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Boltzmann equation and hydrodynamic fluctuations

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We apply the method of invariant manifolds to derive equations of generalized hydrodynamics from the linearized Boltzmann equation and determine exact transport coefficients, obeying Green-Kubo formulas. Numerical calculations are performed in the special case of Maxwell molecules. We investigate, through the comparison with experimental data and former approaches, the spectrum of density fluctuations and address the regime of finite Knudsen numbers and finite frequencies hydrodynamics.

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I. INTRODUCTION

The Boltzmann equation (BE) lies at the basis of classical and quantum kinetic theory of gases. It provides a detailed picture of the time evolution of a dilute gas toward a thermal equilibrium state, which constitutes the essence of the H theorem. This celebrated result gave rise, historically, to the first clear insurgence of irreversibility into deterministic equations of motion. The attempt to generalize the BE to dense gases led, successively and in the special case of a fluid of hard spheres, to the development of the Enskog theory [1], featuring the transfer of momentum and energy between two particles at collision—called collisional transfer—as well as the presence of multiple-particle collisions [2].

Meanwhile, the nonlinear integrodifferential nature of the BE prevented, so far, an exact solution for the case of dilute gases. Perturbative methods and kinetic toy models have been devised such to get partial answers. The Chapman-Enskog (CE) expansion was, in particular, the first important success in this direction [1], as it allowed to consistently derive hydrodynamics laws from their microscopic counterpart and to obtain rigorous expressions for transport coefficients. The CE method is based upon a perturbative expansion of the distribution function in terms of the Knudsen number ε, defined as the ratio between the mean-free path and a macroscopic hydrodynamic length. This is supposed to be a "smallness" parameter, in that the series converges only for $\varepsilon \to 0$. By increasing the order of the expansion one should not expect to capture larger extents of the "true" solution of the BE, since, as it was pointed out by Bobylev [3], one has to face divergencies of the acoustic modes in the dispersion relation, which are inherently related to the procedure of truncation.

In order to tackle this unphysical feature of post-Navier-Stokes hydrodynamics, some regularization methods were borrowed from functional analysis in order to restore the H theorem [4]. The route to be followed in this contribution attempts a nonperturbative approach to solve the BE. It is based on the notion of Invariant Manifold [5]. Through this method, one assumes *a priori* a separation of the hydrodynamic time scale and the kinetic time scale and postulates the existence of a stable invariant manifold (IM) in the space of distribution functions, which is parameterized with the values of the hydrodynamic fields: particle number, velocity, and temperature. In this paper we address the study of the spectrum of hydrodynamic excitations in a Maxwell gas, employing the latter nonperturbative approach, which will allow to find exact transport coefficients at arbitrary length scales.

The paper is organized as follows: in Sec. II we review the eigenvalue problem associated with the linearized Boltzmann equation and recall that hydrodynamic modes at finite wave vector can be obtained as eigenvalues of a perturbed linear operator. Next, in Sec. III, we motivate and derive (cf. Sec. III A) the invariance equations (details collected in Appendix A) and consider the case of Maxwell molecules (Sec. III B), whose associated eigenvalue problem for the unperturbed operator is analytically solvable (Appendix B). Postulating the existence of an IM, we solve the eigenvalue problem for arbitrary wave vectors. As part of the results Sec. IV we present hydrodynamic modes (Sec. IV A), find generalized transport coefficients (Sec. IV B) which recover the Green-Kubo formulas (Sec. IV C). Finally, in Sec. IV D, we determine the spectrum of density fluctuations, compare with experiments, and formulate a hypothesis about the features of finite wavelengths hydrodynamics. Conclusions are drawn in Sec. V.

II. EIGENVALUE PROBLEMS FOR THE BOLTZMANN EQUATION AND HYDRODYNAMICS

The dynamics of the fluctuations of hydrodynamic fields (particle number, momentum, and temperature) as induced by the properties of the underlying microscopic or kinetic equation, is an important issue in statistical mechanics which dates back to the seminal work by Onsager [6]. In this section we focus on the BE and show in a general setting how it features equilibration through some generalized frequencies (inverse of characteristic collision times). The way how these generalized frequencies give rise and affect the decay rates of some collective fluctuations (hydrodynamic modes) of the macroscopic fields is still an issue which lacks a rigorous foundation. The reason is that the hydrodynamic equations, as derived from the BE, are not closed and hence, some (semiphenomenological) approximations for higher order moments need to be included. In particular, the celebrated Navier-Stokes-Fourier (NSF) approximation was the first

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TABLE I. Notation used in this manuscript. Terms have been grouped and abbreviated as depicted in this table. f^{GM} and f^{LM} denote global and local Maxwellian, respectively, and Δf and δf their "distance" from f. The third row informs about the closure discussed in this manuscript, while $\mathbf{x}$ is a set of lower order moments of f.

$$\begin{aligned}
f &= \qquad f^{\mathrm{LM}} \qquad + \delta f \\
&= \overbrace{f^{\mathrm{GM}} + f^{\mathrm{GM}}\varphi_0} \quad + f^{\mathrm{GM}}\delta\varphi \\
&= f^{\mathrm{GM}} + \underbrace{f^{\mathrm{GM}}\mathbf{X}^0\cdot\mathbf{x} + f^{\mathrm{GM}}\delta\mathbf{X}\cdot\mathbf{x}} \\
&= f^{\mathrm{GM}} + \qquad f^{\mathrm{GM}}\Delta\mathbf{X}\cdot\mathbf{x} \\
&= f^{\mathrm{GM}} + \qquad \Delta f
\end{aligned}$$

historically relevant attempt in this direction. We start by reviewing some results formerly obtained by Resibois [7]. He shed some preliminary light upon the connection between the generalized frequencies and the hydrodynamic modes by solving, via perturbation theory, the eigenvalue problems associated *independently* to the BE and to the NSF equations of hydrodynamics.

A. Boltzmann equation

The BE for the velocity distribution function f reads as

$$\partial_t f = -\mathbf{v}\cdot\nabla f + Q[f,f], \tag{1}$$

where Q denotes a nonlinear integral collision operator, and $\mathbf{v}$ velocity. It is convenient to introduce the magnitude of the thermal velocity, $v_T = \sqrt{2k_B T_0/m}$ with mass m of a particle, Boltzmann constant k_{B}, the dimensionless peculiar velocity $\mathbf{c}=(\mathbf{v}-\mathbf{u}_0)/v_T$ and the equilibrium values of macroscopic fields: equilibrium particle number n_0, equilibrium mean velocity $\mathbf{u}_0=\mathbf{0}$, and equilibrium temperature T_0. The global Maxwellian is defined as: $f^{\mathrm{GM}}=(n_0/v_T^3)f_0(c)$ where $f_0(c) = \pi^{-3/2}e^{-c^2}$ denotes a Gaussian in velocity space ($c\equiv|\mathbf{c}|$). We consider only small disturbances from the global equilibrium. After passing over to Fourier space, with a wave vector denoted as $\mathbf{k}$, we decompose the distribution function (see also Table I) as

$$f(\mathbf{k},\mathbf{c},t) = f^{\mathrm{LM}} + \delta f, \tag{2}$$

where f^{LM} denotes the linearized local Maxwellian to be made precise in Sec. III, and δf the deviation from local equilibrium. An alternative notation is introduced via $\delta f = f^{\mathrm{GM}}\delta\varphi$. Considering a comoving reference frame and linearizing the collision operator around global equilibrium, one obtains from Eq. (1)

$$\frac{1}{v_T}\partial_t f = -i\mathbf{k}\cdot\mathbf{c}f + \hat{L}\delta f, \quad \hat{L} = \frac{1}{v_T}L, \tag{3}$$

where we made use of the fact that $\hat{L}f^{\mathrm{LM}}=0$. The linearized Boltzmann collision operator, L, assumes the form

$$L\delta f = \int\int d\Omega d\mathbf{c}_1 \sigma(\Omega,g) g f^{\mathrm{GM}}(c_1)[\delta\varphi(\mathbf{k},\mathbf{c}) + \delta\varphi(\mathbf{k},\mathbf{c}_1) - \delta\varphi(\mathbf{k},\mathbf{c}') - \delta\varphi(\mathbf{k},\mathbf{c}_1')]. \tag{4}$$

Here, $\sigma(\Omega,g)$ is the scattering cross section, $g\equiv|\mathbf{v}-\mathbf{v}_1|$, and $\mathbf{v}$, $\mathbf{v}_1$ are the velocities of the two particles entering the binary collision. In the remainder of this section, we will focus our attention upon the operator $\Lambda\equiv\hat{L}-i\mathbf{k}\cdot\mathbf{c}$, whose spectral properties determine the time evolution of the distribution function. This is readily seen by considering the Laplace time transform of Eq. (3)—to be further discussed in Sec. IV D—and by inspection of the inverse transform, which reads as

$$f(\mathbf{k},\mathbf{c},t) = \frac{1}{2\pi i}\oint \frac{e^{zt}}{(z-\Lambda)} dz f(\mathbf{k},\mathbf{c},0), \tag{5}$$

where the closed path encircles all the poles of the integrand function. Through the spectral theorem, we regard these poles as coinciding with the spectrum of the operator Λ. The investigation of the spectral properties of such an operator is, in fact, a longstanding issue in kinetic theory [8]. In order to study the eigenvalue problem associated with Λ, we introduce the Fourier time transform of the distribution function $f(\mathbf{k},\mathbf{c},\omega)=\int_{-\infty}^{\infty}e^{-\omega t}f(\mathbf{k},\mathbf{c},t)dt$, where ω defines a complex-valued quantity. Then, Eq. (3) reduces to

$$\Lambda f = \omega f, \tag{6}$$

which constitutes the starting point of our analysis.

