A Thermokinetic Approach to Radiative Heat Transfer at the Nanoscale

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Abstract

Radiative heat exchange at the nanoscale presents a challenge for several areas due to its scope and nature. Here, we provide a thermokinetic description of microscale radiative energy transfer including phonon-photon coupling manifested through a non-Debye relaxation behavior. We show that a lognormal-like distribution of modes of relaxation accounts for this non-Debye relaxation behavior leading to the thermal conductance. We also discuss the validity of the fluctuation-dissipation theorem. The general expression for the thermal conductance we obtain fits existing experimental results with remarkable accuracy. Accordingly, our approach offers an overall explanation of radiative energy transfer through micrometric gaps regardless of geometrical configurations and distances.

Introduction

There is a general consensus that the search for clean sources of energy with no climatic and environmental impact constitutes a major strategic objective at present. In this sense, nanoscale thermal radiation conversion offers a source for intensive clean energy generation. Thermal radiation has always been an active field of study. Throughout the 19th century, great scientists (Boltzmann, Stefan, Rayleigh, etc.) dedicated a considerable effort to this problem which was completely solved at the turn of the 20th century due to Planck's contribution to the founding of quantum mechanics. After this, it seemed to be a well-established fact that thermal radiation conversion offers a source for intensive clean energy generation. Several reviews on this issue have been written recently, see Ref. [1–3] by way of example.

Nonetheless, as two nanostructures thermalized at different temperatures come closer to each other, the distribution of charges and currents becomes asymmetric and therefore, defies description in terms of dipolar interactions. Hence, it becomes clear that one must bear in mind higher order effects beyond the dipole [14] and consequently, the fluctuation-dissipation theorem (FDT), whose validity is not guaranteed at this level. Thus, an approach based on the contributions of fluctuating dipole effects seems to be the heart of a considerably simplified treatment of energy transfer at the nanoscale [7,8,13]. These approaches include a wide range of phenomena in which the energy between molecules is dominated by dipole-dipole interactions, also known as the Förster energy transfer [14].

Nonetheless, as two nanostructures thermalized at different temperatures come closer to each other, the distribution of charges and currents becomes asymmetric and therefore, defies description in terms of dipolar interactions. Hence, it becomes clear that one must bear in mind higher order effects beyond the dipole [14] and also include other contributions to thermal conductance quite common in disordered amorphous materials, leading to a generalization of the FDT mentioned above [16].
In this article, we will go deeper into these aspects by showing how phonon-phonon coupling effects account for microscale radiative energy transfer by considering non-Debye relaxation due to the excess of modes in the low and high frequencies in the bulk material [15–17]. In the current literature on disordered systems, the non-Debye refers to an excess of modes of vibration over the Debye level observed in inelastic light (Raman) and neutron scattering. From here, we obtain a general expression for the heat transfer coefficient including both Debye and non-Debye contributions, providing an overall explanation of the energy transfer through micrometric gaps. The findings of our theory fit existing experimental results with a high degree of accuracy.

Methods

Our theoretical framework has been described in previous publications [16,17] and is briefly summarized here. We consider a gas of quanta distributed in phase space according to the probability density \( \rho(\Gamma,t) \), where \( \Gamma = (p,x) \), \( p \equiv |p| \), and \( x \equiv |x| \), with \( p \) and \( x \) being the momentum and position of a quanta, respectively. Here, we must pay attention to the fact that \( \rho(\Gamma,t) \) possesses dimensions of \( h^{-3} \), \( h \) being Planck’s constant. The thermodynamic description that we propose entails the formulation of the second law of thermodynamics, which can be carried out by means of the Gibbs entropy postulate [18],

\[
S(t) = -k_B \int_\mathbb{R} \rho(\Gamma,t) \log \frac{\rho(\Gamma,t)}{\rho_{eq}(\Gamma)} d\Gamma dx + S_{eq}. \tag{1}
\]

This equation gives us the nonequilibrium entropy of the gas of quanta plus the bath, with \( S_{eq} \) being the equilibrium entropy and \( \rho_{eq} \) the equilibrium probability density.

