Thermal transport in a higher-order generalized hydrodynamics

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Thermal transport in classical fluids is analyzed in terms of a Higher-Order Generalized Hydrodynamics (or Mesoscopic Hydro-Thermodynamics), that is, depending on the evolution of the energy density and its fluxes of all orders. It is derived in terms of a Kinetic Theory based on the Non-Equilibrium Statistical Ensemble Formalism. The general system of coupled evolution equations is derived. Maxwell times – which are of large relevance to determine the character of the motion – are derived. They also have a quite important role for the choice of the contraction of description (limitation in the number of fluxes to be retained) in the study of the hydrodynamic motion. In a description of order 1 it is presented an analysis of the technological process of thermal prototyping. Keywords: thermal transport; thermal prototyping; hydro-thermodynamics.

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I. INTRODUCTION

The modern advanced technologies and their resulting end use for obtaining improved and novel products, creates stress on the basic sciences of Physics and Chemistry. This is a result of trying to maintain a balance in the triad ST&I (Science, Technology and Innovation). A particular question involves the dissipation of energy and heat transport in, for example, devices under high-levels of excitation, namely, working in far-removed-from equilibrium conditions and eventually involving ultrafast relaxation and transport processes as well as spatial non-metric scales. Another important aspect is the one of fluids under flow present in certain production processes (e.g., in food engineering, petrochemistry, etc.) whose performance depends on their hydrodynamic properties.

We address here, under the scope of a Higher-Order Generalized Hydrodynamics (HOGH) the question of heat transport in a fluid embedded in a thermal bath (i.e., mixed with other fluid acting as such). On this, it has been noticed that one of the complicated problems of the non-equilibrium theory of transport processes in dense gases and liquids is the fact that their kinetics and hydrodynamics are intimately coupled, and must be treated simultaneously (e.g., see Refs. [1-3]).

Along the last decades Hydrodynamics has been extensively treated resorting to the Nonequilibrium Molecular Dynamics (NMD for short). NMD is a computational method created for modelling physical systems at the microscopic level, being a good technique to study the molecular behavior of several physical processes [4,5]. On the other hand, another very satisfactory approach to deal with hydrodynamics within an ample scope of non-equilibrium conditions consists in the kinetic theory based on the Non-Equilibrium Statistical Ensemble Formalism (NESEF for short) [6-15]. NESEF provides a way to go beyond standard (or classical Onsagerian) Hydrodynamics which involves restrictions, namely, local equilibrium; linear relations between fluxes and thermodynamic forces (meaning weak amplitudes in the motion with Onsager’s symmetry laws holding); near homogeneous and static movement (meaning that the motion can be well described with basically Fourier components with long wavelengths and low frequencies, and then involves only smooth variation in space and time); and weak and rapidly regressing fluctuations [16,17]. Hence, more advanced approaches are required to lift these restrictions. Consider first near homogeneity, which implies validity in the limit of long wavelengths (or wavenumber $Q$ approaching to zero), and to go beyond it is necessary to introduce a proper treatment valid, in principle, for intermediate and short wavelengths (intermediate to large wavenumbers). In phenomenological theories this corresponds to go from classical irreversible thermodynamics to extended irreversible thermodynamics [18-21]. This is what has been called generalized hydrodynamics, a question extensively debated for decades by the Statistical Mechanics community. Several approaches have been used, and a description can be consulted in Chapter 6 of the classical book on the subject by Boon and Yip [22]. Introduction of nonlocal effects for describing motion with influence of ever decreasing wavelengths, going towards the very short limit and involving very high frequencies, has been done in terms of what is referred to as Higher-Order Generalized Hydrodynamics (HOGH) or Mesoscopic Hydro-Thermodynamics (MHT) [23,24]. A first construction based on a large expansion of Extended Irreversible Thermodynamics, i.e., on phenomenological basis, and centered on the analysis of heat transport is reported in Ref. [23]. A full construction in the scope

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of Non-Equilibrium Statistical Thermodynamics is described in Refs. [24-26].

We consider here the question of heat transport in classical fluids within the scope of HOGH. It is obtained a hierarchy of equations of motion for the density of energy and its fluxes of all orders, which are all coupled together and including thermostriction terms that couple them with the evolution equations of the particle density and its fluxes of all order. Maxwell-times associated to the different fluxes are evidenced, which, as already noticed, determine the characteristics of the motion playing an important role in the choice of the contraction of description (i.e., to fix the number of fluxes to be retained) appropriate to the study of the hydrodynamics motion under consideration.

Finally, resorting to the use of HOGH of order 1 it is described a full analysis of the physical processes that are involved in a technological procedure of thermal prototyping.