In the present paper, distribution functions $f=f^{\mathrm{GM}}\varphi$ will be regarded as vectors in a Hilbert space, whose scalar product is defined by

$$\langle f_1|f_2\rangle \equiv \frac{1}{n_0}\int (f^{\mathrm{GM}})^{-1} f_1(\mathbf{c}) f_2(\mathbf{c}) d^3v. \tag{7}$$

The spectrum of Λ is analytic in $k=0$ and it can be shown to contain a $D+2$-fold degeneracy at the origin, corresponding to local conserved quantities. In order to solve the eigenvalue problem associated with Eq. (6), it is worth first to attempt the analysis of the eigenvalue problem in the long-wavelength limit $k\to 0$,

$$\hat{L}\Psi_\alpha(\mathbf{c}) = \lambda_\alpha\Psi_\alpha(\mathbf{c}), \tag{8}$$

where $\{\Psi_\alpha\}$ and $\{\lambda_\alpha\}$ denote sets of eigenfunctions and corresponding eigenvalues, respectively. The operator $\hat{L}$ is found to be symmetric and negative semidefinite with respect to scalar product (7); hence, eigenfunctions $\{\Psi_\alpha\}$ are orthogonal and form a complete set. In particular, a subset of them, which spans a $(D+2)$–dimensional subspace of the Hilbert space can be found corresponding to the degenerate zero eigenvalue. These are the collision invariants $f^{\mathrm{GM}}\mathbf{X}^0$, with $\mathbf{X}^0$ denoting a set of lower order Sonine (or associated Laguerre) polynomials [see also Eq. (A2)],

$$\mathbf{X}^0 = \left[1, 2\mathbf{c}, \left(c^2 - \frac{3}{2}\right)\right]. \tag{9}$$

A perturbative approach is followed in order to extract the corresponding eigenvalues from the full spectrum of Λ. These eigenvalues, denoted hereafter by ω_{hydro}, approach zero in the long-wavelength limit (see [9,10] for a detailed discussion). The yet unknown eigenfunctions and eigenvalues are expanded in powers of the wave vector $\mathbf{k}$,

$$|\Psi_\alpha\rangle = |\Psi_\alpha^{(0)}\rangle + k|\Psi_\alpha^{(1)}\rangle + k^2|\Psi_\alpha^{(2)}\rangle + \cdots,$$

$$\omega_\alpha = \omega_\alpha^{(0)} + k\omega_\alpha^{(1)} + k^2\omega_\alpha^{(2)} + \cdots, \tag{10}$$

where $|\Psi_\alpha^{(0)}\rangle$ denotes a linear combination of the eigenfunctions of the unperturbed system. The result of this standard procedure is a polynomial expression for the set $\{\omega_\alpha\}$ of hydrodynamic modes, up to second order,

$$\omega_1 = ic_0k - k^2\langle\Psi_1^{(0)}|(c_x - c_0)\frac{1}{\hat{L}}(c_x - c_0)|\Psi_1^{(0)}\rangle,$$

$$\omega_2 = -ic_0k - k^2\langle\Psi_2^{(0)}|(c_x + c_0)\frac{1}{\hat{L}}(c_x + c_0)|\Psi_2^{(0)}\rangle,$$

$$\omega_3 = -k^2\langle\Psi_3^{(0)}|c_x\frac{1}{\hat{L}}c_x|\Psi_3^{(0)}\rangle,$$

$$\omega_4 = -k^2\langle\Psi_4^{(0)}|c_x\frac{1}{\hat{L}}c_x|\Psi_4^{(0)}\rangle,$$

$$\omega_5 = -k^2\langle\Psi_5^{(0)}|c_x\frac{1}{\hat{L}}c_x|\Psi_5^{(0)}\rangle, \tag{11}$$

where $c_0 = (5k_BT_0/3m)^{1/2}$ is the speed of sound of an ideal gas.

B. Linear hydrodynamics

The hydrodynamic fields n, $\mathbf{u}$, and T are fluctuating in time. We denote by $[n_k, \mathbf{u}_k, T_k]$ the Fourier transforms of the fluctuations of the hydrodynamics fields, for instance: $n_k = \int_{-\infty}^{\infty}dt\int_{-\infty}^{+\infty}d\mathbf{r}e^{-\omega t - i\mathbf{k}\cdot\mathbf{r}}\delta n(\mathbf{r},t)$, where $\delta n(\mathbf{r},t)$ is the fluctuation of the local particle number density at time t and point $\mathbf{r}$. The equations of hydrodynamics considered in [7] are the linearized NSF equations, which represent balance equations for particle number density, momentum and kinetic energy endowed with specific constitutive equations for the stress tensor and heat flux,

$$\omega n_k(\omega) = -in_0\mathbf{k}\cdot\mathbf{u}_k(\omega), \tag{12a}$$

$$\omega\mathbf{u}_k(\omega) = -i\frac{\mathbf{k}}{n_0}\left(\frac{\partial P}{\partial n}\right)_T n_k(\omega) - i\frac{\mathbf{k}}{n_0}\left(\frac{\partial P}{\partial T}\right)_n T_k(\omega) - \frac{\eta}{n_0}k^2\mathbf{u}_k(\omega) - \frac{\mathbf{k}}{n_0}\left(\zeta + \frac{\eta}{3}\right)\mathbf{k}\cdot\mathbf{u}_k(\omega), \tag{12b}$$

$$\omega T_k(\omega) = -i\frac{1}{n_0}\frac{T_0}{C_v}\mathbf{k}\cdot\mathbf{u}_k(\omega) - \frac{\kappa}{C_v n_0}k^2T_k(\omega), \tag{12c}$$

where ζ and η are, respectively, the bulk and shear viscosity, C_v is the specific heat at constant volume and κ is the thermal conductivity. Solving Eq. (12) amounts to determine the eigenvalues of a 5×5 non Hermitian matrix, which represent the decay rates of the collective excitations. The intuition enlightened in the paper [7] was to put into correspondence the macroscopic eigenvalues with their microscopic counterpart, obtained from Eq. (8) by application of perturbation theory. This identification allowed to find an approximate expression for transport coefficients only in terms of the one-body distribution function which turned out to be equivalent to reduced expressions determined by many-body autocorrelation functions. These coefficients properly recover the Chapman-Enskog expressions from classical kinetic theory. Within the above construction it is found that the decay rates of hydrodynamic modes in the NSF approximation are quadratic in the wave vector $\text{Re}(\omega) \propto -k^2$ and unbounded. The use of a suitable projector, on the other hand, to be outlined in the next section, allows us to find proper asymptotics and paves the way to solve the eigenvalue [Eq. (6)] as well as to determine exact transport coefficients.

III. INVARIANT MANIFOLD TECHNIQUE

The notion of invariant manifold is a generalization of normal solution in the Hilbert and Chapman-Enskog method. Given a dynamical system

$$\frac{df}{dt} = J(f), \tag{13}$$

where $J(f)$ can be considered as a vector field which induces the motion in the space of distribution functions, denoted as U. Given bounded and smooth functions $\mathbf{x}(\mathbf{r},t)$ we define the *locally finite-dimensional* manifold $\Omega \subset U$ as the set of functions $f(\mathbf{x}(\mathbf{r},t),\mathbf{c})$. Hence, within the spirit of the invariant manifold technique, we will only consider sets of distribution functions whose dependence upon the space variable $\mathbf{r}$ is parameterized through some "moments" $\mathbf{x}(\mathbf{r},t)$. As it will be discussed in Sec. IV D, once we identify such coarse-grained fields $\mathbf{x}(\mathbf{r},t)$ with the hydrodynamic fields, postulating their existence implies invoking the hypothesis of local thermodynamic equilibrium. Hence, the extent of our predictions is inherently restricted to length scales wherein the concept of a field as ensemble average over a statistically significant number of particles is still meaningful. Let us denote by T_w the tangent space to the manifold Ω at the point w of the phase space, and let us introduce a projection operator P [to be defined in Eq. (18)] which, when acting on $J(f)$, describes the motion of the vector field along the manifold. The dynamics is, hence, splitted into a fast motion on the affine subspace $w+\ker[P]$: (where $\ker[P]$ denotes the null space of the projection operator P) and a slow motion, which occurs along the tangent space T_w [5]. The set of eigenvalues ω_{hydro} is determined as follows:

(1) we seek for an invariant manifold $\Omega \subset U$ such that the following invariance equation (IE) is fulfilled;

$$(1-P)\Lambda\Delta f=0 \tag{14}$$

where $\Delta f\equiv f-f^{\mathrm{GM}}$ (see also Table I);

(2) after determining the nonequilibrium distribution function from Eq. (14), we derive equations of linear hydrodynamics via integration of the kinetic equation (3). By construction, the decay rates of the macroscopic excitations then coincide with ω_{hydro}.

