, the retarded Coulomb Green's function is given by a vacuum term plus a condensed matter ''image'' term. The usual solution to the ''image problem'' is the Coulomb Green's function

$$G(\mathbf{r},\mathbf{r}',\zeta)=\frac{1}{R}-\left(\frac{\varepsilon(\zeta)-1}{\varepsilon(\zeta)+1}\right)\frac{1}{R_{\mathrm{image}}},$$

$$[z>0,z'>0,\mathrm{Im}(\zeta)>0], \quad (1)$$

where

$$R=|\mathbf{r}-\mathbf{r}'|=\sqrt{(x-x')^2+(y-y')^2+(z-z')^2}, \quad (2)$$

and

$$R_{\mathrm{image}}=|\mathbf{r}-\mathbf{r}'_{\mathrm{image}}|=\sqrt{(x-x')^2+(y-y')^2+(z+z')^2}. \quad (3)$$

For an Ohm's law conductor we choose

$$\varepsilon(\zeta)=1+\left(\frac{4\pi i\sigma}{\zeta}\right), \quad (|\zeta|\to i0^+). \quad (4)$$

Above any conductor, there will be fluctuations in the Coulomb potential $\phi(\mathbf{r},t)$; i.e., with

$$\mathbf{E}(\mathbf{r},t)=-\nabla\phi(\mathbf{r},t), \quad (5)$$

the spectral fluctuation function

$$S(\mathbf{r},\mathbf{r}',\omega)=\int_{-\infty}^{\infty}\left(\frac{dt}{2\pi}\right)\cos(\omega t)\mathrm{Re}\langle\phi(\mathbf{r},t)\phi(\mathbf{r}',0)\rangle, \quad (6)$$

is given by the fluctuation-dissipation theorem

$$S(\mathbf{r},\mathbf{r}',\omega)=-\left(\frac{\hbar}{2\pi}\right)\coth\left(\frac{\hbar\omega}{2k_BT}\right)\mathrm{Im}G(\mathbf{r},\mathbf{r}',\omega+i0^+). \quad (7)$$

Thus Eqs. (1), (3), and (7) imply

$$S(\mathbf{r},\mathbf{r}',\omega)=\left(\frac{\hbar\coth(\hbar\omega/2k_BT)}{2\pi\sqrt{(x-x')^2+(y-y')^2+(z+z')^2}}\right)\times\mathrm{Im}\left(\frac{\varepsilon(\omega+i0^+)-1}{\varepsilon(\omega+i0^+)+1}\right). \quad (8)$$

Equation (8) will be central to our calculation of friction coefficients for molecules above the metal.

For calculating static forces we shall require the Matsubara frequencies

$$\omega_n=\left(\frac{2\pi k_BT}{\hbar}\right)n, \quad n=0,\pm 1,\pm 2,\pm 3,\ldots, \quad (9)$$

and the imaginary time propagator; i.e.,

$$\langle\phi(\mathbf{r},-i\lambda)\phi(\mathbf{r}',0)\rangle_+=\left(\frac{\mathcal{G}(\lambda)}{\sqrt{(x-x')^2+(y-y')^2+(z+z')^2}}\right), \quad (10)$$

where

$$\mathcal{G}(\lambda)=k_BT\sum_{n=-\infty}^{\infty}\left(\frac{\varepsilon(i|\omega_n|)-1}{\varepsilon(i|\omega_n|)+1}\right)e^{-i\omega_n\lambda}, \quad (11)$$

and where the subscript + in Eq. (10) indicates imaginary time ordering. The relationship between the real time retarded fluctuation-dissipation theorem, as in Eqs. (7) and (8), and the imaginary time fluctuation theorem, as in Eqs. (10) and (11), is discussed in the literature.[4]

Having obtained the potential fluctuations, one may also obtain the electric field fluctuations using Eq. (5). For example, Eqs. (10) and (11) imply for electric field noise that at height $h$, i.e., $\mathbf{r}=(0,0,h)$, the nonzero correlations

$$\lim_{\mathbf{r}'\to\mathbf{r}}\langle E_x(\mathbf{r},-i\lambda)E_x(\mathbf{r}',0)\rangle_+=\lim_{\mathbf{r}'\to\mathbf{r}}\langle E_y(\mathbf{r},-i\lambda)E_y(\mathbf{r}',0)\rangle_+=\left(\frac{\mathcal{G}(\lambda)}{8h^3}\right), \quad (12)$$

$$\lim_{\mathbf{r}'\to\mathbf{r}}\langle E_z(\mathbf{r},-i\lambda)E_z(\mathbf{r}',0)\rangle_+=\left(\frac{\mathcal{G}(\lambda)}{4h^3}\right), \quad (13)$$

and for the potential itself

$$\lim_{\mathbf{r}'\to\mathbf{r}}\langle\phi(\mathbf{r},-i\lambda)\phi(\mathbf{r}',0)\rangle_+=\left(\frac{\mathcal{G}(\lambda)}{2h}\right). \quad (14)$$