In general, entropy is produced due to irreversible processes, in such a manner that irreversible processes in nonequilibrium systems are described by means of currents, thermodynamic forces (affinities), and the entropy production rate, which is always positive. It is precisely this positive character of the entropy production that enables us to derive relaxation equations. Since the probability density is conserved the existence of a density gradient \( \frac{\partial \rho(\Gamma,t)}{\partial \Gamma} = \left( \frac{\partial p}{\partial \Gamma}, \frac{\partial x}{\partial \Gamma} \right) \) yields a current \( J(\Gamma,t) = (J_p,J_x) \) which unleashes a relaxation process \( \frac{\partial \rho}{\partial t} = -\nabla \cdot J(\Gamma,t) \). In addition, this current satisfies the relation \( J(\Gamma,t) = -\nabla \cdot \mathbf{D}(\rho) \frac{\partial \rho(\Gamma,t)}{\partial \Gamma} \), derived from the entropy production, which can be obtained from Eq. (1) [16,18]. Here, \( \mathbf{D}(\rho) \) is a material-dependent quantity, the matrix of diffusion coefficients, satisfying Onsager’s symmetry principle. In general, due to the tensorial character of the diffusion matrix, both currents \( J_x \) and \( J_p \) are coupled

\[
J_x = -D_{\beta\beta} \frac{\partial \rho}{\partial \beta}, \quad \text{with} \quad \alpha, \beta = x, p, \tag{2}
\]

where \( D_{\alpha\beta} \) are the diffusion matrix components.

The main contribution of this article is to apply this formalism to the description of the radiative heat transfer between a nanosphere and a plate at different temperatures, \( T_1 \) (hot) and \( T_2 \) (cold), separated by a distance \( d \) (see Fig. 1). We assume that heat transfer results from two different mechanisms. (I) On one hand, we consider a conventional radiative heat exchange involving the dynamics of quasiparticles as the result of two simultaneous processes: elastic emission and absorption of hot photons from the medium at \( T_1 \) and elastic emission and absorption of cold photons from the medium at \( T_2 \); these processes also involve the presence of surface modes [6,10]. (II) The second mechanism behind heat transfer has to do with the excitation of coupled resonant modes from the collection of acoustic states related to defective soft structures in a disordered regime [19–21]. This process encompasses inelastic scattering of the impinging radiation, which is linked to nonequilibrium contributions. In both scenarios, there is no diffusion in configuration space since quanta are massless particles [16], and as a consequence \( J_p = 0 \), which brings about \( J(\Gamma,t) \rightarrow J_p(\Gamma,t) \). Hence, from Eq. (2) one obtains the appropriate diffusion current in momentum space

\[
J_p(\Gamma,t) = \left( \frac{D_{pp}}{D_{xx}} - D_{xp} \right) \frac{\partial \rho(\Gamma,t)}{\partial \Gamma} = -\frac{h}{\tau(\rho)} \frac{\partial \rho(\Gamma,t)}{\partial x}, \tag{3}
\]

where \( \tau(\rho) \) is the relaxation time, which depends on the diffusion matrix components.