II. THEORETICAL BACKGROUND

According to theory, immediately after the open system of $N$ particles, in contact with external sources and reservoirs, has been driven out of equilibrium, the description of its state requires to introduce all its observables. But this is equivalent to have access to the so-called one-particle (or single-particle), $\tilde{n}_1$, and two-particle, $\tilde{n}_2$, dynamical operators for any subset of the particles involved. This is so because all observable quantities can be expressed at the microscopic mechanical level in terms of these operators (e.g. Refs. [27,28]). At the classical mechanical level used here they are given by

$$\tilde{n}_1(\mathbf{r}, \mathbf{p}; \Gamma) = \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j) \delta(\mathbf{p} - \mathbf{p}_j),$$

$$\tilde{n}_2(\mathbf{r}, \mathbf{p}; \mathbf{r}', \mathbf{p}'; \Gamma) = \sum_{j \neq k=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j) \delta(\mathbf{p} - \mathbf{p}_j) \times$$

$$\delta(\mathbf{r}' - \mathbf{r}_k) \delta(\mathbf{p}' - \mathbf{p}_k).$$

In these equations $\mathbf{r}$ and $\mathbf{p}$ are the so called position and momentum field variables and $\Gamma$ is a point in phase space of particles at position $\mathbf{r}_j$, and with linear momentum $\mathbf{p}_j$.

The non-equilibrium statistical operator, $\varrho_\varepsilon(t)$, is a functional of $\tilde{n}_1(\mathbf{r}, \mathbf{p})$ and $\tilde{n}_2(\mathbf{r}, \mathbf{p}; \mathbf{r}', \mathbf{p}')$, each multiplied by the associated non-equilibrium thermodynamic variable, which we call $F_1(\mathbf{r}, \mathbf{p}; t)$ and $F_2(\mathbf{r}, \mathbf{p}; \mathbf{r}', \mathbf{p}'; t)$ [8,9,9,9].

The non-equilibrium thermodynamic state [8,9,29,30] associated to the basic dynamic variables $\tilde{n}_1$ and $\tilde{n}_2$ are the one-particle and two-particle distribution functions

$$f_1(\mathbf{r}, \mathbf{p}; t) = \text{Tr}\{\tilde{n}_1(\mathbf{r}, \mathbf{p}) \varrho_\varepsilon(t)\},$$

$$f_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}'; t) = \text{Tr}\{\tilde{n}_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') \varrho_\varepsilon(t)\},$$

that is, the average over the nonequilibrium ensemble of $\tilde{n}_1$ and $\tilde{n}_2$. The trace operator is in this classical approach to be understood as an integration over phase space; $\tilde{n}_1$ and $\tilde{n}_2$ are functions defined on phase space and $\varrho_\varepsilon$, as stated, is a functional of these two. For the sake of completeness we write down its expression, namely

$$\varrho_\varepsilon(t) = \exp\left\{\ln \varrho(t, 0) - \int_{-\infty}^{t} dt' e^{\varepsilon(t' - t)} \frac{d}{dp} \ln \varrho(t', t' - t)\right\},$$

(5)

where

$$\varrho(t_1, t_2) = \exp\left\{-\phi(t_1) - \int d^3r d^3p F_1(\mathbf{r}, \mathbf{p}; t_1) \times \right.$$  

$$\tilde{n}_1(\mathbf{r}, \mathbf{p}; t_2) - \int d^3r d^3p d^3r' d^3p' F_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}'; t_1) \times \right.$$  

$$\tilde{n}_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}'; t_2)\right\}.$$  

(6)

and, we recall, $\varepsilon$ is a positive real number that goes to zero after the trace operator in the calculation of averages has been performed [8,9]. $t_1$ refers to the evolution in time of the non-equilibrium thermodynamic variables and $t_2$ to the evolution in time of the mechanical quantities.

The knowledge of the two distribution functions $f_1$ and $f_2$ allows to determine the value and evolution of any observable of the system as well as of response functions and transport coefficients. In continuation we consider the case of a unique kind of particle (the solute) in a fluid (the solvent). The former is subjected to external forces driving it out of equilibrium, and the latter (the thermal bath) is taken in a steady state of constant equilibrium with an external reservoir at temperature $T_0$. An analogous case, but at the quantum mechanical level, is the one of the carriers embedded in the ionic lattice in doped or photo-injected semiconductors (see for example Refs. [31-34]).

We write for the Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{H}',$$

(7)

where $\hat{H}_0$ is the kinetic energy operator and

$$\hat{H}' = \hat{H}_1 + W + \hat{H}_P,$$

(8)

contains the internal interactions energy operator $\hat{H}_1$, while $W$ accounts for the interaction of the system with the thermal bath, and $\hat{H}_P$ is the energy operator associated to the coupling of the system with external pumping sources. They are given by

$$\hat{H}_0 = \int d^3r \int d^3p \frac{p^2}{2m} \tilde{n}_1(\mathbf{r}, \mathbf{p}),$$

$$\hat{H}_1 = \frac{1}{2} \int d^3r d^3p \int d^3r' d^3p' V(|\mathbf{r} - \mathbf{r}'|) \tilde{n}_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}'),$$

$$+ \frac{1}{2} \sum_{\mu \neq \nu=1}^{N_0} \Phi(\mathbf{R}_\mu - \mathbf{R}_\nu),$$

(9)

(10)
\[ \dot{W} = \int d^3r \int d^3p \sum_{\mu=1}^{N_p} w(|r - R_\mu|) \hat{n}_1(r, p), \]

\[ \hat{H}_P = \int d^3r \int d^3p U_P(r, t) \hat{n}_1(r, p), \]

where \( V \) and \( \Phi \) stand for the interaction potential between two-particles in the system and thermal bath, respectively; \( w \) is the interaction potential between system and thermal bath, and \( U_P \) is the potential describing the interaction of the system with the external pumping source; \( R_\mu \) and \( P_\mu \) are the position and linear momentum of the particle of mass \( M \) in the thermal bath and \( m \) is the mass of the particles in the fluid.

