Chapter from the book *Thermodynamics*
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1. Introduction

Systems in conditions of equilibrium strictly follow the rules of thermodynamics (Callen, 1985). In such cases, despite the intricate behaviour of large numbers of molecules, the system can be completely characterized by a few variables that describe global average properties. The extension of thermodynamics to non-equilibrium situations entails the revision of basic concepts such as entropy and its related thermodynamic potentials as well as temperature that are strictly defined in equilibrium. Non-equilibrium thermodynamics proposes such an extension (de Groot & Mazur, 1984) for systems that are in local equilibrium. Despite its generality, this theory is applicable only to situations in which the system manifests a deterministic behaviour where fluctuations play no role. Moreover, non-equilibrium thermodynamics is formulated in the linear response domain in which the fluxes of the conserved local quantities (mass, energy, momentum, etc.) are proportional to the thermodynamic forces (gradients of density, temperature, velocity, etc.). While the linear approximation is valid for many transport processes, such as heat conduction and mass diffusion, even in the presence of large gradients, it is not appropriate for activated processes such as chemical and biochemical reactions in which the system immediately enters the non-linear domain or for small systems in which fluctuations may be relevant.

To circumvent these limitations, one has to perform a probabilistic description of the system, which in turn has to be compatible with thermodynamic principles. We have recently proposed such a description aimed at obtaining a simple and comprehensive explanation of the dynamics of non-equilibrium systems at the mesoscopic scale. The theory, mesoscopic non-equilibrium thermodynamics, has provided a deeper understanding of the concept of local equilibrium and a framework, reminiscent of non-equilibrium thermodynamics, through which fluctuations in non-linear systems can be studied. The probabilistic interpretation of the density together with conservation laws in phase-space and positiveness of global entropy changes set the basis of a theory similar to non-equilibrium thermodynamics but of a much broader range of applicability. In particular, the fact of its being based on probabilities instead of densities allows for the consideration of mesoscopic systems and their fluctuations. The situations that can be studied with this formalism...
include, among others, slow relaxation processes, barrier crossing dynamics, chemical reactions, entropic driving, non-linear transport, and anomalous Brownian motion, processes which are generally non-linear. From the methodological point of view, given the equilibrium properties of a system, this theory provides a systematic and straightforward way to obtain stochastic non-equilibrium dynamics in terms of Fokker-Planck equations.

To set the groundwork for the development of the formalism, we discuss first the basic concepts of mesoscopic non-equilibrium thermodynamics and proceed afterwards with the application of the theory to non-equilibrium radiative transfer at the nanoscale.

2. Mesoscopic non-equilibrium thermodynamics

Mesoscopic non-equilibrium thermodynamics is based on the assumption of the validity of the second law in phase-space, which requires the appropriate definition of the non-equilibrium entropy

$$S(t) = -k_B \int \rho(\Gamma,t) \ln \frac{\rho(\Gamma,t)}{\rho_{eq}(\Gamma)} d\Gamma + S_{eq},$$

(1)

where $\rho(\Gamma,t)$ is the probability density of the system with $\Gamma$ a point of the phase space of the system, $S_{eq}$ is the equilibrium entropy of the system plus the thermal bath and $\rho_{eq}(\Gamma)$ is the equilibrium probability density. Note here that the non-equilibrium entropy given through Eq. (1) constitutes the expression of the Gibbs entropy postulate (de Groot & Mazur, 1984). In general, the phase-space point is a set of internal coordinates which univocally determine the state of the system. For a particle or a meso-structure, the set of internal coordinates could include the position and velocity of the particle, number of constituent atoms (as in the case of clusters), reaction coordinates, geometrical parameters, or any other mesoscopic quantity characterizing the state of the meso-structure (Pagonabarraga et al., 1997), (Rubí & Pérez-Madrid, 1999).

Changes in the entropy are related to changes in the probability density which, since the probability is conserved, are given through the continuity equation

$$\frac{\partial}{\partial t} \rho(\Gamma,t) = -\frac{\partial}{\partial \Gamma} \cdot J(\Gamma,t).$$

(2)

The continuity equation defines the probability current $J(\Gamma,t)$ whose expression follows from the entropy production.