A. Derivation of the invariance equation

Let $\mathbf{x}=[\tilde{n},\tilde{\mathbf{u}},\tilde{T}]$ denote the set of dimensionless hydrodynamic fluctuations: $\tilde{n}\equiv(n-n_0)/n_0=$(particle number perturbation), $\tilde{\mathbf{u}}\equiv\mathbf{u}/v_T=$(velocity perturbation) and $\tilde{T}\equiv(T-T_0)/T_0$ (temperature perturbation). By linearizing around the global equilibrium, we write the local Maxwellian contribution to f in (2) as $f^{\mathrm{LM}}=f^{\mathrm{GM}}(1+\varphi_0)$ where φ_0 takes a simple form, $\varphi_0=\mathbf{X}^0\cdot\mathbf{x}$ (linear quasi equilibrium manifold); $\mathbf{X}^0(\mathbf{c})$ was defined in Eq. (9). It is conveniently considered as four-dimensional vector using the four-dimensional version $\mathbf{x}=[\tilde{n},u^{\parallel},\tilde{T},u^{\perp}]$, and is then given by Eq. (A2). The four-dimensional version is obtained by splitting the mean velocity $\tilde{\mathbf{u}}$ uniquely as $\tilde{\mathbf{u}}=u^{\parallel}\mathbf{e}_{\parallel}+u^{\perp}\mathbf{e}_{\perp}$, where the unit vector $\mathbf{e}_{\parallel}$ is parallel to $\mathbf{k}$, and $\mathbf{e}_{\perp}$ orthonormal to $\mathbf{e}_{\parallel}$, i.e., $\mathbf{e}_{\perp}$ lies in the plane perpendicular to $\mathbf{k}$. Due to isotropy, $u^{\perp}$ alone then fully represents the twice degenerated (shear) dynamics. The remainder of this subsection is valid for both four- and five-dimensional versions.

It further proves convenient to introduce a vector of velocity polynomials, $\boldsymbol{\xi}(\mathbf{c})$, which is similar to $\mathbf{X}^0$ and defined by Eq. (A3), such that $\langle f^{\mathrm{GM}}\xi_\mu|f^{\mathrm{GM}}X^0_\nu\rangle=\delta_{\mu\nu}$. Hence, the fields $\mathbf{x}$ are obtained as $\langle\boldsymbol{\xi}(\mathbf{c})\rangle_{f^{\mathrm{LM}}}=\mathbf{x}$, where averages are defined as

$$\langle\boldsymbol{\xi}(\mathbf{c})\rangle_f\equiv\frac{1}{n_0}\int\boldsymbol{\xi}(\mathbf{c})f(\mathbf{c})d^3\mathbf{v}=\langle f^{\mathrm{GM}}\boldsymbol{\xi}(\mathbf{c})|f\rangle. \tag{15}$$

We introduce yet unknown fields $\delta\mathbf{X}(\mathbf{c},\mathbf{k})$ which characterize the part δf of the distribution function. As long as deviations from the local Maxwellian stay small, we seek for a nonequilibrium manifold which is also linear in the hydrodynamic fields $\mathbf{x}$ themselves. Therefore, we set:

$$\delta\varphi=\delta\mathbf{X}\cdot\mathbf{x}. \tag{16}$$

The "eigen"-closure (16), which formally and very generally addresses the fact that we wish to *not* include other than hydrodynamic variables, implies a closure between moments of the distribution function, to be worked out in detail below. By using the above form [Eq. (16)] for $\delta f=f^{\mathrm{GM}}\delta\varphi$, with $\hat{L}\delta f=f^{\mathrm{GM}}L[\delta\mathbf{X}]\cdot\mathbf{x}$, and the canonical abbreviation $\Delta\mathbf{X}\equiv\mathbf{X}^0(\mathbf{c})+\delta\mathbf{X}(\mathbf{c},\mathbf{k})$, Eq. (6) reads as

$$\omega f^{\mathrm{GM}}\Delta\mathbf{X}\cdot\mathbf{x}=\Lambda\Delta f=-i\mathbf{k}\cdot\mathbf{c}f^{\mathrm{GM}}\Delta\mathbf{X}\cdot\mathbf{x}+f^{\mathrm{GM}}\hat{L}\delta\mathbf{X}\cdot\mathbf{x}. \tag{17}$$

The microscopic projected dynamics is obtained from Eq. (14) by introducing the thermodynamic projection operator [5], defined by its action on the vector field $J(f)$,

$$PJ(f)\equiv D_{\mathbf{x}}\Delta f\cdot\int\boldsymbol{\xi}(\mathbf{c})J(f)d^3v, \tag{18}$$

where $D_{\mathbf{x}}\Delta f\equiv\partial\Delta f/\partial\mathbf{x}$. The quantity inside the integral in Eq. (18) represents the time evolution equations for the moments $\mathbf{x}$, when $J(f)=\Lambda\Delta f$. These are readily obtained by integration of weighted Eq. (6) as

$$\omega\langle\boldsymbol{\xi}(\mathbf{c})\rangle_f=-i\mathbf{k}\cdot\langle\boldsymbol{\xi}(\mathbf{c})\mathbf{c}\rangle_f+\langle\boldsymbol{\xi}(\mathbf{c})\rangle_{\hat{L}\delta f}. \tag{19}$$

As shown in Table I, $D_{\mathbf{x}}\Delta f=f^{\mathrm{GM}}\Delta\mathbf{X}$ holds, whereas Eq. (19) is linear in $\mathbf{x}$ and can be written as $\omega\mathbf{x}=\mathbf{M}\cdot\mathbf{x}$. Hence, Eq. (18), with $J(f)=\Lambda\Delta f$, attains the form

$$P\Lambda\Delta f=f^{\mathrm{GM}}\Delta\mathbf{X}\cdot\mathbf{M}\cdot\mathbf{x}. \tag{20}$$

In the derivation of Eq. (20), one needs to take into account that $\langle\boldsymbol{\xi}(\mathbf{c})\rangle_{\delta f}=0$ (as the fields $\mathbf{x}$ are defined through the local Maxwellian part of the distribution function only) and that $\langle\boldsymbol{\xi}(\mathbf{c})\rangle_{\hat{L}\delta f}=0$. The dependence of the matrix elements of $\mathbf{M}$ upon moments of δf is explicitly given in Tab. II. Combining Eqs. (17) and (20), and requiring that the result holds for any $\mathbf{x}$ (invariance condition), we obtain a closed, singular integral equation (invariance equation) for complex-valued $\delta\mathbf{X}$,

$$\Delta\mathbf{X}\cdot\mathbf{M}=-i\mathbf{k}\cdot\mathbf{c}\Delta\mathbf{X}+\hat{L}\delta\mathbf{X}. \tag{21}$$

where $\Delta\mathbf{X}\equiv\mathbf{X}_0+\delta\mathbf{X}$. Notice that $\delta\mathbf{X}$ vanishes for $k=0$, which implies that the invariant manifold $\Omega_{k\to0}$ in that limit is given by the set of local Maxwellians f^{LM}. Implicit Eq. (21) for $\delta\mathbf{X}$ (or $\Delta\mathbf{X}$, as $\mathbf{X}^0$ is known) is identical with eigen-closure (16), and is our main and practically useful result. The Bhatnagar-Gross-Krook (BGK) collision model treated in [11] is recovered for $\hat{L}(\delta\mathbf{X})=-\delta\mathbf{X}$.

B. Solving the invariance equation

Invariance Eq. (21) as well as some symmetry relations for the components δX_μ of the nonequilibrium distribution function (worked out in Appendix A for the interested reader) are exact. Solutions to this equation can be obtained in simple cases. Considering the BGK kinetic equation, for instance, the IE could recently be solved numerically and the spectrum of hydrodynamic modes at arbitrary wavelength has been successfully determined [11]. In the present case, our strategy to solve Eq. (21) is to confine ourselves with a special kind of interaction potential (Maxwell molecules) and is based on the results obtained by Chang-Uhlenbeck [9]. They provided an analytical solution to the eigenvalue problem associated with the collision operator for Maxwell molecules operator (i.e.,: gas molecules interacting via a potential $V\propto r^{-4}$, see also [12]). Their analysis showed that due to the isotropy of the operator $\hat{L}$ (i.e., it commutes with rotation operators in velocity space), it admits the following set of eigenfunctions $\Psi_{r,l}(\mathbf{c})$,

$$\Psi_{r,l}=\sqrt{\frac{r!\left(l+\frac{1}{2}\right)\sqrt{\pi}}{\left(l+r+\frac{1}{2}\right)!}}c^lP_l(z)S^{(r)}_{l+1/2}(c^2), \tag{22}$$

where P_l and $S_{l+\frac{1}{2}}$ denote, respectively, Legendre and Sonine polynomials, $c\equiv|\mathbf{c}|$ and $z\equiv\mathbf{c}\cdot\mathbf{e}_{\parallel}/c$ (see also Appendix A).

