Fourier Law

Federico Bonetto

School of Mathematics, Georgia Institute of Technology, Atlanta, GA
30332-0160, Email: bonetto@math.gatech.edu

Luc Rey-Bellet

Department of Mathematics and Statistics, University of Massachusetts,
Amherst, MA 01003, Email: lr7q@math.umass.edu

1   Introduction

In the famous 1822 treatise by Jean Baptiste Joseph Fourier, "Théorie analytique de la chaleur", the "Discours préliminaire" opens with:

"Primary causes are unknown to us; but are subject to simple and constant laws, which may be discovered by observation, the study of them being the subject of natural philosophy.

Heat, like gravity, penetrates every substance of the universe, its ray occupy all parts of space. The object of our work is to set forth the mathematical laws which this element obeys. The theory of heat will hereafter form one of the most important branches of general physics."

After a brief discussion of rational mechanics he continues with the sentence:

"But whatever may be the range of mechanical theories, they do not apply to the effects of heat. These make up a special order of phenomena, which cannot be explained by the principles of motion and equilibria" .

Fourier goes on with a thorough description of the phenomenology of heat transport and the derivation of the partial differential equation describing heat transport: the Heat Equation. A large part of the treatise is then devoted to solving the Heat Equation for various geometries and boundary conditions. Fourier's treatise marks the birth of Fourier analysis.

After Boltzmann, Gibbs, and Maxwell and the invention of statistical mechanics in the decades after Fourier's work, we believe that Fourier was wrong and that, in principle, heat transport can and should be explained "by the principles of motion and equilibria", i.e. within the formalism of

1

Statistical Mechanics. But well over a century after the foundations of Statistical Mechanics were laid down, we still lack a mathematically reasonable derivation of Fourier's Law from first principles.

Fourier's Law describes the macroscopic transport properties of heat, *i.e.* energy, in nonequilibrium systems. Similar laws are valid for the transport of other locally conserved quantities, e.g. charge, particle density, momentum, etc... We will not discuss these laws here, except to point out that in none of these cases either, macroscopic transport laws have been derived from microscopic dynamics.

As Peierls once put it: *"It seems there is no problem in modern physics for which there are on record as many false starts, and as many theories which overlook some essential feature, as in the problem of the thermal conductivity of [electrically] non-conducting crystals"*.

2   Macroscopic Law

Consider a macroscopic system characterized at some initial time, say $t = 0$, by a nonuniform temperature profile $T_0(\mathbf{r})$. This temperature profile will generate a heat, *i.e.* energy, current $\mathbf{J}(\mathbf{r})$. Due to energy conservation and basic Thermodynamics:

$$c_v(T)\frac{\partial}{\partial t}T(\mathbf{r}, t) = -\nabla \cdot \mathbf{J}\,, \tag{1}$$

where $c_v(T)$ is the specific heat per unit volume. On the other side we know that if the temperature profile is uniform, *i.e.* $T_0(\mathbf{r}) \equiv T_0$ there is no current in the system. It is then natural to assume that, for small temperature gradients, the current is given by:

$$\mathbf{J}(\mathbf{r}) = -\kappa(T(\mathbf{r}))\nabla T(\mathbf{r})\,, \tag{2}$$

where $\kappa(T)$ is the conductivity. Here we have assumed that there is no mass flow or other mode of energy transport beside heat conduction (we also ignore for simplicity any variations in density or pressure). Equation (2) is normally called Fourier's Law. Putting together eqs. (1) and (2) we get the Heat Equation:

$$c_v(T)\frac{\partial}{\partial t}T(\mathbf{r}, t) = \nabla \cdot [\kappa(T)\nabla T]\,. \tag{3}$$

This equation must be completed with suitable boundary conditions. Let us consider two distinct situations in which the Heat Equation is observed experimentally to hold with high precision:

(1) An isolated macroscopic system, *e.g.* a fluid or solid in a domain Λ surrounded by effectively adiabatic walls. In this case Eq.(3) is to be solved subject to the initial condition $T(\mathbf{r}, 0) = T_0(\mathbf{r})$ and no heat flux across the boundary of Λ (denoted by $\partial\Lambda$), *i.e.* $\mathbf{n}(\mathbf{r}) \cdot \nabla T(\mathbf{r}) = 0$ if $\mathbf{r} \in \partial\Lambda$ with $\mathbf{n}$ the normal vector to $\partial\Lambda$ at $\mathbf{r}$. As $t \to \infty$, the system reaches a stationary state characterized by a uniform temperature $\bar{T}$ determined by the constancy of the total energy.