Assuming local equilibrium in $\Gamma$-space, variations of the entropy $\delta S$ are related to changes in the probability density $\rho(\Gamma,t)$. By performing variations over our non-equilibrium entropy given through Eq. (1) and taking into account that $\delta \rho_{eq} = 0$ and $\delta S_{eq} = 0$, we obtain

$$\delta S = \int \frac{\mu(\Gamma,t)}{T} \delta \rho(\Gamma,t) d\Gamma \geq 0,$$

(3)

where we have introduced the non-equilibrium chemical potential

$$\mu(\Gamma,t) = k_B T \ln \frac{\rho(\Gamma,t)}{\rho_{eq}(\Gamma)} + \mu_{eq}.$$  

(4)
with $\mu_{eq}$ being the equilibrium chemical potential. For the photon gas we will consider in the next section, this quantity vanishes at equilibrium due to the massless character of these quasi-particles. Since $-T\delta S = \delta F$, with $F$ being the non-equilibrium free energy, from Eq. (3) we obtain

$$\delta F = \int \mu(\Gamma, t) \delta \rho(\Gamma, t) d\Gamma,$$

which shows the direct relation existing between the free energy and the non-equilibrium chemical potential. Hence, Eq. (3), which constitutes the Gibb’s equation of thermodynamics formulated in the phase-space, underlines the non-equilibrium chemical potential in physical terms. From Eqs. (2) and (3) we obtain the entropy production

$$\frac{\partial}{\partial t} S = -\int J(\Gamma, t) \cdot \left[ \frac{\partial \mu(\Gamma, t)}{\partial \Gamma} / T \right] d\Gamma \geq 0$$

as the product of a thermodynamic current and the conjugated thermodynamic force $\partial[\mu(\Gamma, t) / T] / \partial \Gamma$. The sign of entropy production determines the direction of evolution of the system and from this same quantity we infer linear laws relating thermodynamic currents and conjugated forces in the absence of non-local effects

$$J(\Gamma, t) = -L(\rho) \cdot \frac{\partial}{\partial \Gamma} \frac{\mu(\Gamma, t)}{T},$$

with $L(\rho)$ being the matrix of Onsager coefficients which, as required for the second law, should be positive-definite. The phenomenological law, Eq. (7), together with the expression of the non-equilibrium chemical potential, Eq. (4), lead to the Fick’s law of diffusion formulated in the mesoscale

$$J(\Gamma, t) = -D(\rho) \cdot \frac{\partial}{\partial \Gamma} \rho,$$

where $D(\rho) = k_B L / \rho$ is the matrix of diffusion coefficients. When Eq. (8) is substituted into the continuity equation (2), we obtain the diffusion equation for the probability distribution function

$$\frac{\partial}{\partial t} \rho(\Gamma, t) = \frac{\partial}{\partial \Gamma} D(\rho) \cdot \frac{\partial}{\partial \Gamma} \rho.$$

This equation governs the evolution of the probability distribution in the space of the internal coordinates and constitutes the basis for the study of the stochastic dynamics of the non-equilibrium system.

In the case where the equilibrium probability density is a non-homogeneous quantity, i.e. $\rho_{eq} = \exp(-\phi / k_B T)$, Eq. (8) becomes

$$J(\Gamma, t) = -D(\rho) \left( \frac{\partial}{\partial \Gamma} \rho - \frac{\rho}{k_B T} \frac{\partial}{\partial \Gamma} \phi \right)$$

and instead of Eq. (9) we write
the Fokker-Planck equation for evolution of the probability density in $\Gamma$-space which includes a drift term $\partial \phi / \partial \Gamma$ related to the potential $\phi = -k_B T \log \rho_{eq}$. In this sense, by knowing the equilibrium thermodynamic potential of a system in terms of its relevant variables it is possible to analyze its dynamics away from equilibrium. A particularly interesting circumstance is the case of a purely entropic barrier, often encountered in biophysics and soft-condensed matter.

3. Thermal radiation

Thermal radiation is a long-studied problem in the field of macroscopic physics. The analysis based on equilibrium thermodynamic grounds led to Planck’s blackbody radiation law. In addition, as Planck already realized, there are some limitations to his law due to the finite character of the thermal wavelength of a photon, i.e. when diffraction effects are negligible (Planck, 1959). In fact, once the characteristic length scales are comparable to the wavelength of thermal radiation Planck’s blackbody radiation law is no longer valid. In such a situation, the finite size of the system may give rise to non-equilibrium effects. In order to better understand these effects it becomes necessary to employ a non-equilibrium theory. The aforementioned finite-size effects become evident in all kinds of nanostructures where radiative heat transfer occurs. Radiative heat transfer in nanostructures constitutes an issue that, owing to the rapid advancement of nanotechnology, is the object of great research activity. Understanding and predicting heat transfer at the nanoscale poses wide implications both from the theoretical and applied points of view. There is a great variety of situations involving bodies separated by nanometric distances exchanging heat in an amount not predicted by the current macroscopic laws. We can mention the determination of the cellular temperature (Peng et al., 2010), near-field thermovoltaics (Narayanaswamy & Chen, 2003) and thermal radiation scanning tunneling microscope (De Wilde et al., 2006), just to cite some examples. In most of these cases the experimental length scales are similar to or even less than certain characteristic sizes of the system, i.e. the so-called near-field limit. For example, for two interacting nanoparticles (NPs) we would consider the distance between them as the experimental length scale and their diameter as the characteristic size of the system. Near-field radiative heat transfer becomes manifest through an enhancement of the power absorbed, which exceeds in several orders of magnitude the blackbody radiation limit (Rousseau et al., 2009).