Equations (12), (13), and (14) will be required for our computations of static forces.

For the friction coefficient, we shall need the spectral function for electric field fluctuations above the metal; i.e.,

$$S_{ij}(\mathbf{r},\mathbf{r}',\omega)=\int_{-\infty}^{\infty}\left(\frac{dt}{2\pi}\right)\cos(\omega t)\mathrm{Re}\langle E_i(\mathbf{r},t)E_j(\mathbf{r}',0)\rangle. \quad (15)$$

From Eqs. (5) and (6),

$$S_{ij}(\mathbf{r},\mathbf{r}',\omega)=\partial_i\partial'_jS(\mathbf{r},\mathbf{r}',\omega).$$

Equations (4), (8), and (15) imply the nonzero classical electric field noise

$$\lim_{\omega\to 0}\lim_{\mathbf{r}'\to\mathbf{r}}S_{xx}(\mathbf{r},\mathbf{r}',\omega)=\lim_{\omega\to 0}\lim_{\mathbf{r}'\to\mathbf{r}}S_{yy}(\mathbf{r},\mathbf{r}',\omega)=\left(\frac{k_BT}{16\pi^2\sigma h^3}\right), \quad (16)$$

and

$$\lim_{\omega\to 0}\lim_{\mathbf{r}'\to\mathbf{r}}S_{zz}(\mathbf{r},\mathbf{r}',\omega)=\left(\frac{k_BT}{8\pi^2\sigma h^3}\right). \quad (17)$$

## III. STATIC ATTRACTIVE POTENTIALS

If $H_{\rm int}$ denotes any perturbation Hamiltonian with an unperturbed vanishing mean value $\langle H_{\rm int}\rangle=0$, then second order thermal perturbation theory yields the (free) energy change

$$U=-\left(\frac{1}{2\hbar}\right)\int_0^\beta d\lambda\langle H_{\rm int}(-i\lambda)H_{\rm int}(0)\rangle_+ ,\qquad \beta=\left(\frac{\hbar}{k_BT}\right). \tag{18}$$

For an ion with charge $Ze$ above the metal

$$H_{\rm int}^{(Z)}=Ze\phi(\mathbf{r}), \tag{19}$$

the potential implied by Eqs. (11), (14), (18), and (19) is given by

$$U_Z=-\left(\frac{Z^2e^2}{4h}\right)\lim_{\omega\to 0}\left(\frac{\varepsilon(i|\omega|)-1}{\varepsilon(i|\omega|)+1}\right), \tag{20}$$

which is a well known classical result. For a metal obeying Eq. (4),

$$U_Z=-\left(\frac{Z^2e^2}{4h}\right)\quad(\text{conductor}), \tag{21}$$

which is a classical result usually derived in a much more simple way.

For a dipole interaction

$$H_{\rm int}^{(\mathbf{p})}=-\mathbf{p}\cdot\mathbf{E}(\mathbf{r}), \tag{22}$$

with a polar molecule where $\mathbf{p}$ may be regarded as a constant, Eqs. (11), (12), (13), (18), and (22) imply that

$$U_{\mathbf{p}}=-\left(\frac{p_x^2+p_y^2+2p_z^2}{16h^3}\right)\lim_{\omega\to 0}\left(\frac{\varepsilon(i|\omega|)-1}{\varepsilon(i|\omega|)+1}\right). \tag{23}$$

Hence, for a polar molecule near a metal

$$U_{\mathbf{p}}=-\left(\frac{|\mathbf{p}|^2}{8h^3}\right)(1+\cos^2\theta),\qquad p_z=|\mathbf{p}|\cos\theta\quad(\text{conductor}), \tag{24}$$

which can also be understood in classical image charge terms. The interaction $U_{\mathbf{p}}$ is such that the dipole moment $\mathbf{p}$ finds the *lowest energy* if it is oriented pointing away, $\theta=0$, or pointing toward, $\theta=\pi$, the conducting surface.