Near-field analysis

In the near-field regime, confinement of the electromagnetic waves in a micrometric gap separating neighboring nanostructures introduces peculiar effects in the spectrum of the thermal radiation. Here is where the collective modes (phonons) excited in the material by the impinging radiation come into play. To discern whether confinement effects are important or absent we shall assume a cut-off wavelength, the thermal wavelength of a photon \( \lambda_T = \hbar c/k_B T \), which is proportional to the Wien’s displacement law through a proportionality constant, i.e. \( \lambda_T = \beta/T \), where \( \beta \approx 2.82143937212 \). Actually, when \( d \gg \lambda_T \) we have a blackbody spectrum of radiation. One may wonder what happens when \( d \ll \lambda_T \). Since according to Heisenberg’s principle \( \Delta x \Delta p \geq \hbar \), assuming that the maximum value of \( \Delta x \) is \( d \), one obtains \( \Delta p \geq \hbar/d \), and thus the minimum value of \( \Delta p \) is \( \hbar/d \), leading to \( \Delta E \geq \hbar c \varepsilon/d \), with \( 0 < \varepsilon \ll 1 \). Here, \( \varepsilon \), is precisely, the inverse of the refractive index. Hence, not all frequencies are possible and the frequency of resonance \( \omega_R = 2\pi\varepsilon/c \) appears.

In these circumstances, integrating by parts the resultant continuity equation gives us

\[
\int_0^\infty \int_{-\infty}^{\infty} \left( -\frac{\partial \rho}{\partial t} \right) dp dx = J_p \tag{4}
\]

with \( J_p = p/\hbar \varepsilon^2 \), where we have assumed that \( J_p(\Gamma,t) = 0 \) at \( p = -\infty \). Performing a second integration of Eq. (3) through from \( 1 \) to \( 2 \), we find the net current

\[
J(p,t) = -\frac{h}{\tau(\rho)} (\rho_2 - \rho_1), \tag{5}
\]

where \( \rho_j(p,t) = \rho(p,x_j,t) \) is related to the population of quasiparticles at \( x_j \) and \( \rho_1 + \rho_2 = 1 \). Moreover, \( J(p,t) = (1/\tau(\rho)) \int_0^{\infty} \tau(\rho) J_p dp dx \), with \( \tau(\rho) = \int_0^{\infty} \tau(\rho) dp dx \) corresponding to a hierarchy of relaxation times ubiquitous in complex systems.

In the stationary state, once the system has thermalized at temperatures \( T_1 \) and \( T_2 \), \( J(p,t) = 2N(\omega_0,T)/\hbar^2 \); the factor 2 comes from the polarization of a photon and \( N(\omega,T) \) the being the averaged number of quasiparticles in a elementary cell of volume \( \hbar^3 \) of the phase-space given by Planck’s distribution [22], \( N(\omega,T) = 1/\exp(h\omega/k_B T) - 1 \). Besides, \( \tau(\rho) = \tau(\omega_0 \rho) \); therefore leading to a stationary value, i.e. \( J(p,t) \rightarrow J_\omega(p,\omega) \). Thus, the heat flow \( \dot{Q} \) can be obtained from the sum of all the contributions as

\[
\dot{Q} = -\int_0^{\infty} J(p,t) dp dx = -\int_0^{\infty} \left( -\frac{h}{\tau(\rho)} (\rho_2 - \rho_1) \right) dp dx.
\]
At this point, it is worthwhile to make a short digression about the physical meaning of the time scale $\tau^*(\omega)$. It has been known for a long time [23] that for most condensed systems in time-dependent fields, the orientation polarization behavior can, as a good approximation, be characterized by a relaxation time distribution ($\tau^*(t)$); this behavior is generally meant as dielectric relaxation. In harmonic fields, this implies that the complex dielectric permittivity in the frequency range corresponding to the characteristic times for the molecular reorientation can be written as

$$\epsilon(\omega) = \epsilon_\infty + (\epsilon_s - \epsilon_\infty) \frac{1}{1 + i \omega \tau},$$

where $\epsilon_s$ is the static dielectric constant and $\epsilon_\infty$ is the permittivity at the infinite frequency. Here, the relaxation time distribution $\zeta(t)$ satisfies the normalization condition, $\int_0^\infty \zeta(t) dt = 1$ and Eq. (8) constitutes a generalization of the Debye treatment based on Clausius-Mossotti equation [24]

$$\epsilon(\omega) = \epsilon_\infty + (\epsilon_s - \epsilon_\infty) \frac{1}{1 + i \omega \tau}.$$ 