(2) A system in contact with heat reservoirs. Each reservoir α fixes the temperature of some portion $(\partial\Lambda)_\alpha$ of the boundary $\partial\Lambda$. The rest of the boundary is insulated. When the system reaches a stationary state (again assuming no matter flow) its temperature will be given by the solution of Eq.(3) with the left side set equal to zero,

$$\nabla \cdot \tilde{J}(\mathbf{r}) = \nabla \cdot (\kappa \nabla \tilde{T}(\mathbf{r})) = 0 \,, \tag{4}$$

subject to the boundary condition $\tilde{T}(\mathbf{r}) = T_\alpha$ for $\mathbf{r} \in (\partial\Lambda)_\alpha$ and no flux across the rest of the boundary.

The simplest geometry for a conducting system is that of a cylindrical slab of height h and cross sectional area A. It can be either a cylindrical container filled with a fluid or a piece of crystalline solid. In both cases one keeps the lateral surface of the cylinder insulated. If the top and the bottom of the cylinder are also insulated we are in case (1). If one keeps the top and the bottom in contact with thermostats at temperatures T_h and T_b respectively this is (for a fluid) the usual set up for a Benard experiment. To avoid convection one has to make $T_h > T_b$ or keep $|T_h - T_b|$ small. Assuming uniformity in the direction perpendicular to the vertical x-axis one has, in the stationary state, a temperature profile $\tilde{T}(x)$ with $\tilde{T}(0) = T_b$, $\tilde{T}(h) = T_h$ and $\kappa(\tilde{T})\frac{d\tilde{T}}{dx} =$Const. for $x \in (0, h)$.

In deriving the Heat Equation we have implicitly assumed that the system is described fully by specifying its temperature $T(\mathbf{r}, t)$ everywhere in Λ. What this means on the microscopic level is that we imagine the system to be in local thermal equilibrium (LTE). Heuristically we might think of the system

as being divided up (mentally) into many little cubes, each big enough to contain very many atoms yet small enough on the macroscopic scale to be accurately described, at a specified time t, as a system in equilibrium at temperature $T(\mathbf{r}_i, t)$, where $\mathbf{r}_i$ is the center of the i-th cube. For slow variation in space and time we can then use a continuous description $T(\mathbf{r}, t)$.

The theory of the Heat Equation is very developed and, together with its generalizations, play a central role in modern analysis. In particular one can consider more general boundary conditions. Here we are interested in the derivation of eq.(2) from first principles. This clearly presupposes, as a first fundamental step, a precise definition of the concept of LTE and its justification within the law of mechanics.

3   Empirical Argument

A theory of heat conduction has as a goal the computation of the conductivity $\kappa(T)$ for realistic models, or, at the very least, the derivation of behavior of $\kappa(T)$ as a function of T. The early analysis was based on "kinetic theory". It application to heat conduction goes back to the works of Clausius, Maxwell and Boltzmann who obtained a theoretical expression for the heat conductivity of gases, $\kappa \sim \sqrt{T}$, independent of the gas density. This agrees with experiment (when the density is not too high) and was a major early achievement of the atomic theory of matter.

3.1   Heat Conduction in Gases

Clausius and Maxwell used the concept of a "mean free path" λ: the average distance a particle (atom or molecule) travels between collisions in a gas with particle density ρ. Straightforward analysis gives $\lambda \sim 1/\rho\pi\sigma^2$, where σ an "effective" hard core diameter of a particle. They considered a gas with temperature gradient in the x-direction and assumed that the gas is (approximately) in local equilibrium with density ρ and temperature $T(x)$. Between collisions a particle moves a distance λ carrying a kinetic energy proportional to $T(x)$ from x to $x + \lambda/\sqrt{3}$, while in the opposite direction the amount carried is proportional to $T(x + \lambda\sqrt{3})$. Taking into account the fact that the speed is proportional to $\sqrt{T}$ the amount of energy J transported per unit

area and time across a plane perpendicular to the x-axis is approximately,

$$J \sim \rho\sqrt{T}\left[T(x) - T(x + \lambda\sqrt{3})\right] \sim -\sigma^{-2}\sqrt{T}\frac{dT}{dx} , \tag{5}$$

and so $\kappa \sim \sqrt{T}$ independent of ρ, in agreement with experiment.