These eigenfunctions are orthonormal with respect to scalar product (7), with corresponding eigenvalues,

$$\lambda_{r,l}=2\pi\int \sin(\vartheta)F(\vartheta)T_{r,l}(\vartheta)d\vartheta, \quad r,l\in 0,1\ldots \tag{23}$$

where the explicit expressions for the functions $F(\vartheta)$ and $T_{rl}(\vartheta)$ are required to numerically solve Eq. (21) and hence delegated to Appendix A, where we also summarize a number of implementation details toward solving the invariance equation. Whereas the construction outlined in Sec. II deduces the eigenvalues of perturbed system (8), which vanish in the $k\rightarrow 0$ limit, just from the knowledge of $\ker[\hat{L}]$ (i.e., the "ground states" of the unperturbed system), here we attempt a different route. We introduce, first, a decomposition of the microscopic particle velocity, where its components can be expressed through the absolute value of velocity, c, and the cosine of the angle between velocity and wave vector, already denoted as z. Next, we expand our functions $[\mathbf{X}^{(0)},\delta\mathbf{X}]$ in terms of the orthonormal basis $\Psi_{r,l}=\Psi_{r,l}(c,z)$ up to some finite order N,

$$X_{\mu}^{(0)}(c,z)=\sum_{r,l}^{N} a_{\mu}^{(0)(r,l)}\Psi_{r,l}(c,z), \tag{24a}$$

$$\delta X_{\mu}(k,c,z)=\sum_{r,l}^{N} a_{\mu}^{(r,l)}(k)\Psi_{r,l}(c,z). \tag{24b}$$

The equilibrium coefficients $a_{\mu}^{(0)}$ are known, and can be determined, by taking advantage of the orthogonality of the eigenfunctions, as

$$\mathbf{a}^{(0)(r,l)}=\pi^{3/2}\int e^{-c^2}\Psi_{r,l}(c,z)\mathbf{X}^{(0)}(c,z)d^3\mathbf{c}. \tag{25}$$

Inserting Eq. (24) into IE (21), we obtain the following nonlinear set of algebraic equations for the unknown coefficients $a_{\mu}^{(r,l)}(k)$:

$$b_{\nu}^{(r',l')}M_{\nu\mu}=-i\mathbf{k}\cdot\sum_{r,l}^{N} b_{\mu}^{(r,l)}\mathbf{\Omega}_{(r,l,r',l')}+\sum_{r,l}^{N} a_{\mu}^{(r,l)}\mathcal{L}_{(r,l,r',l')}, \tag{26}$$

where $\forall_{\nu,r,l}b_{\nu}^{(r,l)}\equiv a_{\nu}^{(0)(r,l)}+a_{\nu}^{(r,l)}$, and where we identify

$$\mathcal{L}_{(r,l,r',l')}=\langle f^{\mathrm{GM}}\Psi_{r',l'}|\hat{L}|f^{\mathrm{GM}}\Psi_{r,l}\rangle, \tag{27a}$$

$$\mathbf{\Omega}_{(r,l,r',l')}=\langle f^{\mathrm{GM}}\Psi_{r,l}|\mathbf{c}|f^{\mathrm{GM}}\Psi_{r',l'}\rangle. \tag{27b}$$

For any order N of expansion, the solutions of Eq. (26) characterize an invariant manifold in the phase space. The matrix elements $\mathcal{L}_{(r,l,r',l')}$ can be easily evaluated in few kinetic models, as for the BGK collision operator, hard spheres and Maxwell molecules. In particular, the latter case is recovered by setting

$$\mathcal{L}_{(r,l,r',l')}^{\mathrm{Maxw}}=\lambda_{r,l}\delta_{r,r'}\delta_{l,l'}. \tag{28}$$

Furthermore, the simplest case is BGK where all nonvanishing eigenvalues attain the constant value: $\lambda_{\mathrm{BGK}}=-1$.

IV. RESULTS

The calculation of the coefficients $\mathbf{a}^{(r,l)}$ via reformulated invariance Eq. (26) is easily achieved. All implementation details, in particular the switch to spherical coordinates, and symmetry features, have been worked out and summarized in Appendix A. In order to make this contribution self contained, also the eigenvalues for the Maxwell gas, entering the calculations, are given in Appendix B.

Through the obtained expansion coefficients, the invariant manifold $\Omega\subset U$ is fully characterized: that is, the distribution function is determined and the corresponding matrix $\mathbf{M}$ of linear hydrodynamics as well as moments $A-Z$, are made accessible. Solving the invariance equation, and thus obtaining the distribution function (via $\mathbf{a}^{(r,l)}$) (cf. Fig. 1) required minor computational effort. Results for both the distribution function and its moments will be further discussed below.

Generalized transport coefficients such as viscosity and diffusion coefficients, can be expressed in terms of the moments (components $A-Z$ of $\mathbf{M}$), which further enter the definition of the stress tensor and heat flux. In the regime of large Knudsen numbers the coefficients $\mathbf{a}^{(r,l)}$ may be used to, e.g., directly calculate phoretic accelerations onto moving and rotating convex particles [13], while in the opposite limit of small k we recover classical hydrodynamic equations.

A. Hydrodynamic modes

With $\mathbf{M}$ at hand, the hydrodynamic modes are obtained from Eq. (20). The damping rates of the fluctuations (given by the real part of the hydrodynamic modes) are obtained by truncating the series [Eq. (24)] at the fourth order and represented in Fig. 2. The picture does not qualitatively change upon further increase of the order N. The first important finding is that, for any finite order of expansion, the modes extend smoothly over all the wave vector domain and, for large k, they attain an asymptotic value. This reflects the fact that, below a certain length scale (more specifically, for lengths less than the mean-free path), we reach the free-streaming limit; i.e., the regime in which the collisions cease to occur and particles move along straight lines. Hence, when reducing further the length scale, we may not expect an increase of the damping rate without the "thermalizing" effect of collisions. These physical arguments were already supported by the study of the BGK kinetic Eq. [11], wherein the hydrodynamic modes, in the limit of small wavelengths, reach all the same value equivalent to the constant eigenvalue of the BGK collision operator. A further indication of the role played by the spectrum of $\hat{L}$ for large k is provided by the observation that, when taking into account all the set of the eigenvalues of $\hat{L}$ which are unbounded below, also the hydrodynamic modes grow unboundedly.

B. Transport coefficients

Generalized transport coefficients are obtained by the nontrivial eigenvalues of $-k^2\,\mathrm{Re}(\mathbf{M})$: $\lambda_2=-A$ (elongation viscosity), $\lambda_3=-\frac{2}{3}Y$ (thermal diffusivity) and $\lambda_4=-D$ (shear viscosity). The abbreviation of moments $A-Z$, defined in Tab. II, is chosen to agree with notation used earlier [11] and

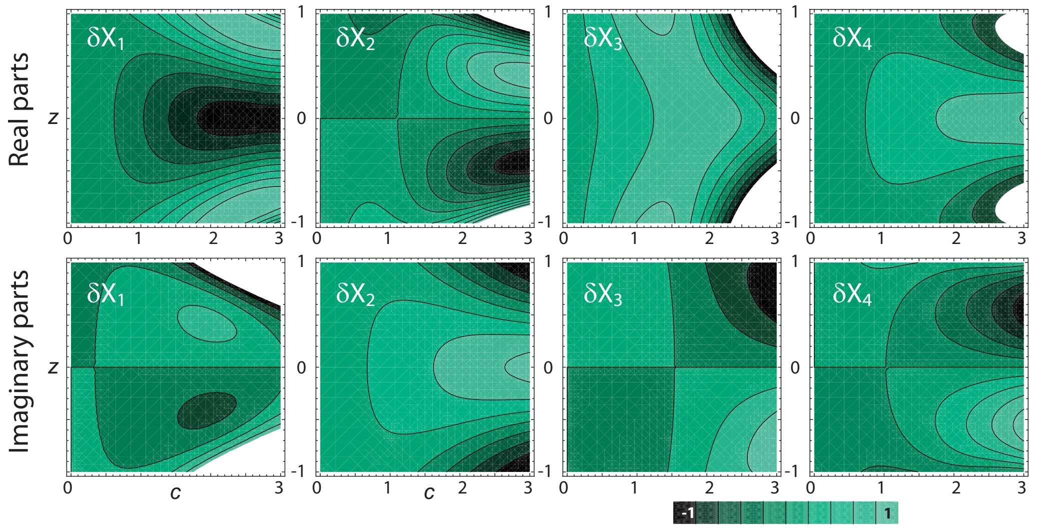

FIG. 1. (Color online) All contributions $\delta X_{1-4}(\mathbf{c},\mathbf{k})$ vs c (horizontal, $c=|\mathbf{c}|$) and $z\in[-1,1]$ (vertical axis, z is the cosine of the angle between $\mathbf{k}$ and peculiar velocity $\mathbf{c}$) to the nonequilibrium distribution function $\delta f=f^{\mathrm{GM}}\delta X_\mu x_\mu$ [Eq. (16)] at $k=1$, obtained with the fourth order expansion, $N=4$. Shown here are both their real (top) and imaginary parts (bottom row). Values range from −1 (black) to 1 (bright and green). Values outside these artificial bounds are uncolored (white) in order to increase the resolution in the remaining parts of the figure.

in textbooks such as [5]. Expressions for stress and heat flux are given in Appendix A. In the limit $k\to 0$, we recover the hydrodynamic limit. This limit had been worked out in detail in [14,15]. In that limit, our generalized transport coefficients $A-Z$ become the classical transport coefficients. As can be seen from Fig. 3 (below), and also by inspecting the invariance equation (in the limit of small k), all moments $A-Z$ approach constant values in the limit of small k. These constants are compatible with those obtained earlier for the case of Navier-Stokes equations and the Burnett correction. The stress tensor and heat flux are given in terms of these moments in Table II. For example, the parallel component of the stress tensor related to density fluctuations, $\sigma_1^{\parallel}$, cf. Eq. (A6), is given by $-k^2B$ so that it approaches $-k^2$ for small k, as it results from the Burnett approximation.