If the dipole moment undergoes quantum fluctuations, e.g., as for a spherical atom, then Eqs. (11), (12), (13), (18), and (22) imply

$$U_{\rm atom}=-\left(\frac{1}{2\hbar}\right)\int_0^\beta d\lambda\langle\mathbf{p}(-i\lambda)\mathbf{p}(0)\rangle_{\rm atom}:\times\langle\mathbf{E}(\mathbf{r},-i\lambda)\mathbf{E}(\mathbf{r}',0)\rangle, \tag{25}$$

or equivalently

$$U_{\rm atom}=-\left(\frac{C_{\rm atom}}{h^3}\right), \tag{26}$$

where

$$C_{\rm atom}=\left(\frac{1}{16\hbar}\right)\int_0^\beta d\lambda\;\mathcal{G}(\lambda)\langle p_x(-i\lambda)p_x(0)+p_y(-i\lambda)p_y(0)+2p_z(-i\lambda)p_z(0)\rangle_{\rm atom}. \tag{27}$$

With $\alpha(\zeta)$ denoting the polarizability tensor of a spherical atom,

$$\langle p_i(-i\lambda)p_j(0)\rangle_{\rm atom,+}=k_BT\delta_{ij}\sum_{n=-\infty}^{\infty}\alpha(i|\omega_n|)e^{-i\omega_n\lambda}, \tag{28}$$

so that Eqs. (11) and (28) yield

$$C_{\rm atom}=\left(\frac{k_BT}{4}\right)\sum_{n=-\infty}^{\infty}\alpha(i|\omega_n|)\left(\frac{\varepsilon(i|\omega_n|)-1}{\varepsilon(i|\omega_n|)+1}\right). \tag{29}$$

In the limit of low temperature Eqs. (9) and (29) imply

$$\lim_{T\to 0}C_{\rm atom}=\left(\frac{\hbar}{4\pi}\right)\int_0^\infty\alpha(i\omega)\left(\frac{\varepsilon(i\omega)-1}{\varepsilon(i\omega)+1}\right)d\omega. \tag{30}$$

$U_{\rm atom}=-(C_{\rm atom}/h^3)$ is the well known energy for the asymptotic van der Waals interaction between a spherical atom and a solid. It has been derived previously by Lifshitz and co-workers.[3] Similar expressions have been used by Harris and Feibelman[12] to get the asymmetry of the van der Waals interaction between a molecule and a surface. Later, Rauber, Klein, and Cole[13] have used Eq. (30) to numerically compute the value of $C_{\rm atom}$.

## IV. FRICTION ON A MOVING ION

The friction coefficient tensor $\mathbf{\Gamma}$ in the case of a linear friction force $\mathbf{F}_{\rm friction}$ versus velocity $\mathbf{V}$ law,

$$\mathbf{F}_{\rm friction}=-\mathbf{\Gamma}\cdot\mathbf{V}, \tag{31}$$

obeys a Kubo formula

$$\Gamma_{ij}=\left(\frac{1}{k_BT}\right)\int_0^\infty dt\,{\rm Re}\langle F_i(t)F_j(0)\rangle, \tag{32}$$

where $\mathbf{F}(t)$ is a random (in general quantum) force exerted on the molecule by the metal.

To see what is involved, consider a charged ion with a random force

$$\mathbf{F}(t)=Ze\mathbf{E}(r,t), \tag{33}$$

due to the electric field fluctuations above the metal. Equations (15), (32), and (33) imply

$$\Gamma_{ij}^{(Z)}=\left(\frac{\pi Z^2e^2}{k_BT}\right)\lim_{\omega\to 0}\lim_{\mathbf{r}'\to\mathbf{r}}S_{ij}(\mathbf{r},\mathbf{r}',\omega). \tag{34}$$

Equations (16), (17), and (34) imply that the nonzero friction coefficients for a charged ion moving above the metal are given by

$$\Gamma_{\parallel}^{(Z)}\equiv\Gamma_{xx}^{(Z)}=\Gamma_{yy}^{(Z)}=\left(\frac{Z^2e^2}{16\pi\sigma h^3}\right), \tag{35}$$

and

$$\Gamma_{\perp}^{(Z)} \equiv \Gamma_{zz}^{(Z)} = \left(\frac{Z^2 e^2}{8\pi\sigma h^3}\right). \tag{36}$$