It was clear to the founding fathers that starting with a local equilibrium situation the process described above will produce, as time goes on, a deviation from LTE. They reasoned however that this deviation from local equilibrium will be small when $(\lambda/T)dT/dx << 1$, the regime in which Fourier's law is expected to hold, and the above calculation should yield, up to some factor of order unity, the right heat conductivity.

To have a more precise theory one can describe the state of the gas through the probability distribution $f(\mathbf{r}, \mathbf{p}, t)$ of finding a particle in the volume element $d\mathbf{r}d\mathbf{p}$ around the phase space point $(\mathbf{r}, \mathbf{v})$. Here LTE means that $f(\mathbf{r}, \mathbf{p}, t) \simeq \exp\left(-\frac{\mathbf{p}^2}{2mkT(\mathbf{r})}\right)$, where m is the mass of the particles. If one computes the heat flux at a point $\mathbf{r}$ by averaging the microscopic energy current at $\mathbf{r}$, $j = \rho\mathbf{v}(\frac{1}{2}mv^2)$, over $f(\mathbf{r}, \mathbf{p}, t)$ then it is only the deviation from local equilibrium which makes a contribution. The result however is essentially the same as Eq.(5). This was shown by Boltzmann who derived an accurate formula for κ in gases by using the Boltzmann equation. If one takes κ from experiment the above analysis yields a value for σ, the effective size of an atom or molecule, which turns out to be close to other determinations of the characteristic size of an atom. This gave an evidence for the reality of atoms and the molecular theory of heat.

3.2   Heat conduction in insulating crystals

In (electrically) conducting solid heat is mainly transported by the conduction electron. In this case one can adapt the theory discussed in the previous section. In (electrically) insulating solids instead heat is transmitted through the vibrations of the lattice. In order to use concepts of kinetic theory, it is useful to picture a solid as a gas of phonons which can store and transmit heat. A perfectly harmonic crystal, due to the fact that phonons do not interact, has an infinite thermal conductivity: in the language of kinetic theory the mean free path λ is infinite. In a real crystal the anharmonic forces produce interactions between the phonons and therefore a finite mean free path. Another source of finite thermal conductivity may be the lattice imperfections and impurities which scatter the phonons.

Debye devised a kind of kinetic theory for phonons in order to describe thermal conductivity. One assumes that a small gradient of temperature is imposed and that the collisions between phonons maintain local equilibrium. An elementary argument gives a thermal conductivity analogous to Eq.(5) obtained in Section 3.1 for gases, (remembering however that the density of phonon is itself a function of T)

$$\kappa \sim c_v c^2 \tau \, . \tag{6}$$

where, with respect to eq.(6), ρ has been replaced by c_v the specific heat of phonons, $\sqrt{T}$ by c the (mean) velocity of the phonons, and λ by $c\tau$, where τ is the effective mean free time between phonon collisions. The thermal conductivity depends on the temperature via τ and a more refined theory is needed to account for this dependence. This was done by Peierls via a Boltzmann equation for the phonons. In phonons collisions the momentum of phonons is conserved only modulo a vector of the reciprocal lattice. One calls normal processes those where the phonon momentum is conserved and Umklap processes those where the initial and final momenta differ by a non-zero reciprocal lattice vector. Peierls theory may be summarized (very roughly) as follows: in the absence of Umklap processes the mean free path and thus the thermal conductivity of an insulating solid is infinite.

A success of Peierls theory is to describe correctly the temperature dependence of the thermal conductivity. Furthermore, on the basis of this theory, one does not expect a finite thermal conductivity in 1-dimensional mono-atomic lattices with pair interactions. This seems so far to be a correct prediction, at least in the numerous numerical results performed on various models.

