On anomalously large nano-scale heat transfer between metals

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Abstract: The non-contact heat transfer between two bodies is more efficient than the Stefan–Boltzmann law, when the distances are on the nanometer scale (shorter than Wien’s wavelength), due to contributions of thermally excited near fields. This is usually described in terms of the fluctuation electrodynamics due to Rytov, Levin, and co-workers. Recent experiments in the tip–plane geometry have reported “giant” heat currents between metallic (gold) objects, exceeding even the expectations of Rytov theory. We discuss a simple model that describes the distance dependence of the data and permits to compare to a plate–plate geometry, as in the proximity (or Derjaguin) approximation. We extract an area density of active channels which is of the same order for the experiments performed by the groups of Kittel (Oldenburg) and Reddy (Ann Arbor). It is argued that mechanisms that couple phonons to an oscillating surface polarisation are likely to play a role.

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Introduction

Thermal radiation provides a seminal topic in physics and beyond [1]. Since Planck explained its spectrum, at the dawn of quantum mechanics, it is clear that over distances shorter than the Wien wavelength (a few microns at room temperature), heat transfer can be more efficient than the Stefan–Boltzmann law because near fields are involved. Fluctuating electromagnetic near fields are successfully described by a statistical approach to macroscopic electrodynamics (Maxwell–Langevin equations) developed by Rytov, Levin, and co-workers [2]. This theory has been developed in the field of nano-optics [3] and is also relevant for colloidal forces [4] and Casimir forces [5,6]. Detailed studies of the radiative heat transfer at short distances go back to Polder and van Hove [7] and others [8]. They have been motivated by experiments where a sharp tip is scanned over a sample and the changes in tip temperature are monitored to measure the heat current [9–11]. This gives access to surface properties that are complementary to electronic tunnelling, with a somewhat worse spatial resolution.

The framework of Rytov theory has been shaken, since data are being reported that it cannot explain. Relevant examples are the temperature dependence of the Casimir force between metals [5,6], and the anomalous electric field noise observed in ion traps [12]. In this paper, we address the heat transfer observed at distances between 1 and 10 nm by the groups of A. Kittel (Oldenburg, Kloppstech & al. [13]) and of P. Reddy (Ann Arbor, Cui & al. [14]). Comparison to different models and numerical calculations based on Rytov theory performed by the authors of Ref. [13] shows that the observed heat transfer is orders of magnitude larger and that its distance dependence is not well understood. In the experiment of Cui & al. [14], the results are interpreted in a different way: the authors apply a sequence of cleaning procedures to their tip and find a change in the dependence of heat conductivity on distance. The “cleanest” setting gives a
heat current consistent with Rytov theory, though close to the limit of detection sensitivity. In a related experiment, the heat current through a molecular (single channel) contact was studied, showing discrete steps given by the quantum of thermal conductance [15]. The spatial resolution of scanning images obtained by the authors of Ref. [13] suggests, however, that the presence of adsorbed molecules on the tip is unlikely in their setup. It is not surprising that the conflicting interpretations of these experiments have given rise to overt discussions.

In this paper, we motivate a simple model to describe the observed data and show that the experiments of Refs. [13, 14] can be put into a common perspective (section 1). The merit of the model is mainly its simplicity, it does not yet provide a physical explanation. It generates heat current densities that apply to a plate-plate geometry and are disturbingly close, however, despite obvious differences between the experimental setups. Fluctuation electrodynamics predicts much smaller numbers (section 2.1). This state of affairs invites questions on the role of additional channels for heat transport and how these could be “activated” at short distances. Obvious candidates for heat carriers are phonons, and indeed, the idea of “phonon tunneling” has become increasingly popular in recent years [16–21]. At the moment, these proposals do not reproduce the observed distance dependence consistently, as pointed out in Ref. [13]. The basic mechanism for phonon tunneling goes back to investigations in the 1980s when anomalous infrared absorption has been found in metallic nanoparticles, see Section 2.2.

1. Model for experimental data

Two sets of experimental data on heat transport between a tip and a planar sample are illustrated in Fig. 1. A striking common feature is the relatively pronounced change in the distance dependence: at large distance, the heat transfer is below the detector noise, but upon approaching the sample, it increases linearly up to the closest distances. An overview on the relevant experimental parameters is given in Table 1. We note that the two setups have opposite ‘polarities’: Kloppstech & al. [13] use a hotter tip, while Cui & al. [14] use a colder one. Table 1 is based on data from Figs. 2(a) and (b) in Ref. [14], but not from Fig. 2(c) there where no significant linear increase is visible. In both experiments, the data do not suggest that electron tunneling plays a significant role for the heat transfer, because the heat and tunnel currents depend on distance in a very different way.