This Debye’s equation, Eq. (9), follows after Fourier-transforming the relaxation function $\phi(t) = \exp(-t/\tau)$ which coincides with the normalized dielectric function $(\epsilon_s - \epsilon(t))/(\epsilon_s - \epsilon_\infty)$. Note that if we assume a time-independent time scale $\tau$ in Eq. (5), after integration we shall obtain the Debye relaxation function in terms of $\exp(-t/\tau)$. Hence, we can understand $\tau^*(\omega)$ as defined through the relation

$$\int_0^\infty \frac{\zeta(t)}{1 + i \omega \tau} dt = \frac{1}{1 + i \omega \tau^*(\omega)},$$

which shows that the Callen-Welton FDT [25] is not valid at this level. In fact, unlike here, the FDT is related to decaying equilibrium fluctuations characterized, precisely, by a single relaxation time.

Now, let’s return to the main topic after that brief digression. Note that according to Eq. (6), in the limit $d \to \infty$,

$$Q = \frac{1}{2} h^3 \varepsilon c \int_0^\infty J_\nu(\omega) g(\omega) d\omega,$$

giving us the blackbody radiation limit provided $\tau^*(\omega)^{-1} \propto \omega$, $Q \propto \left(k_B T_1\right)^4 - \left(k_B T_2\right)^4$. On the other hand, in the limit $d \to 0$, $Q \to 0$ which in contrast to the descriptions based on evanescent surface waves avoids divergences in the heat flux in a self-consistent way. Nonetheless, for finite $d$ we can rephrase the expression of the heat current given by Eq. (6) introducing a new variable $\omega = 1/s$

$$Q = \frac{1}{2} h^3 \varepsilon c \int_0^{\omega^{-1}} J_\nu [\omega(s)] g(\omega) ds$$

$$\approx \frac{h^3 c \varepsilon R_0}{2 \omega} J_\nu [\omega(\chi \omega R_0^{-1})] \left[\omega(\chi \omega R_0^{-1})\right]$$

where the mean value theorem has been used to approximate the integral, with $0 < \chi < 1$. Hence, since $\omega(\chi \omega R_0^{-1}) = \chi^{-1} \omega R_0$, Eq. (12)
Here, in the proposed case, we assume that the density of vibrational states anomalies [27]. Therefore, this accounts for the high nonlinear Raman spectra is fitted using a lognormal function first proposed by Denisov and Rylev [19]. This lognormal distribution is a cumulative effect of incident photons ends perturbing the material, thus triggering collective oscillations. In addition, the lognormal accounts for an excess of ways of adsorbing energy by the system with respect to the ways obtained when merely the Debye squared-frequency law describes the relaxation. Therefore, this provides a reasonable description of the non-Debye law [20,21], which as in Raman scattering also becomes manifest in radiation problems.

Accordingly, the heat transfer coefficient, Eq. (16), results from the addition of the elastic and inelastic contributions mentioned above

\[
H(d,T_0) = \frac{k_B}{\tau_0 d^2} \left[ 1 + \frac{(2\pi)^2 v c}{\sigma \omega d} \exp \left\{ - \frac{\ln^2(\omega/\omega_0)}{2\sigma^2} \right\} \right]
\]

(20)

where \( \tau_0 = \frac{1}{k_B T_0} \) and \( v = \omega / \omega_0 \). In Eq. (20), the first term inside the square brackets corresponds to the usual contributions found up to now in the current literature [6], taking into account surface phonon-polaritons owing to the presence of evanescent waves close to the interface. As we have mentioned above, the second term takes into account cooperative phenomena, becoming manifest through the existence of collective modes of vibration in the system, which appear in the density of states. Consequently, a more general formulation for the radiative heat transfer problems must come from the superposition of Debye and non-Debye relaxation mechanisms, combining in this way the contributions from the material surfaces as well as the bulk.