These friction coefficients for a moving charge above a metal could have been derived on a purely classical basis from Coulomb's law and Ohm's law. Equation (35) has been previously discussed in the literature.[14] The derivation given above relies on the Kubo formalism.[3]

## V. DIPOLAR FRICTION

For a dipole moment, the random force exerted on the molecule is given by

$$\mathbf{F}(t) = (\mathbf{p}(t)\cdot\nabla)\mathbf{E}(\mathbf{r},t). \tag{37}$$

From Eqs. (32) and (36), it is evident that the gradient of the electric field correlations can be defined

$$S_{ikjl}(\mathbf{r},\mathbf{r}',\omega) = \int_{-\infty}^{\infty}\left(\frac{dt}{2\pi}\right)\cos(\omega t)\,\mathrm{Re}\langle \partial_i E_k(\mathbf{r},t)\,\partial_j' E_l(\mathbf{r}',0)\rangle, \tag{38}$$

where Eqs. (5), (7), and (38) imply

$$S_{ikjl}(\mathbf{r},\mathbf{r}',\omega) = \partial_i \partial_k \partial_j' \partial_l' S(\mathbf{r},\mathbf{r}',\omega). \tag{39}$$

From Eq. (3), it follows from straightforward (but tedious) differentiation that

$$\lim_{\mathbf{r}'\to\mathbf{r}} \partial_i \partial_k \partial_j' \partial_l' \left(\frac{1}{R_{\rm image}}\right) = \left(\frac{1}{32h^5}\right)[\mathcal{F}_{ikjl}^{(0)} - \mathcal{F}_{ikjl}^{(2)} + \mathcal{F}_{ikjl}^{(4)}], \tag{40}$$

where

$$\mathcal{F}_{ikjl}^{(0)} = 3\,\eta_j \eta_l(\delta_{jk}\delta_{il} + \delta_{jl}\delta_{ik} + \delta_{ji}\delta_{kl}), \tag{41}$$

$$\mathcal{F}_{ikjl}^{(2)} = 15\,\eta_j \eta_l(\delta_{ij}N_k N_l + \delta_{ik}N_j N_l + \delta_{il}N_k N_j + \delta_{jk}N_i N_l + \delta_{lj}N_k N_i + \delta_{kl}N_i N_j), \tag{42}$$

$$\mathcal{F}_{ikjl}^{(4)} = 105\,\eta_j \eta_l N_i N_k N_j N_l, \tag{43}$$

$$\eta_l = -1 \quad \text{if} \quad l = x,y; \qquad \eta_l = +1 \quad \text{if} \quad l = z; \tag{44}$$

and $\mathbf{N}$ is a unit vector normal to the conductor surface. From Eqs. (8), (39), and (40)

$$\lim_{\mathbf{r}'\to\mathbf{r}} S_{ikjl}(\mathbf{r},\mathbf{r}',\omega) = \left(\frac{\hbar}{64\pi h^5}\right)\coth\left(\frac{\hbar\omega}{2k_B T}\right)\mathrm{Im}\left(\frac{\varepsilon(\omega+i0^+)-1}{\varepsilon(\omega+i0^+)+1}\right) \times[\mathcal{F}_{ikjl}^{(0)} - \mathcal{F}_{ikjl}^{(2)} + \mathcal{F}_{ikjl}^{(4)}]. \tag{45}$$

For a fixed dipole moment $\mathbf{p}$, we have

$$\lim_{\omega\to 0}\lim_{\mathbf{r}'\to\mathbf{r}} \sum_{i,j} p_i p_j S_{ikjl}(\mathbf{r},\mathbf{r}',\omega) = \left(\frac{k_B T}{64\pi^2 \sigma h^5}\right)\sum_{i,j} p_i p_j(\mathcal{F}_{ikjl}^{(0)} - \mathcal{F}_{ikjl}^{(2)} + \mathcal{F}_{ikjl}^{(4)}). \tag{46}$$