But, for simplicity, considering a dilute solution (large distance in average between the particles) or that the potential \( V \) is screened (e.g., molecules in a saline solvent, e.g. \([35]\)), we can disregard \( \hat{n}_2 \), retaining only \( \hat{n}_1 \). In that case, we choose the single particle density \( \hat{n}_1(r, p|\Gamma) \) as the only relevant dynamical variable required. Hence, the auxiliary non-equilibrium statistical operator for the particles embedded in the fluid is

\[
\overline{\gamma}(t, 0) = \exp \left\{ -\phi(t) - \int d^3r \int d^3p F_1(r, p; t) \hat{n}_1(r, p) \right\},
\]

\[
\overline{\gamma}(t, 0) = \prod_{j=1}^{N} \overline{\gamma}_j(r_j, p_j; t, 0),
\]

with

\[
\overline{\gamma}_j(r_j, p_j; t, 0) = \exp \left\{ -\phi_j(t) - \int d^3r \int d^3p \times \right.
\]

\[
F_1(r, p; t) \delta(r - r_j) \delta(p - p_j) \right\}
\]

which is a probability distribution in phase space for an individual particle, with \( \phi(t) \) and \( \phi_j(t) \) ensuring the normalization conditions of \( \overline{\gamma} \) and \( \overline{\gamma}_j \).

The HOGH built in the framework of NESEF-kinetic theory is characterized by the microdynamical variables consisting of the density particles \( \hat{n}(r) \), the density of energy, \( \hat{h}(r) \), and their fluxes of all order, i.e., the tensors of rank \( \ell \), \( \overline{\gamma}_n^{[\ell]}(r) \), and \( \overline{\gamma}_h^{[\ell]}(r) \), with \( \ell = 1, 2, \ldots \), given by

\[
\hat{n}(r) = \int d^3p \hat{n}_1(r, p),
\]

\[
\overline{\gamma}_n^{[\ell]}(r) = \int d^3p \frac{p^2}{2m} \hat{n}_1(r, p),
\]

\[
\overline{\gamma}_h^{[\ell]}(r) = \int d^3p \frac{p^2}{2m} \frac{P}{m} \hat{n}_1(r, p),
\]

where

\[
\hat{n}_1^{[\ell]}(r) = \int d^3p u^{[\ell]}(p) \hat{n}_1(r, p),
\]

\[
\overline{\gamma}_h^{[\ell]}(r) = \int d^3p \frac{p^2}{2m} u^{[\ell]}(p) \hat{n}_1(r, p),
\]

is the tensorial product of \( \ell \) vectors \( P/m \), defining a \( \ell \)-rank tensor (it has the dimensions of velocity to the power \( \ell \)).

The average over the non-equilibrium ensemble of the quantities above provides the set of macrovariables,

\[
\{ n(r, t), I_n(r, t), \{ I_n^{[\ell]}(r, t) \} \},
\]

which we call the family of variables describing the particle motion, and

\[
\{ h(r, t), I_h(r, t), \{ I_h^{[\ell]}(r, t) \} \},
\]

which we call the family of variables describing the heat motion, which define the HOGH.

It can be noticed that in the present case those associated to the energy are contained in those associated to the movement of matter. Beginning with \( \overline{\gamma}_n^{[1]} \) the contraction of the two first indexes provide the expression for the energy, such contraction in \( \overline{\gamma}_n^{[2]} \) results in the flux of energy (heat current), and so on.

According to Eqs. (3) and (13) we have that

\[
f_1(r, p; t) = \text{Tr} \left\{ \hat{n}_1(r, p) \prod_{j=1}^{N} \overline{\gamma}_j(r_j, p_j; t, 0) \right\},
\]

is NESEF single-particle distribution function is space \( (r, p) \); \( \text{Tr} \) indicates integration in phase space and we recall that the average values of the basic dynamical values, and only for them, there is coincidence of the one calculated with the statistical operator \( g_c(t, 0) \) and the calculation with the auxiliary “instantaneous quasi-equilibrium distribution” \( \overline{\gamma}(t, 0) \).

Hence, the basic macrovariables of HOGH, that is, the average values of the microdynamical quantities in Eqs. (15) to (20) are expressed in terms of the single-particle distribution, namely

1. For the family describing particle motion

\[
\overline{\gamma}_n^{[\ell]}(r, t) = \int d^3p u^{[\ell]}(p) f_1(r, p; t),
\]

2. For the family describing heat motion

\[
\overline{\gamma}_h^{[\ell]}(r, t) = \int d^3p \frac{p^2}{2m} u^{[\ell]}(p) f_1(r, p; t),
\]
with \( \ell = 0 \) corresponding to the densities, \( n(r,t) \) and \( h(r,t) \), \( \ell = 1 \) to the first (vectorial) fluxes, \( \ell \geq 2 \) to the higher order fluxes. Moreover, it can be shown that we can write for the flux

\[
I_\ell(r,t) = n(r,t)v(r,t),
\]

where \( v(r,t) \) is the field of barycentric velocity, and for the second-order flux that

\[
m_{h}^{[2]}(r,t) = P^{[2]}(r,t) + m[v(r,t)v(r,t)],
\]

where \( P^{[2]} \) is the pressure tensor and the last term on the right is the convective pressure tensor. Next we proceed to derive in the HOCH context the kinetic equations that govern the hydrodynamic motion.