### Results and Discussion

The thermal conductance is obtained by integrating the heat transfer coefficient over the surface of a sphere of radius \( R \) divided by its area (\( A = 4\pi R^2 \)), i.e. \( G = (1/A) \int_0^R H(d(r), T_0) 2\pi r dr \). Since the distance \( d \) between both surfaces depends on geometrical characteristics, the local distance between the sphere and the plane surface must be measured through the local radius \( r \), assuming the effective distance as \( d(r) = d + b + R - \sqrt{R^2 - r^2} \), with \( b \) being a surface roughness parameter [7].

We have calculated numerically the surface average by adjusting the parameters mentioned above to the experimental results obtained in the Ref [9], which takes into account only the near-field contribution when decreasing the sphere-plate distance. In Fig. 2, we show the near-field conductance fitting the value of the integral of Eq. (20) to the data for glass-glass [8] and gold-gold materials [9]. For both the material we have used \( (\tau_0)^{-1} = 2.1 \times 10^9 \) Hz, \( \omega_0 = 1.7 \times 10^{-11} \) Hz, and \( \sigma = 6.0 \times 10^{18} \). For the glass-glass material we have obtained \( \nu = 3.2 \times 10^{-3} \) and for gold-gold \( \nu = 7.9 \times 10^{-4} \). The near-field heat transfer described using evanescent waves as solutions of classical electrodynamics equations leads to heat flux divergences as the gap vanishes [28]. However, in our approach this divergence does not occur,
reaching a constant-conductance value as the distance between the nanoparticles decreases (shown in the inset). In essence, this is due to the fact that the time relaxation distribution herein described by lognormal distribution incorporates two effects: (I) Phonon branches in a real structure affecting the density of states in different frequency regions, similar to actual behavior observed in metals [29]; and (II) the vibrational modes in the bulk material absorbing the energy excess. Hence, since our assumption of a distribution of relaxation times accurately describes the dynamics of radiative systems at the microscale, we conclude that the FDT in the Callen-Welton formulation [25] is not applicable at the nanoscale and must be modified. By going beyond the Debye theory, a way for this generalization is offered here.

Conclusions

In summary, we have evaluated thermal conductance in the near-field, giving a thermokinetic description of some experiments involving heat radiation through a very narrow gap. Although near-field radiative transfer is a highly complex phenomenon, we have been able to provide a unified and highly accurate explanation of heat exchange processes at the nanoscale. Our theory covers all distances from the far-field up to contact. Since the experiments examined may involve a great variety of nanostructures, our theory possesses a wide scope of applications. The general methodology presented here may also be used in the study of other heat exchange processes such as those occurring in phonon systems and in the analysis of thermal contributions to Casimir forces, even in charge conduction problems in nanosystems.

Supporting Information

Appendix S1 Supporting Information.

Author Contributions

Conceived and designed the experiments: APM LCL JMR. Performed the experiments: APM LCL JMR. Analyzed the data: APM LCL JMR. Contributed reagents/materials/analysis tools: APM LCL JMR. Wrote the paper: APM LCL JMR.

References

1. Zhang Z (2007) Nano Microscale Heat Transfer. New York: McGraw-Hill.
2. Morozhenko V (2012) Nanoscale radiative heat transfer and its applications. In infrared radiation. InTech.
3. S Basu YBC, Zhang ZM (2007) Microscale radiation in thermophotovoltaic devices - a review. Int J Energy Res 31: 689–716.
4. Polder D, van Hove M (1971) Theory of radiative heat transfer between closely spaced bodies. Phys Rev B 4: 3303–3314.
5. Rytov SM (1959) Theory of electric fluctuations and thermal radiation. Bedford: AFCRC-TR. Air Force Cambridge Research Center, Air Research and Development Command, U.S. Air Force.
6. Mulet JP, Joulain K, Carminati R, Greffet J (2002) Enhanced radiative heat transfer at nanometric distance. Microscale Thermophys Eng 6: 209–222.
7. Rousseau E, Siria A, Jourdan G, Volz S, Comin F, et al. (2009) Radiative heat transfer at the nanoscale. Nature Photon 3: 514–517.
8. Shen S, Narayanawamy A, Chen G (2009) Surface phonon polaritons mediated energy transfer between nanoscale gaps. Nano Lett 9: 2899–2913.
9. Shen S, Mavrokefalos A, Sambegoro P, Chen G (2012) Nanoscale thermal radiation between two gold surfaces. Appl Phys Lett 100: 233114.
10. Pendry JB (1999) Radiative exchange of heat between nanostructures. J Phys: Condens Matter 11: 6621–6633.