From Eqs. (31), (37), and (38) we find the friction coefficient tensor for a dipole moment $\mathbf{p}$; i.e.,

$$\Gamma_{kl}^{(\mathbf{p})} = \left(\frac{\pi}{k_B T}\right)\lim_{\omega\to 0}\lim_{\mathbf{r}'\to\mathbf{r}} \sum_{i,j} p_i p_j S_{ikjl}(\mathbf{r},\mathbf{r}',\omega), \tag{47}$$

is then given by

$$\Gamma_{kl}^{(\mathbf{p})} = \left(\frac{1}{64\pi\sigma h^5}\right)\sum_{i,j} p_i p_j(\mathcal{F}_{ikjl}^{(0)} - \mathcal{F}_{ikjl}^{(2)} + \mathcal{F}_{ikjl}^{(4)}). \tag{48}$$

The dimensional arguments discussed in Sec. I, i.e., $\Gamma^{(\mathbf{p})} \sim (p^2/\sigma h^5)$ is verified in Eq. (48) along with the detailed values of the friction coefficient tensor elements in Eqs. (41), (42), and (43). Particular values of the friction coefficients are evaluated and discussed in the Appendix.

## VI. QUANTUM DIPOLE FLUCTUATIONS

For a spherical atom with polarizability $\alpha(\zeta)$, the quantum dipole moment fluctuation spectral function

$$S_{ij}^{(\rm atom)}(\omega) = \int_{-\infty}^{\infty}\left(\frac{dt}{2\pi}\right)\cos(\omega t)\,\mathrm{Re}\langle p_i(t)p_j(0)\rangle, \tag{49}$$

is given by

$$S_{ij}^{(\rm atom)}(\omega) = \delta_{ij}\left(\frac{\hbar}{2\pi}\right)\coth\left(\frac{\hbar\omega}{2k_B T}\right)\mathrm{Im}\,\alpha(\omega+i0^+). \tag{50}$$

From Eq. (32), it follows, for example, that

$$\Gamma_{xx} = \left(\frac{\pi\hbar}{k_B T}\right)\sum_{\rm initial} P_{\rm initial}\sum_{\rm final} \times\delta(\mathcal{E}_{\rm final} - \mathcal{E}_{\rm initial})|\langle{\rm final}|F_x|{\rm initial}\rangle|^2, \tag{51}$$

where $P_{\rm initial} = Z^{-1}\exp(-E_{\rm initial}/k_B T)$,

$$F_x = (\mathbf{p}\cdot\mathbf{g}_x), \quad \mathbf{g}_x = \nabla E_x. \tag{52}$$

In lowest order perturbation theory $|{\rm state}\rangle = |{\rm atom}\rangle|{\rm metal}\rangle$, i.e.,

$$|{\rm initial}\rangle = |i\rangle|I\rangle, \quad |{\rm final}\rangle = |f\rangle|F\rangle, \tag{53}$$

so that

$$\Gamma_{xx} = \left(\frac{\pi\hbar}{k_B T}\right)\sum_{i,I} P_I P_i \sum_{f,F} \delta(E_F + \varepsilon_f - E_I - \varepsilon_i) \times|\langle f|\mathbf{p}|i\rangle\langle F|\mathbf{g}_x|I\rangle|^2, \tag{54}$$

where $|I\rangle,|F\rangle$ represent metal states and $|i\rangle,|f\rangle$ represent spherical atom states.

To evaluate Eq. (54), let us define for the spherical atom

$$S_{\rm atom}^{(\pm)}(\omega) = \left(\frac{\hbar}{3}\right)\sum_i \sum_f P_i|\langle f|\mathbf{p}|i\rangle|^2\delta(\hbar\omega \mp \varepsilon_f \pm \varepsilon_i), \tag{55}$$

and for the metal

$$S^{(\mp)}_{\text{metal}}(\omega)=\hbar\sum_{I}\sum_{F}P_I|\langle F|\mathbf{g}_x|I\rangle|^2\delta(\hbar\omega\pm E_F\mp E_I). \tag{56}$$

Equation (54) then reads

$$\Gamma_{xx}=\left(\frac{\pi}{k_BT}\right)\int_0^\infty d\omega[S^{(+)}_{\text{atom}}(\omega)S^{(-)}_{\text{metal}}(\omega)+S^{(-)}_{\text{atom}}(\omega)S^{(+)}_{\text{metal}}(\omega)]. \tag{57}$$