### III. EVOLUTION EQUATIONS IN NESEF-HOGH

First we noticed that in NESEF-based kinetic theory [8,12,36,37] the evolution equation for a macrovariable \( A(r,p,t) \), being the average over the non-equilibrium ensemble of the microdynamical variable \( \hat{A}(r,p) \), consists into the average over such ensemble of the mechanical equation of motion, namely,

\[
\frac{\partial}{\partial t} \hat{A}(r,p,t) = \frac{\partial}{\partial t} \text{Tr}\{\hat{A}(r,p)\phi_{\tau}(t)\} = \text{Tr}\{\hat{A}(r,p),\hat{H}\phi_{\tau}(t)\},
\]

where \{\ldots\} stands for Poisson bracket. A practical way to handle this equation, in the form of a perturbative series, ordered according to increasing powers of the interaction strength, is fully described in Refs. [8,37]. The successive terms in the series invoke pair collisions, triple and higher-order collisions, all of them including memory and vertex renormalization. A truncation of the series in lowest order (keeping only the terms quadratic in the interaction strengths) is a Markovian approximation [37,38].

From now on we concentrate the attention on the evolution of the thermal quantities

\[
\{h(r,t), I_{\ell}(r,t), \{I_{\ell}^{[\ell]}(r,t)\}\},
\]

with \( \ell = 2,3,\ldots \), that is, the density of energy and its fluxes of all orders given in Eq. (26). The evolution equations are:

\[
\frac{\partial}{\partial t} I_{\ell}^{[\ell]}(r,t) = \int d^{3}p \frac{P^{2}}{2m}u^{[\ell]}(p) \frac{\partial}{\partial t} f_{1}(r,p;t),
\]

in which we need to introduce the kinetic equation for the single-particle \( f_{1}(r,p;t) \) which is given in Ref. [25] and briefly described in Appendix A. Performing the lengthy calculations involved we finally arrive at the general evolution equations (\( \ell = 0,1,2,\ldots \))

\[
\frac{\partial}{\partial t} I_{\ell}^{[\ell]}(r,t) + \nabla \cdot I_{\ell}^{[\ell+1]}(r,t) = - \mathcal{F}(r,t) I_{\ell}^{[\ell+1]}(r,t) + \sum_{s=1}^{\ell} \varphi(1,s) \left[ \mathcal{F}(r,t) I_{\ell}^{[\ell+1]}(r,t) + \varphi_{\ell+1} I_{\ell}^{[\ell+1]}(r,t) + a_{L0} \sum_{s=1}^{\ell} \varphi(1,s) \left[ \nabla I_{\ell}^{[\ell+1]}(r,t) \right] + 2(\ell + 3) a_{L1} \nabla \cdot I_{\ell}^{[\ell+1]}(r,t) + S_{\ell}(r,t),
\]

where

\[
\varphi_{\ell+1} = (\ell + 2) |a_{\tau 0}| + |\varphi_{\ell+2} + 5(\ell + 1) |b_{\tau 1}|,
\]

is the reciprocal of the Maxwell time [39,40] associated to the \( \ell \)-th order flux. Moreover

\[
S_{\ell}(r,t) = (2\ell + 3) b_{\tau 0} \frac{m}{2} I_{\ell}^{[\ell]}(r,t) + b_{\tau 0} \left[ \frac{1}{\ell} \left[ I_{\ell}^{[\ell-2]}(r,t) \right] \right] + b_{\tau 1} \left[ \frac{2}{\ell} \left[ I_{\ell}^{[\ell-2]}(r,t) \right] \right] + a_{\tau 0} \frac{2}{\ell} \nabla \cdot I_{\ell}^{[\ell+1]}(r,t) + a_{\tau 1} \frac{2}{\ell} I_{\ell}^{[\ell+1]}(r,t) + 3(\ell + 2) a_{\tau 1} \frac{2}{\ell} I_{\ell}^{[\ell+1]}(r,t) + R_{\ell}(r,t),
\]

is a contribution which couples the thermal motion to the material motion (thermal-striction effect), \( R_{\ell}(r,t) \) contains the contribution of all the other higher-order fluxes (\( \ell + 2 \)).

The several kinetic coefficients are presented in Appendix B. Taking into account that (see Appendix B)

\[
|b_{\tau 1}| = \frac{1}{5(1 + x)} |a_{\tau 0}|,
\]

it follows that Maxwell times have the property that

\[
\frac{\theta_{\ell+1}}{\theta_{\ell}} = \frac{5(\ell + 2)(1 + x) + \ell^{2} + 5(\ell + 1)}{5(\ell + 3)(1 + x) + (\ell + 2)^{2} + 5(\ell + 2)} < 1,
\]

for \( \ell = 0,1,2,\ldots \) and where \( x = m/M \). The ordered sequence

\[
\theta_{0} > \theta_{1} > \theta_{2} > \theta_{3} > \ldots > \theta_{\ell} > \theta_{\ell+1} > \ldots
\]

is verified, and may be noticed that for large \( \ell, \theta_{\ell} \) goes as \( \ell^{-2} \), i.e., going to zero as \( \ell \rightarrow \infty \).