C. Relationship with Green-Kubo expressions

After some algebra it is possible to cast the expression for the higher order moments in terms of time-correlation functions, in order to show the connection with the Green-Kubo expressions [16]. To this aim, we first write the nonequilibrium distribution function at time τ as

$$\delta f(\mathbf{k},\mathbf{c},\tau) = e^{\Lambda\tau}\delta f(\mathbf{k},\mathbf{c},0). \tag{29}$$

Then, due to Eq. (24), by integrating both sides of Eq. (21), we find

$$M_{\mu\nu} = \sum_{r,l}^{N} \left(a_\nu^{(0)(r,l)} + a_{\nu;R}^{(r,l)}\right)\langle f^{\mathrm{GM}}\xi_\mu|\Lambda e^{\Lambda\tau}|f^{\mathrm{GM}}\Psi_{r,l}\rangle + \sum_{r,l}^{N} a_{\nu;I}^{(r,l)} \times\langle f^{\mathrm{GM}}\xi_\mu|\Lambda e^{\Lambda\tau}|f^{\mathrm{GM}}\Psi_{r,l}\rangle, \tag{30}$$

where $a_{\nu;R}^{(r,l)}$ and $a_{\nu;I}^{(r,l)}$ are, respectively, real and imaginary-valued coefficients. The equality $\langle f^{\mathrm{GM}}\xi_\mu|\Lambda e^{\Lambda\tau}|f^{\mathrm{GM}}\Psi_{r,l}\rangle = -ik\langle f^{\mathrm{GM}}\xi_\mu|c_\parallel e^{\Lambda\tau}|f^{\mathrm{GM}}\Psi_{r,l}\rangle$ holds because lower order mo-

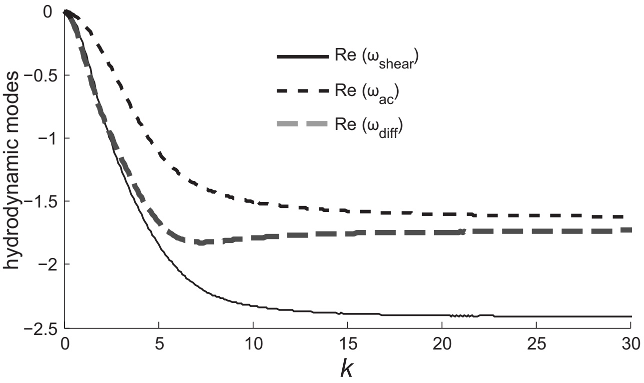

FIG. 2. Hydrodynamic modes ω of the Boltzmann kinetic equation with Maxwell-molecules collision operator as a function of wave number k. Shown are two complex conjugated acoustic modes ω_{ac}, twice degenerated shear mode ω_{shear} and a thermal diffusion mode ω_{diff}.

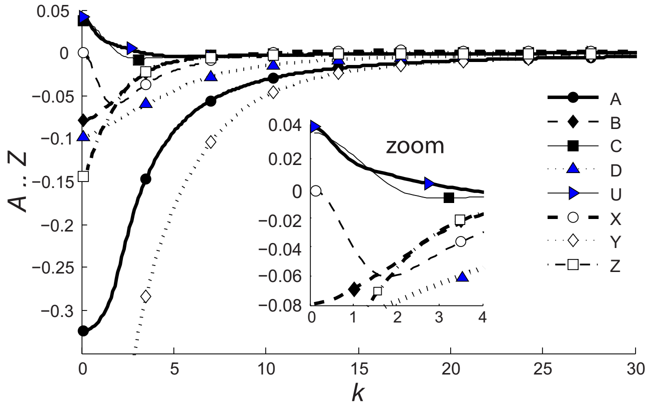

FIG. 3. (Color online) Moments A-Z of the distribution function [see Table II and Eq. (A7)[vs wave number k obtained with the solution of Eq. (21). Nontriangles (black symbols): moments entering only the longitudinal component of hydrodynamic equations. Triangles (blue symbols): moments entering the transverse component of hydrodynamic equations.

TABLE II. Symmetry adapted components of (nonequilibrium) stress tensor $\boldsymbol{\sigma}$ and heat flux $\mathbf{q}$, both introduced in Eq. (A6). Row 2: microscopic expression of these components (averaging with the global Maxwellian). Short-hand notation used: $\lambda^{\parallel}=c_{\parallel}^2-\frac{c^2}{3}$ and $\gamma^{\parallel}=(c^2-\frac{5}{2})c_{\parallel}$. Row 3: expression of the components in terms of (as we show, real valued) functions $A-Z$ (see text). Row 4: parity with respect to z—symmetric ($\oplus$) or antisymmetric ($\ominus$)—of the part of the corresponding δX entering the averaging in row 2, and whether this part is imaginary or real valued (see Fig. 1). Row 3 is an immediate consequence of row 4.

$\sigma_1^{\parallel}$	$\sigma_2^{\parallel}$	$\sigma_3^{\parallel}$	σ_4
$\langle\lambda^{\parallel}\delta X_1\rangle$	$\langle\lambda^{\parallel}\delta X_2\rangle$	$\langle\lambda^{\parallel}\delta X_3\rangle$	$\langle c_{\parallel}c_{\phi}\delta Y_4\rangle$
$-k^2B$	ikA	$-k^2C$	ikD
Real, $\oplus$	Imag, $\oplus$	Real, $\oplus$	Imag, $\ominus$
$q_1^{\parallel}$	$q_2^{\parallel}$	$q_3^{\parallel}$	q_4
$\langle\gamma^{\parallel}\delta X_1\rangle$	$\langle\gamma^{\parallel}\delta X_2\rangle$	$\langle\gamma^{\parallel}\delta X_3\rangle$	$\langle(c^2-\frac{5}{2})c_{\phi}\delta Y_4\rangle$
ikX	$-k^2Z$	ikY	$-k^2U$
Imag, $\ominus$	Real, $\ominus$	Imag, $\ominus$	Real, $\oplus$

ments of the collision operator identically vanish. Next, using the operator identity,

$$\Lambda e^{\Lambda\tau}=-\Lambda\Big(\int_{\tau}^{\infty}e^{\Lambda t}dt\Big)\Lambda, \tag{31}$$

we find for the real part of the $\mathbf{M}$ matrix in Eq. (30), evaluated with $\tau=0$,

$$\mathrm{Re}(M_{\mu\nu})=-\sum_{r,l}^{N}a_{\nu;I}^{(r,l)}\int_0^{\infty}dt\langle\dot{\xi}_{\mu}(0)\dot{\Psi}_{r,l}(t)\rangle_{f^{\mathrm{GM}}}, \tag{32}$$

where $\dot{\Psi}_{r,l}=\Lambda\Psi_{r,l}$. Eq. (32) extends the Green-Kubo relations for transport coefficients to arbitrary wave vector. These relations hold in the hydrodynamic regime, when the system, as a result of many collisions, has reached local equilibrium. The opposite regime ($k\gg 1$) is represented by a simple gas of noninteracting point particles. Importantly, as it is evident from Fig. 3, and as already noticed in [17,18], the transport coefficients vanish in the limit of small wavelengths. This is due to the fact that the real and imaginary-valued coefficients solving Eq. (26), $a_{\nu;R}^{(r,l)}$ and $a_{\nu;I}^{(r,l)}$, respectively, vanish in that limit. This vanishing character of transport coefficients (and, hence, of the heat flux and the stress tensor as is evident from Table II) for large k, corresponds to Eulerian (inviscid) hydrodynamics. We are led, then, to similar conclusions to those traced when we discussed, in Sec. III, the $k\to 0$ limit of invariance Eq. (14): in the free-streaming regime, the local equilibrium manifold (local Maxwellian) becomes an invariant manifold. Let us recall that the Maxwellian distribution constitutes the zero point of the collision integral, in the sense that, in local equilibrium, the net flux of molecules entering and leaving an infinitesimal volume in space, due to the scattering processes, is zero. What we observe here is that, at a sufficiently short length scale, the distribution function reduces to a Maxwellian, since the contribution from the scattering event, again, vanishes: but now this is because collisions ceased to occur.