The linear relation between heat transfer and distance suggests the following toy model that is related to the proximity force (or Derjaguin) approximation [4]. Let us assume that as the distance $d$ between two bodies drops below a critical value $d_c$ (much shorter than the radius of curvature), a strong mechanism of heat transport sets in and leads to a heat current $\dot{q}_c$ (a power per area). Assume further that heat is transferred in this way at a rate that does not depend on distance. Using elementary geometry and the “blunt tip” approximation (radius of curvature $R \gg d_c$, cf. Fig. 2), we find that the “active” area grows linearly with $d_c - d$, as one approaches the sample closer than the critical distance $d_c$. The model can thus be summarized by the following formula for the heat power [thick black lines in Fig. 1]

$$ P = 2\pi R (d_c - d) \dot{q}_c, \quad \text{for } d \leq d_c. \quad (1) $$

Let us note that due to the large heat current, it is likely that one gets a nontrivial temperature distribution in the tip-sample contact area. Indeed, the hot tip generates a small “hot spot” [17], and the large current $\dot{q}_c$ is “draining heat”, competing with thermal conduction in the bulk of the material. If the tip diameter is comparable to the thermal phonon wavelength, it is conducting
Fig. 1. Experimental data on heat transfer between a tip and a planar sample. The data were taken with thermal scanning microscopes [10,22] that allow for a simultaneous measurement of the electronic tunnelling current (onset at distances shorter than $d \sim 0.5\ldots1$ nm, right scale). The shaded areas illustrate the typical measurement uncertainties. Typical experimental parameters are collected in Table 1. The thick solid lines give the trend of our model (1).

Left plot: heat power $P$, adapted from Fig.2 of Kloppstech et al., Nature Commun. 8 (2017) 14475, Ref. [13], International License: Creative Commons Attribution 4.0.

Right plot: thermal conductance $G$ for a tip cleaned with an organic solvent. Adapted from Fig.2(a) of Cui et al., Nature Commun. 8 (2017) 14479, Ref. [14], International License: Creative Commons Attribution 4.0.

significantly less heat than a bulk sample [23]. This situation probably does not apply to the experiments discussed here, because the phonon wavelengths within the thermal spectrum are much shorter ($<1$ nm).

The simple model (1) describes the experimental data surprisingly well. The linear distance dependence of the heat power corresponds indeed, by the proximity force approximation, to a distance-independent heat current density $\dot{q}_c$ in a plate-plate geometry. The parameters that can be extracted by fitting the model to the data of Refs. [13,14], are given in Table 2. A striking

|                  | Kloppstech & al. [13] | Cui & al. [14] |
|------------------|----------------------|----------------|
| tip temperature $T_t$ | 280 K               | 303 K          |
| sample temperature $T_s$ | 120 K               | 343 K          |
| tip radius $R$      | 30 nm                | 150 nm         |
| max. power $P$      | 0.5 $\mu$W           | 1.2 $\mu$W     |
| max. conductance $G$ | 3 nW/K              | 20 \ldots 30 nW/K |
| onset distance $d_c$ | 5 \ldots 6 nm       | 2 \ldots 3 nm  |

Table 1. Typical data for two experiments that measure the heat transfer between a tip and a planar substrate. To convert the heat power $P$ to the thermal conductance $G$, use the formula $P = |T_t - T_s|G$ where $T_t$, $T_s$ are the tip and sample temperatures, respectively. These temperatures are not measured right at the tip apex, but further away along the tip shaft and below the sample. Note that the difference $T_t - T_s$ is not small.
Fig. 2. Sketch of the tip area that contributes to the anomalous heat transfer.

A relevant tip area is

\[ A = \pi r^2 \]

\[ = \pi (R^2 - (R - d_c + d)^2) \]

\[ \approx 2\pi R(d_c - d) \]

if \( R \gg d_c - d \)

The observation is how close together are the values for the heat current density \( \dot{q}_c \), despite the relatively large differences in the measured heat power and the tip radius. We do not expect the difference in hot and cold bodies to play a significant role here, as for the metallic materials used, the conditions for a thermal diode (strongly temperature-dependent thermal parameters) are not met.