For the Brownian particle \( (m/M \gg 1) \) the ratio in Eq. (36) tends asymptotically to \( (\ell + 2)/(\ell + 3) \), while for Lorentz particles \( (m/M \ll 1) \) the ratio tends to \( (\ell^{2} + 5(\ell + 3)/(5(\ell + 1)^{2} + 5(\ell + 5)) \). Considering that the Maxwell time of the first flux of matter, \( \theta_{\tau 0} \) (which is the linear momentum relaxation time), in Ref. [24], is
Moreover, for general \( \ell \) equilibrium thermodynamic state of the system, variables space to be used for the description of the non-equilibrium thermodynamic space of states.

The more restricted contraction can be used when larger and larger are the prevalent wavelengths in the motion and larger are the prevalent wavelengths in the motion, therefore, in simpler words, when the motion becomes more and more smooth in space and time, the more restricted contraction can be used when larger and larger are the prevalent wavelengths in the motion.

As shown elsewhere [42], it can be conjectured a general criterion of contraction, namely, a truncation of order \( r \) (meaning keeping the densities and their fluxes up to order \( r \)) can be introduced, once we can show that in the spectrum of wavelengths, which characterizes the motion, predominate those larger than a “frontier” one, \( \lambda^2_{(r,r+1)} = \lambda^2 \theta_r \theta_{r+1} \), where \( \lambda \) is of the order of the thermal velocity and \( \theta_r \) and \( \theta_{r+1} \) the corresponding Maxwell times associated to the fluxes of order \( r \) and \( r + 1 \).

We shall try to illustrate the matter using a contraction of order 1.

IV. CONTRACTION OF DESCRIPTION

Equation (32) represents the coupled set of evolution equations involving the density and all its fluxes in its most general form. It must be noticed that it is linear in the basic variables; no approximation has been introduced. Nonlinearities should arise out of the inclusion of inter-particle interaction which we have disregarded in the present communication (case of a dilute solution). However, as already noticed, such set of equations is intractable, and, of course, we need to look in each case on how to find the best description using the smallest possible number of variables. In other words to introduce an appropriate – for each case – contraction of description: this contraction implies in retaining the information considered as relevant for the problem in hands, and to disregard non-relevant information [41].

Elsewhere [42] we have discussed the question of the contraction of description (reduction of the dimensions of the non-equilibrium thermodynamic space of states). As shown a criterion for justifying the different levels of contraction is derived: It depends on the range of wavelengths and frequencies which are relevant for the characterization, in terms of normal modes, of the hydrodynamic motion in the non-equilibrium open system. Maxwell times have a particular relevance for establishing such contractions, for which a truncation criterion can be derived, which rests on the characteristics of the hydrodynamic motion that develops under the given experimental procedure.

Since inclusion of higher and higher order fluxes implies in describing a motion involving increasing Knudsen numbers per hydrodynamic mode (that is governed by smaller and smaller wavelengths - larger and larger wave numbers - accompanied by higher and higher frequencies), in a qualitative manner, we can say, as a general “thumb rule”, that the criterion indicates that a more and more restricted contraction can be used when larger and larger are the prevalent wavelengths in the motion. Therefore, in simpler words, when the motion becomes more and more smooth in space and time, the more reduced can be the dimension of the basic macrovariables space to be used for the description of the non-equilibrium thermodynamic state of the system.

As shown elsewhere [42], it can be conjectured a general criterion of contraction, namely, a truncation of order \( r \) (meaning keeping the densities and their fluxes up to order \( r \)) can be introduced, once we can show that in the spectrum of wavelengths, which characterizes the motion, predominate those larger than a “frontier” one, \( \lambda^2_{(r,r+1)} = \lambda^2 \theta_r \theta_{r+1} \), where \( \lambda \) is of the order of the thermal velocity and \( \theta_r \) and \( \theta_{r+1} \) the corresponding Maxwell times associated to the fluxes of order \( r \) and \( r + 1 \). We shall try to illustrate the matter using a contraction of order 1.

V. HOGH OF ORDER 1

In this section, we consider very briefly a relation of the theory so far presented and the analysis of a particular techno-industrial process, namely, laser thermal stereolithography. Stereolithography is a technological process that allows solid parts to be made directly and rapidly from computer data (prototyping) without the necessity of tooling or cutting machining. The presently available industrial process is based on the use of photopolymers, with the solid sections built using laser ultraviolet light which induces a photochemical reaction solidifying the resin and thus providing a prototype (matrix) of the part of the object (in machines, cars, medical implants, etc.) to be produced. An alternative procedure involves the use of thermo sensitive resins, like some waxes and compounds, and with them the solid sections are formed by a sintering process produced by application of heat generated by an infrared-light laser [43]. This alternative rapid prototyping method has the economic advantage of using much cheaper and easily available thermo-sensitive resins instead of the rare and expensive photosensitive resins used with the other, original, approach. We consider next some hydrodynamic aspects of this technique.