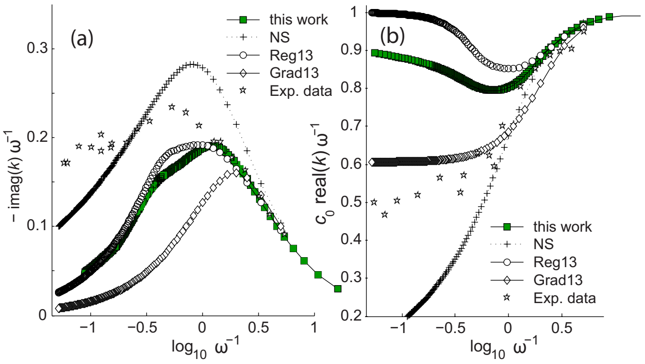

FIG. 4. (Color online) (a) Damping spectrum, i.e., the negative imaginary part of k divided by frequency ω vs the negative logarithm of ω. Results obtained in this work [by solving Eq. (21), and subsequently Eq. (20) for $w(k)$ with complex valued k and real valued ω] are compared with previous approaches including Navier-Stokes (NS), regularized 13 moment (Reg13) [19], Grad 13 moment (Grad13), and experimental data presented in [20]. (b) Phase spectrum, i.e, real part of k times velocity of sound c_0 and divided by ω vs the negative logarithm of ω. Again, we compare with reference results.

D. Finite wavelengths hydrodynamics and comparison with experiments

The existence of short wavelengths collective modes in real fluids is a long-standing issue (see in particular the excellent reference [21]). Ford and Foch [10] illustrated, on the basis of a model kinetic equation approximating the linearized BE, that the sound modes could be extended to length scales comparable with the mean-free path in the gas. Our analysis showed, on the other hand, that hydrodynamic modes and the generalized transport coefficients extend smoothly over all the k domain (there is no occurrence of any critical point as in the case of a Grad kinetic system, studied in [14,15]). Hence our approach, here and in [11], tends to predict that the notion of invariant manifold holds also for very short length scales. This would be in agreement with the celebrated papers by Alder *et al.* [17,22] on dense fluids, showing that hydrodynamic laws remain valid down to times comparable with the time between collisions, t_{coll}, and that the k-dependent zero-frequency transport coefficients decay until they vanish at short length scales. It would be significant, therefore, to investigate the features of our model at finite frequencies and wavelengths and verify whether the procedure of truncation we introduced in Eq. (24) introduces a length scale below which our coarse-grained description breaks down. In Fig. 4 a comparison is shown about inverse phase velocity and damping for acoustic waves between our results, former approaches [19,23] and experimental data performed by Meyer and Sessler [20]. As it is seen, our results are very close to the predictions of the regularized 13 (Reg13) moments method [19] and closer to experimental data than Reg13 concerning the phase spectrum. Our theory is capable in predicting a phase speed which remains finite also at high frequencies, a feature which is not possessed by any hydrodynamics derived from the CE expansion.

A further clue about the features of our predictions in the regime of finite frequencies and wave vectors can be achieved by a closer inspection upon the spectrum of density fluctuations. To this aim, we introduce the Laplace transform of the hydrodynamic fields $\mathbf{x}_{\mathbf{k}}(z)=\int_0^\infty e^{-zt}\mathbf{x}_{\mathbf{k}}(t)dt$ and write the equation of linear hydrodynamics as

$$\mathbf{x}_{\mathbf{k}}(z) = (z\mathbf{I}-\mathbf{M})^{-1}\mathbf{x}_{\mathbf{k}}(t=0). \tag{33}$$

By inverting the Laplace transform one obtains

$$\mathbf{x}_{\mathbf{k}}(t) = \frac{1}{2\pi i}\oint \frac{e^{zt}}{(z\mathbf{I}-\mathbf{M})}dz\,\mathbf{x}_{\mathbf{k}}(t=0). \tag{34}$$

In order to proceed further and to calculate the intermediate scattering functions $C_{\mathbf{x},\mathbf{x}}(\mathbf{k},t)=\langle\mathbf{x}_{\mathbf{k}}(t)\mathbf{x}_{-\mathbf{k}}(0)\rangle$, we need to define the averages which are employed in the calculation of correlation functions. These are, in fact, no longer ensemble averages, as in Eq. (15), but, due to Eq. (34), are averages over initial conditions, weighted by the probability density of thermodynamic fluctuation theory [24,25]. Finally, the power spectrum of $C_{\mathbf{x},\mathbf{x}}$ is given by its Fourier transform,

$$S_{\mathbf{x},\mathbf{x}}(k,\omega) = \int_{-\infty}^{\infty} C_{\mathbf{x},\mathbf{x}}(\mathbf{k},t)e^{-i\omega t}dt. \tag{35}$$

It is worth focusing upon a quantity which is experimentally accessible: the spectrum of density fluctuations, $S_{\tilde{n},\tilde{n}}$, which is related to the scattering cross section. The calculation of $S_{\tilde{n},\tilde{n}}$ proceeds along the lines indicated above. It just suffices to notice how the solution for $\tilde{n}_{\mathbf{k}}(z)$ involves terms proportional to the initial values of $\tilde{n}_{\mathbf{k}}, \tilde{\mathbf{u}}_{\mathbf{k}}, \tilde{T}_{\mathbf{k}}$, but, following standard recipes [24], only the term proportional to $\tilde{n}_{\mathbf{k}}(t=0)$ needs to be retained in the calculation. By considering just the lower order terms in k, one obtains

$$\tilde{n}_k(t) = \left[\frac{2}{5}e^{-\chi k^2 t} + \frac{3}{10}e^{-\Gamma k^2 t}\cos(c_0 k t)\right]\tilde{n}_k(0). \tag{36}$$

The first term in Eq. (36) represents a fluctuation which decays according to a purely diffusive process, with a lifetime proportional to D_T, whereas the second term represents a fluctuation propagating through the fluid at the (dimensionless) speed of sound $c_0=\sqrt{5/3}$ and decaying with a lifetime given by Γ. The coefficient D_T generalizes the standard thermal conductivity, while Γ generalizes the combined effect of both thermal conductivity and longitudinal kinetic viscosity. In the limit of small k, and following standard text books [26], their expression is given by

$$D_T = \frac{2}{5}(X-Y), \tag{37a}$$

$$\Gamma = -\left(\frac{1}{2}A + \frac{1}{5}X + \frac{2}{15}Y\right), \tag{37b}$$

where the moments A, X, and Y we had already defined and related to material properties (see also Table II). Unlike standard treatments of hydrodynamic fluctuations, the generalized transport coefficient X enters the expression of the coefficients D_T and Γ, even though its contribution, as it is evident from Fig. 3 is fairly small. The (approximate) intermediate correlation function is then obtained by averaging

$$C_{\tilde{n},\tilde{n}}(\mathbf{k},t) = \delta_{\mathbf{k},0} + \langle\tilde{n}_{\mathbf{k}}(0)\tilde{n}_{-\mathbf{k}}(0)\rangle\left[\frac{2}{5}e^{-D_T k^2|t|} + \frac{3}{10}e^{-\Gamma k^2|t|}\cos(c_0 k t)\right], \tag{38}$$

and the dynamical structure factor, hence, attains the following form:

$$S_{\tilde{n},\tilde{n}}(k,\omega) = \delta(\omega)\,\delta_{k,0} + \langle\tilde{n}_k(0)\tilde{n}_{-k}(0)\rangle\left[\frac{2}{5}\frac{2D_T k^2}{\omega^2+(D_T k^2)^2} + \frac{3}{10}\frac{2\Gamma k^2}{(\omega\pm c_0 k)^2+(\Gamma k^2)^2}\right]. \tag{39}$$

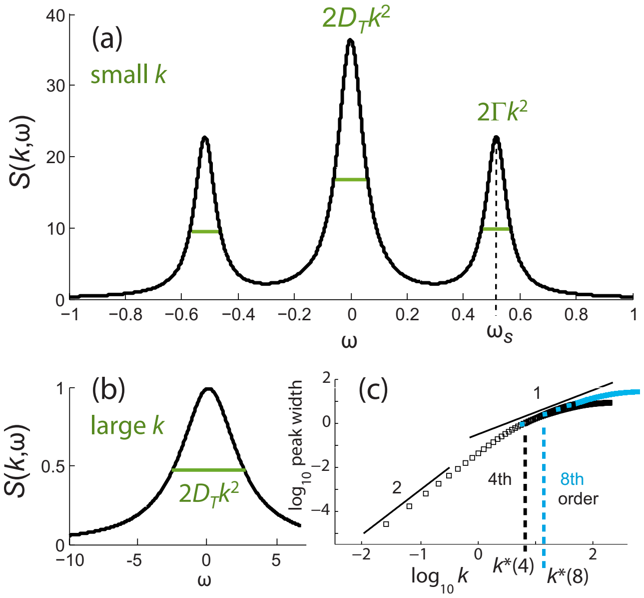

FIG. 5. (Color online) (a) Dynamic structure factor $S_{\tilde{n},\tilde{n}}(k,\omega)$ vs ω for a small $k=0.4$ and (b) large $k=100$. $\omega_s=c_0k$ denotes the hydrodnamics predicted sound mode of the spectrum, and the widths are related to the moments $A-Z$ (see Fig. 3). For small k, these are given by $D_T=\frac{2}{5}(X-Y)$ and $\Gamma=-(\frac{1}{2}A+\frac{1}{5}X+\frac{2}{15}Y)$, where A is the generalized longitudinal kinetic viscosity, Y the generalized thermal diffusion coefficient and X is a cross-coupling transport coefficient, relating heat flux to density gradients. (c) Width D_Tk^2 of the Rayleigh peak vs k (double logarithmic). At small k, $D_Tk^2 \propto k^2$ as all moments $A-Z$, except X, reach a finite value in this limit. The inflection point at $k=k^*(N)\gg 1$ (shown to be increasing with the order of expansion N) denotes the onset of departure from the ideal Maxwellian behavior, where the width of the peak starts to behave sublinearly in k, and is used to quantify the range of validity for results obtained at finite order.

