

# Adsorbate vibrational mode enhancement of radiative heat transfer

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We show that the radiative heat transfer between two solid surfaces at short separation may increase by many order of magnitude when the surfaces are covered by adsorbates. In this case the heat transfer is determined by resonant photon tunneling between adsorbate vibrational modes. We propose an experiment to check the theory.

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It is well known that for bodies separated by  $d \gg d_T = c\hbar/k_B T$ , the radiative heat transfer between them is described by the Stefan–Boltzman law:

$$S = \frac{\pi^2 k_B^4}{60\hbar^3 c^2} (T_1^4 - T_2^4), \quad (1)$$

where  $T_1$  and  $T_2$  are the temperatures of solid **1** and **2**, respectively. In this limiting case the heat transfer is connected with traveling electromagnetic waves radiated by the bodies, and does not depend on the separation  $d$ . For  $d < d_T$  the heat transfer increases by many order of magnitude due to the evanescent electromagnetic waves that decay exponentially into the vacuum; this is often referred to as photon tunneling. At present there is an increasing number of investigations of heat transfer due to evanescent waves in connection with the scanning probe microscopy under ultrahigh vacuum conditions [1–7]. It is now possible to measure extremely small amounts of heat transfer into small volumes [8]. STM (Scanning Tunneling Microscope) can be used for local heating of the surface, resulting in local desorption or decomposition of molecular species, and this offers further possibilities for the STM to control local chemistry at surface.

The efficiency of the radiative heat transfer depends strongly on the dielectric properties of the media. In [3, 5, 6] it was shown the heat flux can be greatly enhanced if the conductivities of the material is chosen to maximize the heat flow due to photon tunneling. At room temperature the heat flow is maximal at conductivities corresponding to semi-metals. In fact, only a thin film ( $\sim 10 \text{ \AA}$ ) of a high-resistivity material is needed to maximize the heat flux [5]. Another enhancement mechanism of the radiative heat transfer can be connected with resonant photon tunneling between states localized on the different surfaces. Recently it was dis-

covered that resonant photon tunneling between surface plasmon modes give rise to extraordinary enhancement of the optical transmission through sub-wavelength hole arrays [9]. The same surface modes enhancement can be expected for the radiative heat transfer (and the van der Waals friction [10]) if the frequency of these modes is sufficiently low to be excited by thermal radiation. At room temperature only the modes with frequencies below  $\sim 10^{13} \text{ s}^{-1}$  can be excited. Recently, enhancement of the heat transfer due to resonant photon tunneling between surface plasmon modes localized on the surfaces of the semiconductors was predicted [7]. Other surface modes which can be excited by thermal radiation are adsorbate vibrational modes.

In this paper we study the radiative heat transfer between small particles, e.g. adsorbed molecules, or dust particles, considered as point dipoles, and situated on the surfaces of different bodies. Using an electromagnetic approach, in the dipolar approximation, we derive a general expression the radiative heat power exchanged between the particles. We show that, if the particles have resonance frequencies which are matched, the heat transfer can be enhanced by many orders of magnitude in comparison with the heat transfer between clean surfaces of the good conductors.

Let us consider two particles with dipole polarizabilities  $\alpha_1(\omega)$  and  $\alpha_2(\omega)$  and with the fluctuating dipole moments  $p_1^f$  and  $p_2^f$  normal to the surfaces. Accordingly to fluctuation-dissipation theorem [11], the spectral density function for the fluctuating dipole moment is given by

$$\langle p_i^f p_j^f \rangle_\omega = \frac{\hbar}{\pi} \left( \frac{1}{2} + n_i(\omega) \right) \text{Im} \alpha_i(\omega) \delta_{ij} \quad (2)$$

where the Bose-Einstein factor

$$n_i(\omega) = \frac{1}{e^{\hbar\omega/k_B T_i} - 1}. \quad (3)$$

Assume that the particles are situated opposite to each other on two different surfaces, at the temperatures  $T_1$  and  $T_2$ , respectively, and separated by the distance  $d$ . The fluctuating electric field of a particle **1** does work on a particle **2**. The rate of working is determined by

$$P_{12} = 2 \int_0^\infty d\omega \omega \text{Im}\alpha_2(\omega) \langle E_{12} E_{12} \rangle_\omega \quad (4)$$

where  $E_{12}$  is the electric field created by a particle **1** at the position of a particle **2**:

$$E_{12} = \frac{8p_1^f/d^3}{1 - \alpha_1\alpha_2(8/d^3)^2}. \quad (5)$$

From Eqs. (2)–(4) we get  $P_{12}$ , and the rate of cooling of a particle **2** can be obtained using the same formula by reciprocity. Thus the total heat exchange power between the particles is given by

$$P = P_{12} - P_{21} = \frac{2\hbar}{\pi} \int_0^\infty d\omega \omega \frac{\text{Im}\alpha_1 \text{Im}\alpha_2 (8/d^3)^2}{|1 - (8/d^3)^2 \alpha_1 \alpha_2|^2} (n_1(\omega) - n_2(\omega)). \quad (6)$$