One may employ Eq. (50) in the form

$$S^{(+)}_{\text{atom}}(\omega)=\left(\frac{\hbar}{\pi}\right)[n(\omega)+1]\text{Im}\alpha(\omega+i0^+), \tag{58}$$

and

$$S^{(-)}_{\text{atom}}(\omega)=\left(\frac{\hbar}{\pi}\right)n(\omega)\text{Im}\alpha(\omega+i0^+), \tag{59}$$

where the Planck distribution is defined as

$$n(\omega)=\frac{1}{e^{\beta\omega}-1}. \tag{60}$$

Similarly, one may employ Eqs. (38), (45), (52), and (56) in the form

$$S^{(+)}_{\text{metal}}(\omega)=\left(\frac{3\hbar}{4\pi h^5}\right)[n(\omega)+1]\text{Im}\left(\frac{\varepsilon(\omega+i0^+)-1}{\varepsilon(\omega+i0^+)+1}\right), \tag{61}$$

and

$$S^{(-)}_{\text{metal}}(\omega)=\left(\frac{3\hbar}{4\pi h^5}\right)n(\omega)\text{Im}\left(\frac{\varepsilon(\omega+i0^+)-1}{\varepsilon(\omega+i0^+)+1}\right). \tag{62}$$

Equations (57), (58), (59), (61), and (62) imply the central power law result of this section, i.e.,

$$\Gamma_{xx}=\left(\frac{D_{xx}}{h^5}\right), \tag{63}$$

where

$$D_{xx}=\left(\frac{3\hbar^2}{2\pi k_BT}\right)\int_0^\infty d\omega\, n(\omega)[n(\omega)+1] \times\text{Im}\left(\frac{\varepsilon(\omega+i0^+)-1}{\varepsilon(\omega+i0^+)+1}\right)\text{Im}\alpha(\omega+i0^+), \tag{64}$$

or equivalently

$$D_{xx}=-\left(\frac{3\hbar}{2\pi}\right)\int_0^\infty d\omega\left(\frac{\partial n(\omega)}{\partial\omega}\right)\text{Im}\left(\frac{\varepsilon(\omega+i0^+)-1}{\varepsilon(\omega+i0^+)+1}\right) \times\text{Im}\alpha(\omega+i0^+). \tag{65}$$

Note that in the quantum limit

$$n(\omega)\rightarrow\exp(-\hbar\omega/k_BT)\quad\text{as}\quad T\rightarrow 0, \tag{66}$$

it follows from Eqs. (65) and (66)

$$\lim_{T\rightarrow 0}D_{xx}(\text{quantum})=\left(\frac{3\hbar}{2\pi}\right)\lim_{\omega\rightarrow 0}\text{Im}\left(\frac{\varepsilon(\omega+i0^+)-1}{\varepsilon(\omega+i0^+)+1}\right) \times\text{Im}\alpha(\omega+i0^+)=0. \tag{67}$$

The approach to zero as $T\rightarrow 0$ is exponential in character; i.e., $D_{xx}\propto\exp(-\Delta/k_BT)$, where $\Delta$ is the energy of the first excited state of the atom relative to the ground state. Thus, it is required to go to higher order perturbation theory[15] for friction on the spherical atom at temperatures $k_BT\ll\Delta$.

On the other hand, in the ‘‘classical limit’’ for, e.g., for rotating polar molecules with large $n(\omega)\gg 1$,

$$n(\omega)\approx\left(\frac{k_BT}{\hbar\omega}\right)\quad(\hbar\omega\ll k_BT), \tag{68}$$

Eq. (65) yields

$$D_{xx}(\text{classical})=\left(\frac{3k_BT}{2\pi}\right)\int_0^\infty\left(\frac{d\omega}{\omega^2}\right) \times\text{Im}\left(\frac{\varepsilon(\omega+i0^+)-1}{\varepsilon(\omega+i0^+)+1}\right)\text{Im}\alpha(\omega+i0^+), \tag{69}$$

which in the additional limit $\omega\ll\sigma$ yields

$$D_{xx}(\text{classical})=\left(\frac{3k_BT}{4\pi^2\sigma}\right)\int_0^\infty\left(\frac{d\omega}{\omega}\right)\text{Im}\alpha(\omega+i0^+) =\left(\frac{3k_BT\alpha_T}{8\pi\sigma}\right), \tag{70}$$

where $\alpha_T$ is the classical polarizability of a tumbling (rotating) dipole moment. With

$$\langle p_x^2\rangle_{\text{classical}}=\langle p_y^2\rangle_{\text{classical}}=\langle p_z^2\rangle_{\text{classical}}=k_BT\alpha_T, \tag{71}$$

one finds, either from Eqs. (70) and (71) or from Eq. (48), that

$$D_{xx}(\text{classical})=\left(\frac{\langle|\mathbf{p}^2|\rangle_{\text{classical}}}{8\pi\sigma}\right). \tag{72}$$