It is essential to the process that the produced prototypes be homogeneous and with well-defined and satisfactorily precise geometry, leading to spatially well-defined solid parts with three-dimensional geometry. Advances in such direction are being obtained, which are related to quite interesting and illustrative aspects of the generalized hydrodynamics so far described.

In a typical experiment, a beam originating from a CO₂ laser is used (\( \lambda = 10.6 \ mu \) m with power, for best technical results, around 25 watts). An optical system directs the laser beam to illuminate and heat the polymeric resin with the laser beam focused to a spot of diameter, say, \( 2r_0 \) (usually in the 1 mm range). The resin (e.g., epoxy, polyester) together with a curing agent (e.g., dimethyltriamine), compounding the media where the sintering process is to proceed, is then locally heated and a solidification follows. The optical system governed by the computer program focuses the beam along the correct path for the prototype to be produced. However, the experience in the laboratory showed that using a pure
material (the resin and the curing substance) the process was not rapid or well localized. The pressure and heating originated on the spot of focalization of the laser beam generated a material wave accompanied by heat motion, resulting in the solidification (sintering) of the resin over large extensions and thus ruining the purpose of the technique that, as noted, requires a quite localized solidification to obtain a well-shaped model. This drawback was corrected to a large degree by resorting to mix the resin with silica (or aluminum) powder with the grains acting as collision centers.

The theory presented in the previous section allows us to analyze and understand those results. In the process we are present, evidently, matter and heat motion in the body of the sample, but neglecting thermostriiction effects (which seems a plausible approximation in the case under consideration), we can apply the theory just presented. Hence, material and thermal motion are decoupled and we concentrate our attention on the equations of motion for energy, whose propagation is of fundamental relevance (perpendicular direction z). Hence, we can separate the planar polar coordinates from the z-coordinate and use the initial and boundary condition of Eq. (45) for solving the result equation, whose solution we write in the form of a superposition of normal modes on the surface sample, namely:

\[ h(r, t) = \int d^2 k \tilde{\varepsilon}(k) e^{i(k \cdot r - \omega_k t)}, \]  



Neglecting the right side of Eq. (42) (i.e., the term that leads to the cooling of the system after a certain time interval has elapsed), we solve it for the case of particular initial and boundary conditions. They consist of taking a laser pulse producing a concentration of energy at the spot of focalization, which is distributed on the material upper thin layer with a Gaussian profile of width \( r_0 \approx 1.0 \text{ mm} \), i.e.,

\[ h(r, 0) = A(\pi/r_0^2)^{1/2} e^{-r^2/4r_0^2}, \]  

where \( A \) is an amplitude related to the intensity of the pumped laser light energy. In Eq. (45), \( r \) is the planar radius and we assume a near uniform heating in depth (perpendicular direction z). Hence, we can separate the planar polar coordinates from the \( z \)-coordinate and use the initial and boundary condition of Eq. (45) for solving the resulting equation, whose solution we write in the form of a superposition of normal modes on the surface sample, namely:

\[ h(r, t) = \int d^2 k \tilde{\varepsilon}(k) e^{i(k \cdot r - \omega_k t)}, \]  



Inserting Eq. (46) in Eq. (42), we obtain the characteristic equation that defines the energy dispersion relation in the propagation of this second sound, which is

\[ \omega_k = -\frac{i}{\tau_c} \pm \sqrt{c_e^2 k^2 - 1/(\tau_c)^2}, \]  

where \( \tau_c = 2D_e/c_e^2 \) is the lifetime.

We can see that depending on the value of \( k \) this dispersion relation separates two types of regimes, namely:

\[ k > \frac{1}{c_e \tau_c} \equiv k_c, \]  

which corresponds to a damped (with lifetime \( \tau_c \)) undulatory motion, while for

\[ k < \frac{1}{c_e \tau_c} \equiv k_c, \]  

there follows an overdamped movement, which, as discussed below, consists of a diffusive motion. Moreover in the case \( k < k_c \), approximately

\[ \omega_k = \frac{-iD_e k^2}{-i/\tau_c} \]  

while for \( k > k_c \), we can write that

\[ \omega_k = -i/\tau_c \pm \tilde{\omega}_k; \quad \tilde{\omega}_k = c_e \sqrt{k^2 - k_c^2}, \]  

with \( \tilde{\omega} \) being a real number frequency. Hence, on the basis of these results, we can separate Eq. (46) in the form

\[ h(r, t) = \int_{k<k_c} d^2 k [a(k) e^{-t/\tau_c} + \tilde{h}(k) e^{-D_e k^2 t}] e^{i k \cdot r} + \int_{k>k_c} d^2 k \tilde{\varepsilon}(k) e^{-t/\tau_c} \cos(\tilde{\omega}_k t) e^{i k \cdot r}, \]  

\[ \]
where \( a(\mathbf{k}) \) and \( \tilde{h}(\mathbf{k}) \) are coefficients to be determined by the initial and boundary conditions of Eq. (45). The latter can be Fourier analyzed to obtain that
\[
h(\mathbf{r},0) = A(\pi/r_0^2) \int d^2k e^{-k^2r_0^2} e^{-\mathbf{k} \cdot \mathbf{r}},
\]
and then
\[
\tilde{h}(\mathbf{k}) = A(\pi/r_0^2)e^{-k^2r_0^2},
\]
and we are neglecting in Eq. (52) the term with coefficient \( a(\mathbf{k}) \) because of the rapid decay of this term in comparison with the other in this region where \( k < k_c \).