4   Statistical Mechanics Paradigm: Rigorous analysis

In a rigorous approach to the above arguments we have first to formulate precisely the problem on a mathematical level. It is natural to adapt the standard formalism of Statistical Mechanics to our situation. To this end we assume that our system is described by the positions Q and momenta P of a (very large) number N of particles particle, with $Q = (\mathbf{q}_1, \ldots, \mathbf{q}_N) \in \Lambda^N$, $\Lambda \subset \mathbb{R}^d$ and $P = (\mathbf{p}_1, \ldots, \mathbf{p}_N) \in \mathbb{R}^{dN}$. The dynamics (in the bulk) is given

by an Hamiltonian function $H(Q, P)$. A state of the system is a probability measure $\mu(P, Q)$ on phase space. As usual in Statistical Mechanics the value of an observable $f(P, Q)$ will be given by the expected value of f with respect to the the measure μ.

In the case of a fluid contained in a region Λ we can assume that the Hamiltonian has the form

$$H(P, Q) = \sum_{i=1}^{N} \left[\frac{\mathbf{p}_i^2}{2m} + \sum_{j \neq i} \phi(\mathbf{q}_j - \mathbf{q}_i) + u(\mathbf{q}_i) \right] = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \mathcal{V}(Q), \quad (7)$$

where $\phi(\mathbf{q})$ is some short range inter particle potential, $u(\mathbf{q}_i)$ an external potential, e.g. the interaction of the particle with fixed obstacles like in the case of the conduction electron interacting with the fixed crystalline ions.

If we want to describe the case in which the temperature at the boundary are kept different in different regions $\partial \Lambda_\alpha$ we have to properly define the dynamics at the boundary of the system. A possibility is to use "Maxwell boundary conditions": when a particle hits the wall in $\partial \Lambda_\alpha$ it get reflected and reemerge with a distribution of velocities

$$f_\alpha(d\mathbf{v}) = \frac{m^2}{2\pi (kT_\alpha)^2} |v_x| \exp\left[-\frac{m\mathbf{v}^2}{2kT_\alpha} \right] d\mathbf{v} \quad (8)$$

Several other ways to impose boundary conditions have been considered in the literature.

The notion of LTE can be made precise here in the so called hydrodynamic scaling limit (HSL) where the ratio of microscopic to macroscopic scales goes to zero. The macroscopic coordinates $\mathbf{r}$ and t are related to the microscopic ones $\mathbf{q}$ and τ, by $\mathbf{r} = \epsilon \mathbf{q}$ and $t = \epsilon^\alpha \tau$, i.e. if Λ is a cube of macroscopic sides l, then its sides, now measured in microscopic length units, are of length $L = \epsilon^{-1} l$. We then suppose that at $t = 0$ our system of $N = \rho L^d$ particles is described by an equilibrium Gibbs measure with a temperature $T(\mathbf{r}) = T(\epsilon \mathbf{q})$: roughly speaking the phase space ensemble density has the form,

$$\mu_0(P, Q) \sim \exp\left\{ -\sum_{i=1}^{N} \beta_0(\epsilon \mathbf{q}_i) \left[\frac{\mathbf{p}_i^2}{2m} + \sum_{j \neq i} \phi(\mathbf{q}_j - \mathbf{q}_i) + u(\mathbf{q}_i) \right] \right\}, \quad (9)$$

where $\beta_0^{-1}(\mathbf{r}) = T_0(\mathbf{r})$.

In the limit $\epsilon \to 0$, ρ fixed, the system at $t = 0$ will be macroscopically in LTE with a local temperature $T_0(\mathbf{r})$ (as already noted we suppress here the variation in the particle density $n(\mathbf{r})$). We are interested in the behavior of a macroscopic system, for which $\epsilon << 1$, at macroscopic times $t \geq 0$, corresponding to microscopic times $\tau = \epsilon^{-\alpha}t$, $\alpha = 2$ for heat conduction or other diffusive behavior. The implicit assumption then made in the macroscopic description given earlier is that since the variations in $T_0(\mathbf{r})$ are of order ϵ on a microscopic scale, then for $\epsilon << 1$, the system will, also at time t, be in a state very close to LTE with a temperature $T(\mathbf{r}, t)$ that evolves in time according to Fourier's law, Eq.(1).