Representative plots of $S(k,\omega)$ are shown in Figs. 5(a) and 5(b). For small k (hydrodynamic limit), the spectrum we obtain recovers the usual results of neutron (or light) scattering experiments and consists of three Lorentzian peaks. The one centered in $\omega=0$ is the Rayleigh peak, which corresponds to the diffusive thermal mode. The two side peaks centered in $\omega \pm c_0 k$ are the Brillouin peaks, and represent the two propagating sound waves. By increasing the wave vector, the structure of Eq. (39) is unchanged except that the generalized coefficients D_T and Γ need to be replaced by more complicate expressions, not given here. The net effect observed is that the Brioullin peaks move outward and tend to become not measurable , whereas the central Rayleigh peak decreases and broadens. Density fluctuations are, therefore, driven only by a diffusive thermal mode for large enough k. A deeper look about the behavior of the width at half maximum of the central Rayleigh peak with increasing wave vectors allows us to bridge the gap between the hydrodynamic continuumlike description and the free particle limit. The hydrodynamic regime is featured by a width increasing with the square wave vector, $\propto k^2$. On the contrary, in the free particle limit, the calculation of the dynamical structure factor $S_{\tilde{n},\tilde{n}}(k,\omega)$ reduces to the Fourier transform of the self part of the van Hove function $G_s(\mathbf{r},t)$ [24], which, upon writing $\mathbf{c}=\mathbf{r}/t$, is given by the Maxwellian distribution: $G_s(\mathbf{r},t) = \pi^{-3/2} v_T^{-3} t^{-3} \exp(-r^2/t^2)$. Hence, the width of the peak is expected to grow up linearly in k, for large k. Our results, see Fig. 5(c), predict a width which is truly quadratic for small enough k, reaches the regime of linear behavior and terminate, for some large k, with a sublinear dependence on k. The onset of the terminal regime at $k=k^*(N)$ marks the range of validity which can be accessed at a given finite order of expansion, N. Increasing N thus does not alter the overall picture we obtained at a moderate order of expansion, and more generally, results obtained with $N+1$ will not change those obtained with N below $k^*(N)$ [cf. Fig. 5(c)].

V. CONCLUSIONS

The main result of our paper is the characterization of the nonequilibrium distribution function, through the method of invariant manifolds, and the calculation of its moments [the functions $A-Z$, cf. Table II, have been related to material properties in Sec. IV B, to the scattering function in Eq. (37), and to expansion coefficients in Eq. (A7)], which constitute the building blocks of the generalized hydrodynamic equations. As we had previously shown in [14], the latter equations are stable and hyperbolic for arbitrary wave vectors. Moreover, we have proposed and applied a route to solve the eigenvalue problem associated with BE (6), by calculating the hydrodynamic modes, which we may regard either as decay rates of hydrodynamic fluctuations or as generalized eigenfrequencies of BE (3). The generalized transport coefficients have been numerically determined and settled into expressions recovering the Green-Kubo formulas. Finally, also by comparing with available experimental data and previous approaches, we discussed the range of validity of our approach, which turned out to be capable of extending the hydrodynamic scenario to length scales below the mean-free path. This offers perspectives toward a deeper comprehension of the transition between a “mesoscopic” particlelike description of matter and the “continuum” macroscopic one.

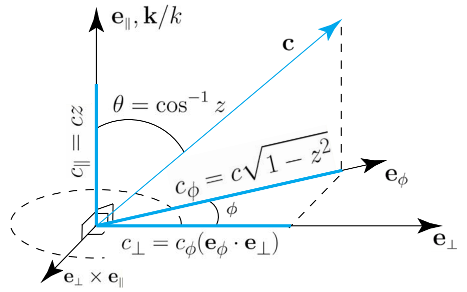

FIG. 6. (Color online) Schematic drawing introducing an orthonormal frame $\mathbf{e}_\parallel$, $\mathbf{e}_\perp$, and $\mathbf{e}_\perp \times \mathbf{e}_\parallel$ which is defined by the wave vector $\mathbf{k} \| \mathbf{e}_\parallel$ and the heat flux $\mathbf{q}$ (not shown), which lies in the $\mathbf{e}_\parallel - \mathbf{e}_\perp$ plane. Shown is the velocity vector $\mathbf{c}$ (A1) relative to this frame (characterized by length c, coordinate z, and angle ϕ) and its various components. The integration over $d^3c = c^2 dc dz d\phi$ is done in spherical coordinates with respect to the local orthonormal basis.

ACKNOWLEDGMENTS

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APPENDIX A: IMPLEMENTATION DETAILS

In order to calculate the averages occurring in Sec. III, like $\langle \mu(\mathbf{c}) \rangle_f$, we switch to spherical coordinates. For each (at present arbitrary) wave vector $\mathbf{k}=k\mathbf{e}_\parallel$, we choose the coordinate system in such a way that its (vertical) z-direction aligns with $\mathbf{e}_\parallel$ and that its x direction aligns with $\mathbf{e}_\perp$. The velocity vector we had been decomposed earlier as $\tilde{\mathbf{u}} = u^\parallel \mathbf{e}_\parallel + u^\perp \mathbf{e}_\perp$. We can then express $\mathbf{c}$, over which we are going to perform all integrals, in terms of its norm c, a vertical variable z and plane vector $\mathbf{e}_\phi$ (azimuthal angle $\mathbf{e}_\phi \cdot \mathbf{e}_\perp = \cos\phi$; the plane contains $\mathbf{e}_\perp$) for the present purpose as

$$\mathbf{c}/c = \sqrt{1-z^2}\,\mathbf{e}_\phi + z\mathbf{e}_\parallel, \tag{A1}$$

as shown in Fig. 6.

The local Maxwellian, linearized around global equilibrium, takes the form: $f^{\mathrm{LM}}/f^{\mathrm{GM}} = 1 + \varphi_0 = 1 + \mathbf{X}^0 \cdot \mathbf{x}$, where the four-dimensional $\mathbf{X}^0$, and the related vector $\boldsymbol{\xi}$, employing four-dimensional $\mathbf{x} = [\tilde{n}, u^\parallel, \tilde{T}, u^\perp]$, are given by

$$\mathbf{X}^0(\mathbf{c}) = \left[1, 2c_\parallel, \left(c^2 - \frac{3}{2}\right), 2c_\perp\right], \tag{A2}$$

$$\boldsymbol{\xi}(\mathbf{c}) = \left[1, c_\parallel, \frac{2}{3}\left(c^2 - \frac{3}{2}\right), c_\perp\right]. \tag{A3}$$

Here, we introduced, for later use, the abbreviations

$$c_\parallel \equiv \mathbf{c} \cdot \mathbf{e}_\parallel, \quad c_\perp \equiv \mathbf{c} \cdot \mathbf{e}_\perp, \quad c_\phi \equiv \mathbf{c} \cdot \mathbf{e}_\phi = \frac{c_\perp}{\mathbf{e}_\perp \cdot \mathbf{e}_\phi}, \tag{A4}$$

such that $i\mathbf{k} \cdot \mathbf{c} = ikc_\parallel$. We can then rewrite Eq. (A1) as $\mathbf{c} = c_\phi \mathbf{e}_\phi + c_\parallel \mathbf{e}_\parallel$ with $c_\parallel = cz$ and $c_\phi = c\sqrt{1-z^2}$. The latter two components, contrasted by $c_\perp$ (and $\mathbf{e}_\phi$), do not depend on the azimuthal angle. We further introduced yet unknown fields $\delta\mathbf{X}(\mathbf{c},\mathbf{k})$ which characterize the nonequilibrium part of the distribution function, $\delta\varphi = \delta f / f^{\mathrm{GM}}$. By analogy with the structure of the local Maxwellian, those are linear in terms of the hydrodynamic fields $\mathbf{x}$ themselves,

$$\delta\varphi = \delta\mathbf{X}\cdot\mathbf{x} = \delta X_1\tilde{n} + \delta X_2 u^{\parallel} + \delta X_3\tilde{T} + \delta X_4 u^{\perp}. \tag{A5}$$