The friction coefficient is then

$$\Gamma_{xx}(\text{classical})=\left(\frac{\langle|\mathbf{p}^2|\rangle_{\text{classical}}}{8\pi\sigma h^5}\right). \tag{73}$$

## VII. DISCUSSION

We have calculated the electronic contribution to the friction coefficients for ions, polar molecules, and spherical atoms moving near a metal in a regime where an image charge argument is physically valid. For an ionic charge $Ze$, $\Gamma\sim(Z^2e^2/\sigma h^3)$. For a polar molecule with a dipole moment $\mathbf{p}$, $\Gamma(\text{classical})\sim(\langle p^2\rangle_{\text{classical}}/\sigma h^5)$.

For the case of a spherical atom, the zero-point dipole moment fluctuations $\langle p^2\rangle_{\text{quantum}}$ contribute to the attraction energy in Eqs. (26) and (30), but do not contribute to the friction coefficient at low temperature $k_BT\ll\Delta$ in the lowest order perturbation theory of Eq. (53). The required higher order perturbation theory results have been discussed elsewhere.[15]

For a nobel gas atom above the metal at a height $h \gg a$, where $a$ is the metallic interatomic spacing, the mean dipole moment in the ground state $\langle 0|\mathbf{p}|0\rangle = \mathbf{0}$. However, for an atom in the first adsorbed monolayer, there exists a net dipole moment $\langle \mathbf{p}\rangle \neq 0$.[16] Thus, for sliding friction in the first adsorbed layer, dipole images and Ohm's law induced friction play a role which is not present when $h \gg a$ and $\langle 0|\mathbf{p}|0\rangle = \mathbf{0}$.

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## APPENDIX

In this appendix we shall explicitly evaluate the friction coefficient for a dipole moment oriented normal to the plane of the metal surface,

$$\mathbf{p} = p\mathbf{N}, \quad p = |\mathbf{p}|. \tag{A1}$$

For motion parallel to the plane, Eqs. (48) and (A1) read

$$\Gamma_{xx}^{(p)} \equiv \Gamma_{\parallel}^{(p)} = \left(\frac{p^2}{64\pi\sigma h^5}\right)(\mathcal{F}_{zxzx}^{(0)} - \mathcal{F}_{zxzx}^{(2)} + \mathcal{F}_{zxzx}^{(4)}). \tag{A2}$$

From Eqs. (41), (42), and (43)

$$\mathcal{F}_{zxzx}^{(0)} = -3, \quad \mathcal{F}_{zxzx}^{(2)} = -15, \quad \mathcal{F}_{zxzx}^{(4)} = 0. \tag{A3}$$

Hence,

$$\Gamma_{\parallel}^{(p)} = \left(\frac{3p^2}{16\pi\sigma h^5}\right). \tag{A4}$$

Similarly, for motion normal to the plane

$$\Gamma_{zz}^{(p)} \equiv \Gamma_{\perp}^{(p)} = \left(\frac{p^2}{64\pi\sigma h^5}\right)(\mathcal{F}_{zzzz}^{(0)} - \mathcal{F}_{zzzz}^{(2)} + \mathcal{F}_{zzzz}^{(4)}), \tag{A5}$$

we have from Eqs. (41), (42), and (43),

$$\mathcal{F}_{zzzz}^{(0)} = 9, \quad \mathcal{F}_{zzzz}^{(2)} = 90, \quad \mathcal{F}_{zzzz}^{(4)} = 105. \tag{A6}$$

Hence

$$\Gamma_{\perp}^{(p)} = \left(\frac{3p^2}{8\pi\sigma h^5}\right). \tag{A7}$$

Equations (A4) and (A7) for a static dipole moment $\mathbf{p} = p\mathbf{N}$ pointing normal to the surface should be compared to Eqs. (35) and (36) for a static charge $Ze$.

The case of a dipole moment pointing normal to the metal surface, i.e., $\mathbf{p} = p\mathbf{N}$ is of potential importance for the case of nobel gas atoms adsorbed on metals. It appears to be true that such atoms (at least in the first monolayer) do grow a net dipole moment normal to the metal surface.

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