From a mathematical point of view the difficult problem is to prove that the system stays in LTE for $t > 0$ when the dynamics are given by a Hamiltonian time evolution. This requires proving that the macroscopic system has some very strong ergodic properties, $e.g.$ that the only time invariant measures locally absolutely continuous w.r.t Lebesgue measure are, for infinitely extended spatially uniform systems, of the Gibbs type. This has only been proved so far for systems evolving via stochastic dynamics, $e.g.$ interacting Brownian particles or lattice gases. For such stochastic systems one can sometimes prove the hydrodynamical limit and derive macroscopic transport equations for the particle or energy density and thus verify the validity of Fourier Law.

Another possibility, as we already saw, is to use the Boltzmann equation. Using ideas of hydrodynamical space and time scaling described earlier it is possible to derive a controlled expansion for the solution of the stationary Boltzmann equation describing the steady state of a gas coupled to temperature reservoirs at the top and bottom. One then shows that for $\epsilon << 1$, ϵ being now the ratio λ/L, the Boltzmann equation for f in the slab has a time independent solution which is close to a local Maxwellian, corresponding to LTE, (apart from boundary layer terms) with a local temperature and density given by the solution of the Navier-Stokes equations which incorporates Fourier's law as expressed in Eq.(2). The main mathematical problem is in controlling the remainder in an asymptotic expansion of f in power of ϵ. This requires that the macroscopic temperature gradient, $i.e.$ $|T_1 - T_2|/h$, where $h = \epsilon L$ is the thickness of the slab on the macroscopic scale, be small.

Even if this apparently technical problem could be overcome we would still be left with the question of justifying the Boltzmann equation for such steady states and of course it would not tell us anything about dense fluids or crystals. In fact the Boltzmann equation itself is really closer to a

macroscopic than to a microscopic description. It is obtained in a well defined kinetic scaling limit in which in addition to rescaling space and time the particle density goes to zero, *i.e.* $\lambda >> \sigma$.

A simplified model of a crystal is characterized by the fact that all atoms oscillate around given equilibrium positions. The equilibrium positions can be thought of as the points of a regular lattice in $\mathbb{R}^d$, say $\mathbb{Z}^d$. Although $d = 3$ is the physical situation one can be interested also in the case $d = 1, 2$. In this situation $\Lambda \subset \mathbb{Z}^d$ with cardinality N and each atom is identified by its position $\mathbf{x_i} = \mathbf{i} + \mathbf{q_i}$ where $\mathbf{i} \in \Lambda$ and $\mathbf{q_i} \in \mathbf{R}^d$ is the displacement of the particle at lattice site $\mathbf{i}$ from this equilibrium position. Since inter atomic forces in real solids have short range, it is reasonable to assume that the atoms interact only with their nearest neighbors via a potential that depends only on the relative distance with respect to the equilibrium distance. Accordingly the Hamiltonians that we consider have the general form

$$ H(P, Q) = \sum_{\mathbf{i} \in \Lambda} \frac{\mathbf{p_i}^2}{2m} + \sum_{|\mathbf{i}-\mathbf{j}|=1} V(\mathbf{q_i} - \mathbf{q_j}) + \sum_{\mathbf{i}} U_{\mathbf{i}}(\mathbf{q_i}) = \sum_{\mathbf{i} \in \Lambda} \frac{\mathbf{p_i}^2}{2m} + \mathcal{V}(Q) \,, \quad (10) $$

where $P = (\mathbf{p_i})_{\mathbf{i} \in \Lambda}$ and analogously for Q. We shall further assume that as $|\mathbf{q}| \to \infty$ so do $U_{\mathbf{i}}(\mathbf{q})$ and $V(\mathbf{q})$. The addition of $U_{\mathbf{i}}(\mathbf{q})$ pins down the crystal and ensures that $\exp[-\beta H(P, Q)]$ is integrable with respect to $dPdQ$ and thus the corresponding Gibbs measure is well defined.

In this case, in order to fix the temperature at the boundary one can add a Langevin term to the equation of particles on the boundaries, *i.e.* if $\mathbf{i} \in \partial\Lambda_\alpha$ the equation for the particle is

$$ \dot{\mathbf{p}}_{\mathbf{i}} = -\partial_{\mathbf{q_i}} H(P, Q) - \lambda\mathbf{p_i} + \sqrt{\lambda\mathbf{T}_\alpha}\dot{w}_{\mathbf{i}} \,, \quad (11) $$

where $\dot{w}_{\mathbf{i}}$ is a standard white noise. Other thermostatting mechanisms can be considered.