The current literature on the subject of radiative energy exchange at the nanoscale is based on the validity of the fluctuation-dissipation theorem (Callen & Welton, 1951), (Landau & Lifshitz, 1980), (Joulain et al., 2005). In the dipole-dipole interaction approximation, dipole moments fluctuate since they are embedded in a heat bath. Consequently, the incident field also fluctuates as well as the energy of a pair of dipoles. Since this quantity is proportional to the dipole moment squared, its second moment is proportional to the dipole-dipole correlation function, which follows from the fluctuation-dissipation theorem. This procedure constitutes the so-called fluctuating electrodynamics (Domingues et al., 2005). Expressions for the fluctuation-dissipation theorem can also be found even when the dipolar approximation is no longer valid since due to the particular charge distribution, higher order multipoles become important (Pérez-Madrid et al., 2008). Such as in the case of two interacting NPs illustrated in Fig. 1.
Mesoscopic Non-Equilibrium Thermodynamics: Application to Radiative Heat Exchange in Nanostructures

Fig. 1. Schematic illustration of the interaction between two nanoparticles (NP1 and NP2) at temperatures $T_1$ and $T_2$, respectively. Each nanoparticle is assimilated to a multipole moment (moments $M_1^{(i)}$ and $M_2^{(m)}$) and separated by a distance $d$ between their centres.

For extremely short length scales, since the relaxation processes involved in the absorption and emission of radiation does not follow a Debye law related to a definite relaxation time, the fluctuation-dissipation theorem ceases to be valid and a collective description becomes necessary.

In the following Sections, we will present a non-equilibrium thermo-statistical theory describing the heat exchange at the nanoscale in the framework of mesoscopic non-equilibrium thermodynamics based on the assumption of the validity of the second law and the existence of local regression laws at the mesoscale (Reguera et al., 2006).

4. Mesoscopic non-equilibrium thermodynamics of thermal radiation

In this section, we will apply the mesoscopic non-equilibrium theory developed in the previous section to study the heat exchange by thermal radiation between two parallel plates at different temperatures separated by a distance $d \gg \lambda_T$, where $\lambda_T = c \omega / k_B T$ is the thermal wavelength of a photon (see Fig. 2). For such distances, diffraction effects can be neglected safely.

Fig. 2. Schematic illustration of the radiation exchanged between two materials maintained at different temperatures, $T_1$ and $T_2$, separated by a distance $d$.

Let us consider the photon gas between two plates at local equilibrium in phase-space. We will assume that the photons do not interact among themselves. The gas is then homogeneous and a phase-space point is merely $\Gamma \rightarrow p$ and thus, the diffusion matrix...
reduces to a scalar $D(\Gamma)$, the diffusion coefficient. Additionally, if there are only hot and cold photons at temperatures $T_1$ and $T_2$, respectively, then

$$J(p,t) = \hat{j}_1(t) \delta(p-p_1) + \hat{j}_2(t) \delta(p-p_2), \quad (12)$$

i.e., the system reaches a state of quasi-equilibrium. Thus, integration of Eq. (8) taking into account (12), leads to

$$\frac{\hat{j}_1(t)}{D_1} + \frac{\hat{j}_2(t)}{D_2} = \rho(p_1,t) - \rho(p_2,t), \quad (13)$$

with $\hat{j}(t) = \mathbf{u} \cdot \hat{j}(t)$ and $\mathbf{u}$ being the unit vector normal to the walls. Additionally, $D_1$ and $D_2$ correspond to the diffusion coefficient of hot and cold photons. From here, by introducing the net current $J(t)$ defined through

$$J(t) = \frac{J_1(t)}{D_1} + \frac{J_2(t)}{D_2}, \quad (14)$$

where $a$ is a dimensionality factor, or equivalently

$$J(t) = aD_1\hat{j}_2(t) + aD_2\hat{j}_1(t), \quad (15)$$

according to Eq. (13) we obtain

$$J(t) = -aD_1D_2 \left[ \rho(p_2,t) - \rho(p_1,t) \right]. \quad (16)$$

Term-by-term comparison of Eqs. (15) and (16) leads to the identification of the currents