Let us firstly consider some general consequences of Eq. (6). There are no constrain on the particle polarizability  $\alpha(\omega) = \alpha' + i\alpha''$  other than that  $\alpha''$  is positive, and  $\alpha'$  and  $\alpha''$  are connected by the Kramers-Kronig relation. Therefore, assuming identical surfaces, we are free to maximize the photon-tunneling transmission coefficient

$$t = \frac{(8\alpha''/d^3)^2}{|1 - (8\alpha/d^3)^2|^2}. \quad (7)$$

This function is a maximum when

$$\alpha'^2 + \alpha''^2 = (d^3/8)^2 \quad (8)$$

so that  $t = 1/4$ . Substituting this result in (6) gives the upper bound for the heat transfer power between two particles

$$P_{\max} = \frac{\pi k_B^2}{3\hbar} (T_1^2 - T_2^2). \quad (9)$$

This result is a particular case of the more general statement [3] about that there is a maximum heat flow in a given channel. A simple interpretation can be given for Eq. (9). The energy transfer between the particles can be considered as a result of the collisions. The maximal rate of energy transfer is of the order of magnitude of

the product of the characteristic thermal energy on the frequency of the collision, equaled to the maximal frequency of the vibration which can be thermally excited, thus  $P_{\max} \sim k_B T \cdot k_B T/\hbar$ . For adsorbed molecules at the concentration  $n_a = 10^{19} \text{m}^{-2}$ , when one surface is at zero temperatures and the other is at the room temperature the maximal heat flux due to the adsorbates  $S_{\max} = n_a P_{\max} = 10^{12} \text{Wm}^{-2}$ , which is nearly 10 order of magnitude larger than the heat flux due to the black body radiation,  $S_{BB} = \sigma T = 4 \cdot 10^2 \text{Wm}^{-2}$ .

We rewrite the denominator of the integrand in Eq. (6) in the form

$$|1 - (8\alpha/d^3)^2|^2 = [(1 - 8\alpha'/d^3)^2 + (8\alpha''/d^3)^2] \times [(1 + 8\alpha'/d^3)^2 + (8\alpha''/d^3)^2] \quad (10)$$

The conditions for resonant photon tunneling are determined by equation

$$\alpha'(\omega_\pm) = \pm d^3/8. \quad (11)$$

Close to resonance we can write

$$(1 \pm 8\alpha'/d^3)^2 + (8\alpha''/d^3)^2 \approx (8\beta_\pm/d^3)^2 [(\omega - \omega_\pm)^2 + ((\alpha''/\beta_\pm)^2)], \quad (12)$$

where

$$\beta_\pm = \left. \frac{d\alpha'_r(\omega)}{d\omega} \right|_{\omega=\omega_\pm}.$$

Assuming  $|\alpha''/\beta_\pm| \ll \omega_\pm$  we get the following contribution to the heat transfer:

$$P = \frac{\hbar}{2} [(\alpha''(\omega_+)/|\beta_+|)\omega_+(n_1(\omega_+) - n_2(\omega_+)) + (+ \rightarrow -)]. \quad (13)$$

Close to a pole we can use the approximation

$$\alpha \approx \frac{a}{\omega - \omega_0 - i\eta}, \quad (14)$$

where  $a$  is a constant. Then from the resonant condition (11) we get

$$\omega_\pm = \omega_0 \pm 8a/d^3.$$

For the two-poles approximation to be valid the difference  $\Delta\omega = |\omega_+ - \omega_-|$  must be greater than the width  $\eta$  of the resonance, so that  $8a/d^3 > \eta$ .

For  $\eta \ll 8a/d^3$ , from Eq. (6) we get

$$P = \frac{\hbar\eta}{2} [\omega_+(n_1(\omega_+) - n_2(\omega_+)) + (+ \rightarrow -)]. \quad (15)$$

Using Eq. (15) we can estimate the heat flux between identical surfaces covered by adsorbates with concentration  $n_a$ :  $S \approx n_a P$ . Interesting, the explicit  $d$  dependence has dropped out of Eq. (15). However,  $P$  may still be  $d$ -dependent, through the  $d$ -dependence of  $\omega_{\pm}$ . For  $\hbar\omega_{\pm} \leq k_B T$  the heat transfer will be only weakly distance independent.

For  $8a/d^3 < \eta$  we can neglect multiple scattering of the photon between the particles, so that the denominator in the integrand in Eq. (6) equal unity. For  $d \gg l$ , where  $l$  is the interparticle spacing, the heat flux between two surfaces covered by adsorbates with concentration  $n_{a1}$  and  $n_{a2}$  can be obtained after integration of the heat flux between two separated particles. We get

$$S = \frac{24\hbar n_{a1} n_{a2}}{d^4} \int_0^{\infty} d\omega \omega \text{Im}\alpha_1 \text{Im}\alpha_2 [n_1(\omega) - n_2(\omega)]. \quad (16)$$

Assuming that  $\alpha$  can be approximated by Eq. (14), for  $\omega_0 \ll \eta$  Eq. (16) gives the heat flux between two identical surface:

$$S = \frac{12\pi\hbar\omega_0 a^2 n_a^2}{d^4 \eta} [n_1(\omega_0) - n_2(\omega_0)]. \quad (17)$$

We note that Eq. (17) can be obtained directly from the heat flux between two semi-infinite solids [3, 5, 6]. In such approach the contribution to the heat flux from adsorbates can be taken into account by appropriate modification of the Fresnel formulas for the reflection factors [12].