Figure 2. Sphere-plate near-field heat transfer coefficients between a gold (or glass) sphere and a gold (or glass) substrate versus gap distances. The data are from Ref [9] for the 50 µm diameter spheres. The dotted lines are comparisons with the theoretical predictions from the proximity theorem. The inset shows a non-divergent regime as the gap vanishes.

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11. Biehs SA, Rousseau E, Greffet JJ (2010) Mesoscopic description of radiative heat transfer at the nanoscale. Phys Rev Lett 105: 234301.
12. Sasihithlu K, Narayanaswamy A (2011) Proximity effects in radiative heat transfer. Phys Rev B 83: 161406(R).
13. Domingues G, Volz S, Joulain K, Greffet JJ (2005) Heat transfer between two nanoparticles through near field interaction. Phys Rev Lett 94: 085901.
14. Förster T (1948) Zwischemolekulare energiewanderung und fluorresenz. Ann Phys (Leipzig) 437: 55–75.
15. Pérez-Madrid A, Rubí JM, Lapas LC (2008) Heat transfer between nanoparticles: Thermal conductance for near-field interactions. Phys Rev B 77: 155417.
16. Pérez-Madrid A, Lapas LC, Rubí JM (2009) Heat exchange between two interacting nanoparticles beyond the fluctuation-dissipation regime. Phys Rev Lett 103: 048301.
17. Pérez-Madrid A, Rubí JM, Lapas LC (2010) Non-equilibrium stefan-boltzmann law. J Non-Equilib Thermodyn 35: 279–288.
18. de Groot SR, Mazur P (1984) Nonequilibrium thermodynamics. New York: Dover.
19. Denisov YV, Rylev AP (1990) Frequency dependence of the density of vibrational states in glasses: Lognormal distribution. JETP Lett 52: 411–414.
20. Shintani H, Tanaka H (2008) Universal link between the boson peak and transverse phonons in glass. Nature Mater 7: 870–877.
21. Chumakov A, Monaco G, Monaco A, Crichton WA, Bosak A, et al. (2011) Equivalence of the boson peak in glasses to the transverse acoustic van hove singularity in crystals. Phys Rev Lett 106: 225501.
22. Planck M (1991) The theory of heat radiation. New York: Dover.
23. Yager W (1936) The distribution of relaxation times in typical dielectrics. Physics 7: 454–456.
24. Debye P (1929) Polar molecules. New York: Chemical Catalog Co.
25. Callen H, Welton T (1951) Irreversibility and generalized noise. Phys Rev 83: 34–40.
26. Graebner JE, Golding B, Allen LC (1986) Phonon localization in glasses. Phys Rev B 34: 5696–5701.
27. Zanatta M, Baldi G, Caponi S, Fontana A, Giloli E, et al. (2010) Elastic properties of permanently densified silica: A raman, brillouin light, and x-ray scattering study. Phys Rev B 81: 212201.
28. Pan JJ (2000) Radiative transfer over small distances from a heated metal. Opt Lett 25: 369–371.
29. Lynn JW, Smith HG, Nicklow RM (1973) Lattice dynamics of gold. Phys Rev B 8: 3493–3499.