$$\hat{j}_1(t) = D_1\rho(p_1,t) \quad (17)$$

and

$$\hat{j}_2(t) = -D_2\rho(p_2,t) \quad (18)$$

Therefore,

$$D_1\hat{j}_2(t) = -D_1D_2\rho(p_2,t) \quad (19)$$

represents the fraction of photons absorbed at the hot surface from the fraction $\hat{j}_2(t)$ of photons emitted at the cold surface. Likewise,

$$D_2\hat{j}_1(t) = D_1D_2\rho(p_1,t) \quad (20)$$

represents the fraction of photons absorbed at the cold surface from the fraction $\hat{j}_1(t)$ of photons emitted at the hot surface.

For a perfect absorbed, i.e. the ideal case, $D_1 = D_2 = 1$ and if the temperatures $T_1$ and $T_2$ remain constant, hot and cold photons will reach equilibrium with their respective baths and the probability current will attain a stationary value.
\[ J_\omega(\omega) = a \left[ \rho_{eq}(\omega, T_1) - \rho_{eq}(\omega, T_2) \right] \]  

\[ \rho_{eq}(\omega, T) = 2 \frac{N(\omega, T)}{h^3} \]  

where \( h \) being the Planck constant and \( N(\omega, T) \) the averaged number of photons in an elementary cell of volume \( h^3 \) of the phase-space given by the Planck distribution (Planck, 1959),

\[ N(\omega, T) = \frac{1}{\exp(\hbar \omega / k_b T) - 1}. \]  

Moreover, the factor 2 in Eq. (22) comes from the polarization of photons. The stationary current (21) provides us with the flow of photons. Since each photon carries an amount of energy equal to \( \hbar \omega \), the heat flow \( Q_{12} \) follows from the sum of all the contributions as

\[ Q_{12} = \int h\omega J_\omega(\omega) dp. \]  

where \( p = (h \omega / c) \Omega_p \), with \( \Omega_p \) being the unit vector in the direction of \( p \). Therefore it follows that by taking \( a = c / 4 \)

\[ Q_{12} = \frac{c}{16\pi} \int d\omega d\Omega \Lambda(\omega) \left[ \theta(\omega, T_1) - \theta(\omega, T_2) \right], \]  

with \( \theta(\omega, T) = \hbar \omega N(\omega, T) \) being the mean energy of an oscillator and where \( \Lambda(\omega) = \omega^2 / \pi^2 c^3 \) plays the role of the density of states. By performing the integral over all the frequencies and orientations in Eq. (25) we finally obtain the expression of the heat interchanged

\[ Q_{12} = \sigma \left( T_1^4 - T_2^4 \right), \]  

where \( \sigma = \pi^2 k_b^4 / 60 h^3 c^2 \) is the Stefan constant. At equilibrium \( T_1 = T_2 \), therefore \( Q_{12} = 0 \). This expression reveals the existence of a stationary state (Saida, 2005) of the photon gas emitted at two different temperatures. Note that for a fluid in a temperature gradient, the heat current is linear in the temperature difference whereas in our case this linearity is not observed. Despite this fact, mesoscopic non-equilibrium thermodynamics is able to derive non-linear laws for the current. In addition, if we set \( T_2 = 0 \) in Eq. (26), we obtain the heat radiation law of a hot plate at a temperature \( T_1 \) in vacuum (Planck, 1959)

\[ Q_1 = \sigma T_1^4. \]  

5. Near-field radiative heat exchange between two NPs

In this section, we will apply our theory to study the radiative heat exchange between two NPs in the near-field approximation, i.e. when the distance \( d \) between these NPs satisfies both \( d < \lambda_t \) and the near-field condition \( 2R \leq d \leq 4R \), with \( R \) being the characteristic radius
of the NPs. These NPs are thermalized at temperatures \( T_1 = T_2 \) (see Fig. 3). In particular we will compute the thermal conductance and compare it with molecular simulations (Domingues et al., 2005).