We have also computed the number \( n \) of transport channels per unit area, taking into account the quantum of thermal conductance \( G_q \). Due to the large differences in temperature, we have generalized the definition of \( G_q \) by using the Landauer formula [24, 25] for the heat current from the tip \((a, T_t)\) to the sample \((b, T_s)\)

\[
\dot{q}_{a\rightarrow b} = n \int_0^\infty \frac{d\omega}{2\pi} \frac{k_B T_t |t_{ab}|^2}{\exp(h\omega / k_B T_t) - 1}
\]

The net current from tip to sample is given by the difference \( \dot{q} = |\dot{q}_{a\rightarrow b} - \dot{q}_{b\rightarrow a}| \). If we assume that the transmission is symmetric, \( |t_{ab}|^2 = |t_{ba}|^2 \), as expected from reciprocity, and limited by unity [24, 25], then the maximum heat current is

\[
\dot{q} \leq n \frac{\pi}{12} \frac{k_B^2}{h} |T_t^2 - T_s^2| = n \frac{\pi}{6} \frac{k_B}{h} \frac{T_t + T_s}{2} |T_t - T_s| G_q
\]

Table 2. Fit parameters for two nanoscale heat transport experiments, based on Eq.(1). The channel density \( n \) is computed by dividing the differential heat current density, \( \dot{q}_c / |T_t - T_s| \), by the effective thermal conductance quantum \( G_q = (\pi/6)(k_B^2/h)^1/2(T_t + T_s) \), evaluated at the average temperature [see Eq.(3)]. The Rytov prediction is the estimation of fluctuation electrodynamics in the parallel plate geometry [7]. We have taken the leading order contribution in the few-nm range, due to thermally excited magnetic near fields [Eq.(4)], and have adapted the result to a large temperature difference.

|                   | Kloppstech & al. [13] | Cui & al. [14] |
|-------------------|-----------------------|----------------|
| onset distance \( d_c \) | 5 . . . 6 nm          | 2 . . . 3 nm   |
| saturated current \( \dot{q}_c \) | 4 . . . 5 \cdot 10^8 W/m² | 5 . . . 6 \cdot 10^8 W/m² |
| channel density \( n \) | 1.6 Å⁻²               | 4.5 Å⁻²       |
| Rytov prediction   | 2.3 \cdot 10^6 W/m²   | 3.8 \cdot 10^6 W/m² |
Coming back to the experimental data extracted from this model (Table 2), we note that the channel densities $n$ differ only by a factor of $\sim 3$. In order of magnitude, they are larger than one channel per unit cell (its cross section is $\sim 16.6 \, \text{Å}^2$ in gold), and this is only a lower limit, provided the Landauer formalism applies [24,25]. The channel density would be higher if the transmission for many channels were below unity, for example. This illustrates that the heat transfer observed in these experiments is indeed a “giant” one [13]. A question that is open so far is which mechanisms can possibly lead to such an efficient coupling between two metallic bodies.

2. Mechanisms for giant heat transfer

2.1. Fluctuation electrodynamics: magnetic near fields

The physical origin of the anomalously large heat transfer has been addressed in previous work. It has been pointed out that the standard fluctuation electrodynamics of Rytov, Levin, and co-workers falls short by a large factor [13]. Ignoring for the moment the shape of the tip, we recall for simplicity an approximate formula obtained by Polder and van Hove [7]. It turns out that at distances in the 10 nm range, the main contribution to the heat transfer between metals comes from the “magnetic near field”, i.e., evanescent waves in the TE-polarization. It is not dominated by surface plasmons, since these appear at frequencies way above the room temperature Planck spectrum and they have only a small mode density in the relevant infrared range. Ref. [7] focuses on the differential heat conductance per unit area and finds the following approximation for the heat current

$$
\dot{Q}_{TE, \text{evan}} \approx \frac{0.574}{4\pi} \frac{\mu_0 k_B^3}{\hbar^2} \sigma T^2 |T_r - T_s| \quad \text{for} \quad |T_r - T_s| \ll T_r, T_s
$$

(4)

where $\mu_0$ is the magnetic constant, $\sigma$ the DC conductivity (in SI units), and $T = \frac{1}{2}(T_r + T_s)$ the average temperature. This formula applies when the distance is smaller than the typical diffusion length for thermal magnetic fields, $\ell_T \sim \left[\hbar / (k_B T \mu_0 \sigma)\right]^{1/2}$ (also known as skin depth). For the range of temperatures considered here, $\ell_T \sim 15 \ldots 9 \, \text{nm}$.