For  $d > d_T$  the dipole field is determined by the expression in the wave zone. The more simplest way to obtain contribution of adsorbates to heat flux in this case is to use macroscopic approach. However without calculation it is clear that in this region the surface contribution to the heat transfer due to adsorbates will be negligibly small in the comparison with the volume contribution, because in the limit of the large wave length the reflection amplitudes of the electromagnetic waves is reduced to classical Fresnel formulas, which do not contain information about surface region. For black bodies this volume contribution is determined by Stefan-Boltzman law. The heat transfer between the clean surfaces of the good conductors was investigated in the details in [13].

In the case of ionic adsorption the dipole polarizability is given by

$$\alpha = \frac{e^* M}{\omega^2 - \omega_0^2 - 2i\omega\eta}, \quad (18)$$

where  $e^*$  is the ionic charge,  $M$  is the ionic mass, and where  $\omega_0$  and  $\eta$  are the vibrational frequency and damping constant, respectively. For the K/Cu(001) system

$\omega_0 = 1.9 \cdot 10^{13}$ , and at low coverage  $e^* = 0.88$  [14], which gives  $a = e^*/2M\omega_0 = 7 \cdot 10^{-17} \text{ m}^3 \cdot \text{s}^{-1}$ . For  $\eta = 10^{12} \text{ s}^{-1}$  and  $d < 10 \text{ \AA}$ , when one surface has  $T = 300 \text{ K}$  and the other  $T = 0 \text{ K}$ , we get distance independent  $P \approx 10^{-9} \text{ W}$ . In this case, for  $n_a = 10^{18} \text{ m}^{-3}$  the heat flux  $S \approx 10^9 \text{ Wm}^{-2}$ . At the same conditions the heat flux between two clean surfaces  $S_{clean} \approx 10^8 \text{ Wm}^{-2}$ . Thus the photon tunneling between the adsorbate vibrational states can strongly enhance the radiative heat transfer between the surfaces.

Let us describe the physical origin of the different regimes in resonant photon tunneling between adsorbate vibrational modes. At sufficiently small separation, when  $8a/d^3 > \eta$ , the photons goes back and forth several time in the vacuum gap, building up coherent constructive interference in the forward direction much as would occur in resonant electron tunneling. In this case the vibrational modes on the isolated surfaces combine to form collective vibrational modes (diatomic "molecule"), where the adsorbates vibrate in phase or out of phase. This will result in a very weak distance dependence of the heat flux, because the transmission probability for photon depends very weakly on  $d$  in this case (see above). For large  $d$ , when  $8a/d^3 < \eta$ , the sequential tunneling is more likely to occur, where the photon excited in a adsorbate vibrational mode, tunnels to the adsorbate vibration at the other surface, and then couples to the other excitations in the media and exit.

The above discussion is for a special case of matching adsorbate vibrational frequencies ( $\omega_1 = \omega_2 = \omega_0$ ), but the picture still applies in the nonsymmetric case ( $\omega_1 \neq \omega_2$ ). Here, adsorbate vibrational modes on the two surfaces have different frequencies and, instead of a vibration mode for diatomic homopolar molecule, we have a diatomic heteropolar molecule.

Finally, let us suggest an experiment to probe the photon-tunneling heat transfer theory. Consider a solid surface (substrate) at low temperature with a low concentration of weakly adsorbed atoms (e.g. noble gas atoms) or molecules. The position of the atoms can mapped out relative to the substrate using a STM. Next, the surface of another solid at higher temperature (e.g. room temperature) is brought in the vicinity (separation  $d$ ) of the substrate. The heat transfer (via photon tunneling) to the substrate will result in a temperature increase on the substrate surface. This will result in the diffusion of the weakly bound adsorbates. The (average) diffusion distance will be a function of the heat transfer. If the two bodies are separated after a given time period, and if the new position of the adsorbates is determined using the STM [15], it is possible to infer the heat transfer from the hot to the cold surface as a

function of the separation  $d$ . This experiment is conveniently performed using as the second (warm) body an AFM (Atomic Force Microscope) tip with a wide flat tip, as recently produced and used for contact mechanics studies [16].

In summary, we have presented a detailed theoretical study of the heat transfer between surfaces covered by adsorbates. We have shown that resonant photon tunneling between adsorbate vibration modes can give rise extraordinary enhanced heat transfer, in the comparison with the heat transfer between clean good conductor surfaces. This result can be used in the scanning probe microscopy for local heating and modification of the surface. Finally, we have suggested an experiment by which the radiative heat transfer due to photon tunneling can be measured.

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