![Fig. 3. Illustration of two interacting nanoparticles of characteristic radius \( R \) separated by a distance \( d \) of the order nm](image)

Since in the present case diffraction effects cannot be ignored \( D_1 \) and \( D_2 \) must be taken as frequency dependent quantities rather than constants and hence, Eq. (25) also applies, now with \( \Lambda(\omega) = D_1(\omega)D_2(\omega)\omega^2 / \pi^2 c^3 \). This density of states differs from the Debye approximation \( \omega^2 / \pi^2 c^3 \) related to purely vibration modes and is a characteristic of disordered systems which dynamics is mainly due to slow relaxing modes. Analogous to similar behaviour in glassy systems, we assume here that (Pérez-Madrid et al., 2009)

\[
D_1(\omega)D_2(\omega) = A \exp \left( \frac{B^2 \omega^2}{2} \right) \delta(\omega - \omega_R),
\]

where the characteristic frequency \( A \) and the characteristic time \( B \) are two fitting parameters, and \( \omega_R = 2\pi c / d \) is a resonance frequency.

The heat conductance is defined as

\[
G_{12}(T_0) / \pi R^2 = \lim_{\omega \to \infty} \frac{Q_{12}(\omega)}{\pi R^2} = \frac{Q_{12}(\omega)}{\pi R^2},
\]

where \( T_0 = (T_1 + T_2) / 2 \) is the temperature corresponding to the stationary state of the system. Therefore,

\[
G_{12}(T_0) = \frac{k_B \omega_R^2 R^2}{4\pi c^2} A \exp \left( \frac{B^2 \omega_R}{2} \right) \left[ \frac{\hbar \omega_R / k_B T_0}{\sinh \left( \hbar \omega_R / 2k_B T_0 \right)} \right]^2.
\]

In Fig. 4, we have represented the heat conductance as a function of the distance \( d \) between the NPs of different radii. This figure shows a significant enhancement of the heat conductance when \( d \) decreases until \( 2D \), which, as has been shown in a previous work by means of electromagnetic calculations and using the fluctuation-dissipation theorem (Pérez-Madrid et al., 2008), is due to multipolar interactions. In more extreme conditions when the NPs come into contact to each other, a sharp fall occurs which can be interpreted as due to an intricate conglomerate of energy barriers inherent to the amorphous character of these NPs generated by the strong interaction. In these last circumstances the multipolar expansion is no longer valid.
Fig. 4. Thermal conductance $G_{12}$ vs. distance $d$ reproducing the molecular dynamics data obtained by (Domingues et al., 2005). The grey points represent the conductance when the NPs with effective radius $R = 0.72$, 1.10, and 1.79 nm are in contact. The lines show the analytical result obtained from Eq. (30) by adjusting $A$ and $B$ to the simulation data.

6. Conclusions

The classical way to study non-equilibrium mesoscopic systems is to use microscopic theories and proceed with a coarse-graining procedure to eliminate the degrees of freedom that are not relevant to the mesoscopic scale. Such microscopic theories are fundamental to understand how the macroscopic and mesoscopic behaviours of the system arise from the microscopic dynamics. However, these theories frequently involve specialized mathematical methods that prevent them from being generally applicable to complex systems; and more importantly, they use much detailed information that is lost during the coarse-graining procedure and that is actually not needed to understand the general properties of the mesoscopic dynamics.

The mesoscopic non-equilibrium thermodynamics theory we have presented here starts from mesoscopic equilibrium behaviour and adds all the dynamic details compatible with the second principle of thermodynamics and with the conservation laws and symmetries inherent to the system. Thus, given the equilibrium statistical thermodynamics of a system, it is a straightforward process to obtain Fokker-Planck equations for its dynamics. The dynamics is characterized by a few phenomenological coefficients, which can be obtained for the particular situation of interest from experiments or from microscopic theories and describes not only the deterministic properties but also their fluctuations.

Mesoscopic non-equilibrium thermodynamics has been applied to a broad variety of situations, such as activated processes in the non-linear regime, transport in the presence of entropic forces and inertial effects in diffusion. Transport at short time and length scales exhibits peculiar characteristics. One of them is the fact that transport coefficients are no longer constant but depend on the wave vector and frequency. This dependence is due to the existence of inertial effects at such scales as a consequence of microscopic conservation.
law. The way in which these inertial effects can be considered within a non-equilibrium thermodynamics scheme has been shown in Rubí & Pérez-Madrid, 1998.

We have presented the application of the theory to the case of radiative heat exchange, a process frequently found at the nanoscale. The obtention of the non-equilibrium Stefan-Boltzmann law for a non-equilibrium photon gas and the derivation of heat conductance between two NPs confirm the usefulness of the theory in the study of thermal effects in nanosystems.

7. References


Progress of thermodynamics has been stimulated by the findings of a variety of fields of science and technology. The principles of thermodynamics are so general that the application is widespread to such fields as solid state physics, chemistry, biology, astronomical science, materials science, and chemical engineering. The contents of this book should be of help to many scientists and engineers.

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