Also in this case we can define LTE using eq.(9) but we run in the same difficulties described above although the problem is somehow simpler due to the presence of the lattice structure and the fact that the particles oscillate close to their equilibrium points. We can obtain Fourier's Law only adding stochastic terms,*e.g.* terms like eq.(11), to the equation of motion of every particle and assuming that $U(\mathbf{q})$ and $V(\mathbf{q})$ are harmonic. These added noises can be thought of as an effective description of the chaotic motion generated by the anharmonic terms in $U(\mathbf{q})$ and $V(\mathbf{q})$.

Just how far we are from establishing rigorously Fourier Law is clear from our very limited mathematical understanding of the stationary nonequilibrium state (SNS) of mechanical systems whose ends are, as in the example of the Benard problem, kept at fixed temperatures T_1 and T_2. Various models have been considered, for example models with Hamiltonian (10) coupled at the boundaries with heat reservoirs described by eqs. (11). The best mathematical results one can prove are the existence and uniqueness of SNS, the existence of a stationary nontrivial heat flow, as well properties of the fluctuations of the heat flow in the SNS, central limit theorem type fluctuations are related to Kubo formula and Onsager relations and large deviation type fluctuations are related to the Gallavotti-Cohen fluctuation theorem. What is missing is information on how the relevant quantities depends on the size of the system N. In this context the heat conductivity in this situation can be defined precisely without invoking LTE. To do this we let $\tilde{J}$ be the expectation value in the SNS of the energy or heat current flowing from reservoir 1 to reservoir 2. We then define the conductivity κ_L as $\tilde{J}/(A\delta T/L)$ where $\delta T/L = (T_1 - T_2)/L$ is the effective temperature gradient for a cylinder of microscopic length L and uniform cross section A and $\kappa(T)$ is the limit of κ_L when $\delta T \to 0$ ($T_1 = T_2 = T$) and $L \to \infty$. The existence of such a limit with κ positive and finite is what one would like to prove.

5   See also

Statistical Mechanics, Nonequilibrium Statistical Mechanics: Overview, Boltzmann equation, Dynamical System and Thermodynamics, Ergodic Theory, Interacting Particle systems and hydrodynamic equations, Dynamical system approach to non-equilibrium statistical mechanics.

References

[1] N.W. Ashcroft and N.D. Mermin: *Solid State Physics*, Saunders College 1988.

[2] R. Berman: *Thermal conduction in solids* Oxford: Clarendon press, 1976

[3] Bonetto, F.; Lebowitz, J. L.; Rey-Bellet, L.: Fourier's law: a challenge to theorists. in *Mathematical physics 2000*, Imp. Coll. Press, London, 2000, pp. 128–150.

[4] S. Brusch: *The kind of motion we call heat*, Elsevier, 1994.

[5] P. Debye: *Vorträge über die Kinetische Theorie der Wärme*, Teubner, 1914.

[6] Jean Baptiste Joseph Fourier: *Théorie Analytique de la Chaleur*. Paris, Firmin Didot, 1822. English Translation in 1878 by Alexander Freeman. New York: Dover Publications, Reprinted in 2003.

[7] C. Kipnis and C. Landim, *Scaling limits of interacting particle systems*, Springer, Berlin 1999.

[8] S. Lepri, R. Livi, and A. Politi: Thermal conduction in classical low-dimensional lattices. Phys. Rep. 377 (2003), no. 1, 1–80.

[9] R.E. Peierls: *Quantum theory of solids*, Oxford, Clarendon Press, 1955

[10] R.E. Peierls: Quantum theory of solids. in *Theoretical physics in the twentieth century*, Interscience, New York, 1960 pp. 140–160

[11] Rey-Bellet, Luc: Statistical mechanics of anharmonic lattices. In *Advances in differential equations and mathematical physics* (Birmingham, AL, 2002), 283–298, Contemp. Math. **327** , Amer. Math. Soc., Providence, RI, 2003.

[12] H. Spohn: *Large Scale Dynamics of Interacting Particle*, Springer Verlag, 1991.