Therefore, we obtain that
\[
h(\mathbf{r},t) = A(\pi/r_0^2) \left[ \int_{k<k_c} d^2k e^{-k^2r_0^2} e^{-D_c k^2 t} e^{i\mathbf{k} \cdot \mathbf{r}} + \int_{k>k_c} d^2k e^{-k^2r_0^2} e^{-t/\tau_c} \cos(\omega_k t) e^{i\mathbf{k} \cdot \mathbf{r}} \right].
\]

Equation (55) clearly tells us that the movement, as already noticed, is composed of a diffusive motion associated to the modes with long wavelengths (\( \lambda > c_\tau \tau_c \)) and damped undulatory motion associated to the intermediate to short wavelengths (\( \lambda < c_\tau \tau_c \)), similarly, to the case of the telegraphist equation in electrodynamics.

Inspection of Eq. (55) leads us to the conclusion that, on account of the Gaussian envelope in the integral, the contributions to the integrals for values of \( k \) such that \( kr_0 > 1 \) are negligible. Therefore, considering the limit that separates the undulatory and diffusive regimes namely, \( k_c = (c_\tau \tau_c)^{-1} \), which we write \( k_c \lambda_c = 1 \); where \( \lambda_c = c_\tau \tau_c \) is the mean free path, we can notice that:

(i) If \( k_c r_0 = r_0/\lambda_c < 1 \), the motion is composed of a diffusive one accompanied by a wave that carries heat at speed \( c_\tau \), and similarly for the expected movement of mass (a material or pressure wave) that expands from the initial burning hole produced by the incidence of the laser pulse (see Fig. 1), and

(ii) if \( k_c r_0 = r_0/\lambda_c > 1 \), then the movement is purely diffusive, and in this case,
\[
h(\mathbf{r},t) = \frac{\pi A}{r_0^2 + D_c t} e^{-r^2/(r_0^2 + D_c t)},
\]
which is illustrated in Figure 2.

On the basis of the analysis above, the prototype in the case when the pure resin is used is ruined, as noticed, because of solidification over a large area, i.e., a large area around the spot of laser beam focalization has been heated. We conclude that in this case, the situation should be such that \( k_c r_0 < 1 \) and the undulatory motion, before decaying, carries heat at distances, in the experiments, of the order of centimeters. On the other hand, addition of silica powder greatly improves the situation, producing an acceptable prototype. We conclude that when \( k_c r_0 > 1 \) the wave propagation of heat is not present, only slow diffusion accompanied by rapid cooling and sinterization on a small space scale (millimeter in the experiment).

That the presence of silica powder increases \( k_c \) can be understood on the basis that \( k_c = (c_\tau D_c)^{-1} = \lambda_c^{-1} \), and the presence of the macroscopic grains of silica decreases the mean free path \( \lambda_c \), increasing therefore \( k_c \). It should be noticed that also the diffusivity \( D_c \) decreases, further improving the results.

Consequently, we can say that the theoretical analysis we performed appears as justified, which corroborates the observed experimental behavior. The study of this industrial and commercial technique, on the basis of the simplest form of the approach to the generalized hydro-

FIG. 1: Description of the domain of propagation of a diffusive character accompanied with undulatory motion. The space dependence amplitude of the density for increasing time indicated by the arrow.

FIG. 2: Description of the domain of propagation of a pure diffusive motion. The space dependence amplitude of the density for increasing time indicated by the arrow.
dynamics described here (i.e., only one step further from the domain of classical hydrodynamics), allows one, on the one hand, to discuss and reinforce some aspects of the theory, and, on the other, to visualize the physical phenomena developing in the process and then to analyze in depth the problem and look for optimization of the technique.

VI. CONCLUDING REMARKS

In summary, the study in depth of the characteristics and responses of materials working, as in devices and industrial processes, under far-from-equilibrium conditions and, eventually, involving complex and nanometric conditions, can presently be performed in terms of two main formalisms, namely, computational modelling [4,5] or a generalized kinetic theory. We have here presented the derivation, based on a Gibbs-style nonequilibrium statistical ensemble formalism, of a kinetic theory which permitted the construction of a generalized kinetic equation having an ample domain of validity and large number of possible applications.

In this communication we have worked at the classical mechanical level. The quantum mechanical approach follows along quite similar lines; in that case the classical single-particle distribution \(f_1(r,p;t)\) is replaced by the Wigner-von Neumann one and, clearly, Heisenberg quantum equations of motion enter in place of the Hamiltonian classical ones. The quantum approaches has been described and applied in the case of semiconductors, where it has an important paper in the determination of heat conductivity at the nanometric scale, when it is described and applied in the case of semiconductors, of a fundamental relation with full details given in Ref. [24]. The symbol \(\odot\) stands for contracted product of tensors.