If this estimate is extrapolated to a large temperature difference (ignoring the change in conductivity), one gets instead of Eq.(3) a heat current proportional to $|T_r^3 - T_s^3|$. The corresponding predictions are included in Table 2 and are two orders of magnitude lower than the values extracted from the experiments. This discrepancy is even larger ($\sim 10^3$) in fluctuation electrodynamics calculations based on the actual tip geometry [13].

2.2. “Activated” phonons

Attractive alternatives to fluctuation electrodynamics are mechanisms related to phonons. Indeed, in metals at not too low temperatures, phonons already give the largest contribution to the specific heat. They are less effective than electrons for heat conduction, however, because the speed of sound is much smaller than the Fermi velocity. In addition, phonons are not “active” in terms of coupling to electric or magnetic fields: due to the fcc symmetry of the unit cell, we do not expect any optical phonons in bulk gold, and the acoustic branch is not accompanied by an oscillating polarisation. (This becomes different for piezoelectric materials, as pointed out in Ref. [16].) Several papers have suggested mechanisms to couple phonons between two vacuum-separated bodies, also called “phonon tunneling”. This is based, for example, on the van der Waals coupling between surface oscillations [19–21] which has also been considered for thermal fluctuations of the van der Waals force on a particle near a surface [26]. The drawback is that these proposals lead to a distance dependence that differs significantly from what is observed in Fig.1 [13].
One should note here that the tips in the experiments are very likely made of amorphous rather than crystalline gold. And even in the case of flat surfaces (surface scans in the experiments of Refs. [13, 17] show atom-scale steps, for example), it is well known that a gold surface is undergoing a reconstruction over a depth of a few layers. This possibly leads to optical surface phonons, featuring a net dipole moment. Hence we may expect an oscillating surface polarization that is excited when bulk phonons scatter from the surface. It is noteworthy that this has been discussed in the 1980s when an anomalously large infrared absorption has been observed in metallic nanoparticles (see references in Ref. [27]). An interesting observation has been made by Andersson and co-workers [28]: they considered a “jellium” half-space and showed that the electron density response to an applied electric field [29,30] oscillates with the depth into the metal, similar to Friedel oscillations. This gives a net charge imbalance in the first few layers. The associated forces on the atomic cores drive an optical surface phonon mode that dissipates by radiating bulk phonons. In reverse, this mechanism may “activate” bulk phonons by generating a surface polarization that couples electrostatically to another body nearby. A similar idea based on the dynamic behaviour of the image charge induced in a metal surface has been put forward in Ref. [17]. The distance dependence of the corresponding heat transfer will be dealt with in a separate theory paper.

Conclusion

We have proposed a simple model that permits to appreciate the experimental data on non-radiative heat transfer observed with scanning thermal microscopes on the sub-10 nm scale [13,14]. Although the two setups differ in their parameters and the two groups give different interpretations of their respective observations, the model puts the “raw data” into a common perspective, with surprisingly close values for the heat conductance per area. The giant or anomalous character of the observations is underlined by the large area density of heat-carrying channels that the model predicts within the Landauer formalism.

It is not likely that the tunnelling of electrons contributes significantly to the observed heat transfer. Just by looking at the distance dependence of the data for the tunnelling current and the heat flux (Fig.1), it seems rather clear that no significant electron transfer occurs in the 2–5 nm range in both experiments. Kloppstech & al. [13] also do not mention electronic heat transfer among their list of candidate mechanisms.

There is a difference in the critical distance $d_c$ between the two setups which suggests that this parameter is not a fundamental quantity. It may depend on local phenomena at the tip like elastic deformations or migrating atoms, and this is likely to depend on tip preparation (pulling, annealing etc.). The resolution of the scanning images shown in the supplementary material by Kloppstech & al [13] does not suggest a contamination by molecules as long as a few nanometers.