When Eq. (A2) is compared with, say, standard Boltzmann kinetic equation, it contains several additional contributions. First, \(\mathbf{P}(r,p;t)\), Eq. (A3), can be interpreted as a modified momentum, composed of the linear one, \(\mathbf{p}\), plus a contribution arising out of the interaction with the thermal bath, \(m\mathbf{A}_1(p)\). The contribution \(m\mathbf{A}_1(p)\) can be considered as implying in a transfer of momentum between system and bath.

The force \(\mathbf{F}(r,p;t)\), in Eq. (A4), is composed of four contributions: the first one, \(-\nabla U_{ext}(r,t)\), is the external applied force; next, \(\mathbf{B}_1(p)\), arising out of the interaction with the thermal bath, is a contribution that, together with the fourth one in Eq. (A2), namely, \(\mathbf{B}(p)f_1\), constitutes a generalization of the so-called effective friction force. In the limit of a Brownian system (\(m \gg M\)) it is recovered the known expression [49] \(\gamma \nabla_p[(\mathbf{p}/m)f_1(r,p;t)]\) with the friction coefficient given by \(\gamma = m/\tau\) where \(\tau\) is the momentum relaxation time. In the limit of a Lorentz system (\(m \ll M\)) \(\mathbf{B}_1(p)\) and \(\mathbf{B}(p)\) tend to zero and then this friction force is practically null.

The third contribution to the force \(\mathbf{F}(r,p;t)\), i.e. \(\mathbf{F}_{NL}(r,t)\), is an interesting one, which is an effective force between pairs of particles generated through the interaction of each of the pair with the thermal bath. A similar presence of an induced effective coupling of this type has been evidenced in the case of two Brownian particles embedded in a thermal bath [50] and also it can
be noticed the similarity with the one that leads to the formation of Cooper pairs in type-I superconductivity. Such contribution is of a nonlinear (bilinear in \( f_1 \)) character, and therefore eventually may lead to the emergence of complex behavior in the system, e. g., the cases of the so-called non-equilibrium Bose-Einstein-like condensation [51-56]. The last contribution, \(-\nabla U\), is usually called the self-consistent or mean field force, containing the proper single-particle distribution and then providing a nonlinear contribution to the kinetic equation.

The fifth term on the left of Eq. (A2) consists of a cross double differentiation, namely the rank-2 tensor \([\nabla_p \nabla_p f_1]\), which takes into account effects of anisotropy caused by non-uniformity. The sixth one consists of a double differentiation in the momentum variable, the rank-2 tensor \([\nabla_p \nabla_p f_1]\), which is related to the so-called diffusion in momentum space. Both contributions have their origins in the interaction of the particles with the thermal bath, that is in those terms of the collision integral \( J_1^{(2)} \) containing the potential \( w \) (see Eq. (11)).

Finally, on the right, \( J_5^{(2)} \) is the collision integral resulting from the interaction between the particles taken in the weak coupling limit, i.e., the so-called weakly coupled gas collision integral [57].

To go beyond the weak-coupling approximation, one needs to go back to the general kinetic equation to include memory effects and higher-order collision integrals, so that to include vertex renormalization [52].

### Appendix B: The Kinetic Coefficients in Eq. (32)

We do have that,

\[
a_{\tau_0} = -\frac{1}{2} \int dQ Q^4 f_{\tau_0}(Q),
\]

(B1)

with

\[
f_{\tau_0}(Q) = -\frac{n_R (M \beta_0)^{3/2} \pi |\psi(Q)|^2}{\sqrt{2 \pi m^2} V Q} \left(\frac{m}{M} + 1\right)
\]

(B2)

where \( \psi(Q) \) is the Fourier transform of the potential energy \( w(\{r_j - R_\mu\}) \), \( n_R \) is the density of particles in the thermal bath, \( V \) is the volume, and \( \beta_0^{-1} = k_B T_0 \). Moreover,

\[
a_{\tau_1} = -\frac{M \beta_0}{10} a_{\tau_0},
\]

(B3)

\[
a_{L_0} = \sqrt{\frac{2}{M \beta_0 \pi \kappa}} a_{\tau_0},
\]

(B4)

\[
\frac{1}{\kappa} = \frac{1}{\int dQ Q^4 |\psi(Q)|^2 \left(1 + \frac{m}{M}\right)}
\]

(B5)

\[
b_{\tau_0} = -\frac{2}{M \beta_0} a_{\tau_0} \left(1 + \frac{m}{M}\right)^{-1},
\]

(B6)

\[
b_{\tau_1} = \frac{a_{\tau_0}}{5} \left(1 + \frac{m}{M}\right)^{-1},
\]

(B7)

\[
a_{L_1} = -\frac{1}{5 \kappa} \sqrt{\frac{2M \beta_0}{\pi}} a_{\tau_0}.
\]

(B8)

### Conflicts of interest

The authors have no competing interests to declare.

### Declarations of interest

None.

### Supplementary data

Supplementary data to this article can be found online at https://doi.org/.
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