We hope that our considerations inspire further experiments and foster the search for a theoretical explanation – which must go beyond traditional Rytov–Levin fluctuation electrodynamics. We have argued that genuine surface properties like optical surface phonons that have been put forward in the 1980s already [27,28], may “catalyze” heat transport. It can thus be expected that in any meaningful model for this thermal anomaly, two significant differences with respect to standard fluctuation electrodynamics appear: (i) due to the large heat current, one probably needs to construct a self-consistent description of the temperature profile (see, e.g., Ref. [31]), and (ii) the models cannot be built from bulk material properties and the response to electromagnetic fields is determined by genuine surface properties [29,32].
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References

1. S. Chandrasekhar, Radiative Transfer (Dover, New York, 1960).
2. S. M. Rytov, Y. A. Kravtsov, and V. I. Tatarskii, Elements of Random Fields, vol. 3 of Principles of Statistical Radiophysics (Springer, Berlin, 1989).
3. L. Novotny and B. Hecht, Principles of Nano-Optics (Cambridge University Press, Cambridge, 2006), 1st ed.
4. V. A. Parsegian, Van der Waals Forces – A Handbook for Biologists, Chemists, Engineers, and Physicists (Cambridge University Press, New York, 2006).
5. S. Y. Buhmann, Dispersion Forces II – Many-Body Effects, Excited Atoms, Finite Temperature and Quantum Friction, vol. 248 of Springer Tracts in Modern Physics (Springer, Heidelberg, 2013).
6. A. I. Volokitin and B. N. J. Persson, Electromagnetic Fluctuations at the Nanoscale – Theory and Applications, NanoScience and Technology (Springer, Berlin, 2017).
7. J. J. Loomis and H. J. Maris, “Theory of heat transfer by evanescent electromagnetic waves,” Phys. Rev. B 4, 3303–14 (1971).
8. J. Dransfeld and J. Xu, “The heat transfer between a heated tip and a substrate: fast thermal microscopy,” J. Microsc. 152, 35–42 (1988).
9. M. Prunnila and J. Meltaus, “Acoustic phonon tunneling and heat transport due to evanescent electric fields,” Phys. Rev. Lett. 105, 115433 (2010).
10. A. Voevodin and A. K. Roy, “Vacuum phonon tunneling,” Phys. Rev. Lett. 105, 166101 (2010).
11. G. D. Mahan, “The tunneling of heat,” Appl. Phys. Lett. 98, 132106 (2011).
12. D. Polder and M. van Hove, “Theory of radiative heat transfer between closely spaced bodies,” Phys. Rev. B 4, 3303–14 (1971).
13. J. J. Loomis and H. J. Maris, “Theory of heat transfer by evanescent electromagnetic waves,” Phys. Rev. B 50, 18517–24 (1994).
14. E. G. Cravalho, C. L. Tien, and R. P. Caren, “Effect of small spacings on radiative transfer between two dielectrics,” J. Heat Transf. 89, 351–58 (1967).
15. Y. Ezzahri and K. Joulain, “Vacuum-induced phonon transfer between two solid dielectric materials: Illustrating the case of Casimir force coupling,” Phys. Rev. B 82, 121419(R) (2010).
16. S.-A. Biehs, E. Rousseau, and J.-J. Greffet, “Mesoscopic description of radiative heat transfer at the nanoscale,” Phys. Rev. Lett. 105, 234301 (2010).
17. C. Henkel and M. Wilkens, “Heating of trapped atoms near thermal surfaces,” Eur. Lett. 47, 414–20 (1999).
27. R. Monreal, J. Giraldo, F. Flores, and P. Apell, “Far-infrared optical absorption due to surface phonon excitations in small metal particles,” Solid State Commun. 54, 661–63 (1985).
28. S. Andersson, B. N. J. Persson, M. Persson, and N. D. Lang, “Long-range electron-phonon coupling at metal surfaces,” Phys. Rev. Lett. 52, 2073–76 (1984).
29. P. J. Feibelman, “Surface electromagnetic fields,” Progr. Surf. Sci. 12, 287–408 (1982).
30. N. D. Lang and W. Kohn, “Theory of metal surfaces: Induced surface charge and image potential,” Phys. Rev. B 7, 3541–50 (1973).
31. R. Messina, W. Jin, and A. W. Rodriguez, “Strongly coupled near-field radiative and conductive heat transfer between planar bodies,” Phys. Rev. B 94, 121410 (2016).
32. D. Bedeaux and J. Vlieger, Optical Properties of Surfaces (World Scientific, Singapore, 2004).