The functions $\delta X_{1,2,3}$, which are associated to the longitudinal fields, inherit the full rotational symmetry of the corresponding Maxwellian components, $\delta X_{1,2,3} = \delta X_{1,2,3}(c,z)$, whereas δX_4 factorizes as $\delta X_4(c,z,\phi) = 2\delta Y_4(c,z)\Sigma_{m=1}^{\infty} y_m \cos m\phi$. In this context it is an important technical aspect of our derivation to work with a suitable orthogonal set of basis functions (irreducible tensors, cf. [30], for models beyond the Maxwell gas) to represent δf uniquely. The matrix $\mathbf{M}$ in Eq. (20) contains the nonhydrodynamic fields, the heat flux $\mathbf{q} \equiv \langle \mathbf{c}(c^2 - \frac{5}{2})\rangle_f$ and the stress tensor $\boldsymbol{\sigma} \equiv \langle \overline{\mathbf{cc}}\rangle_f$, where $\overline{\mathbf{s}}$ denotes the symmetric traceless part of a tensor $\mathbf{s}$ [14,15,27,28], $\overline{\mathbf{s}} = \frac{1}{2}(\mathbf{s}+\mathbf{s}^T) - \frac{1}{3}\mathrm{tr}(\mathbf{s})\mathbf{I}$. Using Eq. (16) and the above mentioned angular dependence of the $\delta\mathbf{X}$ functions (the only term in δX_4 playing a role in our calculations is the first-order term $\cos\phi$, with $y_1 = 1$, see [31]), constraints, such as the required decoupling between longitudinal and transversal dynamics of the hydrodynamic fields, are automatically dealt with correctly when performing integrals over ϕ. More explicitly [31], the stress tensor and heat flux uniquely decompose as follows:

$$\boldsymbol{\sigma} = \sigma^{\parallel}\frac{3}{2}\overline{\mathbf{e}_{\parallel}\mathbf{e}_{\parallel}} + \sigma^{\perp}2\overline{\mathbf{e}_{\parallel}\mathbf{e}_{\perp}}, \tag{A6a}$$

$$\mathbf{q} = q^{\parallel}\mathbf{e}_{\parallel} + q^{\perp}\mathbf{e}_{\perp}, \tag{A6b}$$

with the moments $\sigma^{\parallel} = (\sigma_1^{\parallel}, \sigma_2^{\parallel}, \sigma_3^{\parallel})\cdot(\tilde{n}, u^{\parallel}, \tilde{T})$ and $\sigma^{\perp} = \sigma_4 u^{\perp}$, and similarly for $\mathbf{q}$ (see row 2 of Table II). The prefactors arise from the identities $\overline{\mathbf{e}_{\parallel}\mathbf{e}_{\parallel}}:\overline{\mathbf{e}_{\parallel}\mathbf{e}_{\parallel}} = \frac{2}{3}$ and $\overline{\mathbf{e}_{\parallel}\mathbf{e}_{\perp}}:\overline{\mathbf{e}_{\parallel}\mathbf{e}_{\perp}} = \frac{1}{2}$. We note in passing that, while the stress tensor has, in general, three different eigenvalues, in the present symmetry adapted coordinate system it exhibits a vanishing first normal stress difference. Since the integral kernels of all moments in Eq. (A6) do not depend on the azimuthal angle, these are actually two-dimensional integrals over $c \in [0,\infty]$ and $z \in [-1,1]$, each weighted by a component of $2\pi c^2 f^{\mathrm{GM}}\delta\mathbf{X}$. Stress tensor and heat flux can yet be written in an alternative form which is defined by row 3 of Table II. As we will prove below, due to fundamental symmetry considerations, the hereby introduced generalized transport coefficients $A-Z$ are real valued. They can be expressed in terms of the moments of the distribution function, i.e., expansion coefficients $\mathbf{a}^{(r,l)}$, as follows:

$$A = -\frac{i a_2^{(0,2)}}{\sqrt{3}k}, \quad B = -\frac{a_1^{(0,2)}}{\sqrt{3}k^2},$$

$$C = -\frac{a_3^{(0,2)}}{\sqrt{3}k^2}, \quad X = -\frac{i\sqrt{5}a_1^{(1,1)}}{2k},$$

$$Y = -\frac{i\sqrt{5}a_3^{(1,1)}}{2k}, \quad Z = -\frac{\sqrt{5}a_2^{(1,1)}}{2k^2},$$

$$D = -\frac{i}{k}\sum_{r,l}^{N} a_4^{(r,l)}\langle f^{\mathrm{GM}} c_{\parallel} c_{\phi} | f^{\mathrm{GM}}\Psi_{r,l}\rangle,$$

$$U = -\frac{1}{k^2}\sum_{r,l}^{N} a_4^{(r,l)}\left\langle f^{\mathrm{GM}}\left(c^2 - \frac{5}{2}\right)c_{\phi}\middle| f^{\mathrm{GM}}\Psi_{r,l}\right\rangle. \tag{A7}$$

We proceed by using these functions $A-Z$ to split $\mathbf{M}$ into parts as $\mathbf{M} = \mathrm{Re}(\mathbf{M}) - i\,\mathrm{Im}(\mathbf{M})$,

$$\mathbf{M} = k^2\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & A & 0 & 0 \\ \frac{2}{3}X & 0 & \frac{2}{3}Y & 0 \\ 0 & 0 & 0 & D \end{pmatrix} - ik\begin{pmatrix} 0 & 1 & 0 & 0 \\ \tilde{B} & 0 & \tilde{C} & 0 \\ 0 & \tilde{Z} & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \tag{A8}$$

with abbreviations $\tilde{B} \equiv \frac{1}{2} - k^2 B$, $\tilde{C} \equiv \frac{1}{2} - k^2 C$, and $\tilde{Z} \equiv \frac{2}{3}(1 - k^2 Z)$. The checkerboard structure of matrix $\mathbf{M}$ (A8) is particularly useful for studying properties of the hydrodynamic Eq. (20), such as hyperbolicity and stability (see [14] and below), once the functions $A-Z$ are explicitly evaluated. We remind the reader that we use orthogonal basis functions (irreducible moments, cf. Table II) to solve Eq. (21). In order to show how the above functions enter the definition of the $\mathbf{M}$ matrix, we first notice that its elements are—*a priori*—complex valued. We wish, then, to make use of the fact that all integrals over z vanish for odd integrands. To this end we introduce abbreviations $\oplus$ ($\ominus$) for a real-valued quantity which is even (odd) with respect to the transformation $z \to -z$. One notices $\mathbf{X}^0 = (\oplus, \ominus, \oplus, \oplus)$, and we recall that $A-Z$ are integrals over either even or odd functions in z, times a component of $\delta\mathbf{X}$ (see Table II).

Let us prove the consistency of the specified symmetry of $\mathbf{M}$ and the invariance condition: Start by assuming $A-Z$ to be real-valued functions. Then $M_{\mu\nu} = \oplus$ if $\mu+\nu$ is even, and $M_{\mu\nu} = i\oplus$ otherwise. This implies $\delta X_1 = \oplus + i\ominus$, $\delta X_2 = \ominus + i\oplus$, $\delta X_3 = \oplus + i\ominus$, and $\delta X_4 = \oplus + i\ominus$, i.e., different symmetry properties for real and imaginary parts. With these "symmetry" expressions for $\mathbf{X}^0$, $\delta\mathbf{X}$, and $\mathbf{M}$ at hand, and by noticing that symmetry properties for $\delta\mathbf{X}$ take over to $\hat{L}(\delta\mathbf{X})$ because the $\psi_{r,l}$ are (i) symmetric (antisymmetric) in z for even (odd) l and (ii) eigenfunctions of $\hat{L}$, we can insert into the right-hand side of the equation, $\hat{L}(\delta\mathbf{X}) = (\mathbf{X}^0 + \delta\mathbf{X})\cdot(\mathbf{M} + i\ominus\mathbf{I})$, which is identical with invariance Eq. (21). There are only two cases to consider, because $\mathbf{M}$ has a checkerboard structure, i.e., only two types of columns: Columns $\mu=1$ and $\mu=3$: $\delta X_{\mu} = \oplus + i\ominus$ because $M_{1-3,4} = 0$; Columns $\mu \in \{2,4\}$: $\delta X_{\mu} = \oplus + i\ominus$ if $M_{\mu,1-3} = 0$ (which is the case for column 4) and $\ominus + i\oplus$ if $M_{\mu,4} = 0$ (which is the case for column 2). These observations complete the proof.

APPENDIX B: EXACT SOLUTION TO THE EIGENVALUE PROBLEM FOR A MAXWELL-MOLECULES COLLISION OPERATOR

Given the linearized Boltzmann collision operator,

$$L\delta f = \int\int d\Omega d\mathbf{c}_1 \sigma(\Omega,g) g f^{\mathrm{GM}}(c_1)[\delta\varphi(\mathbf{k},\mathbf{c}) + \delta\varphi(\mathbf{k},\mathbf{c}_1) - \delta\varphi(\mathbf{k},\mathbf{c}') - \delta\varphi(\mathbf{k},\mathbf{c}_1')] \tag{B1}$$

where $g=|v-v_1|$ is the absolute value of the relative velocity and $\sigma(\Omega,g)$ the differential collision cross section. For so-called Maxwell molecules the collision probability per unit time is independent of the relative velocity,

$$g\sigma(\Omega,g) = \sqrt{\frac{2K(M+m)}{Mm}} F(\vartheta), \tag{B2}$$

where m, M are the masses of the colliding particles and $F(\vartheta)$, with $\vartheta \in [0,\pi]$, is given in parametric form through the parameter $\phi \in [0,\pi]$,

$$\vartheta(\phi) = \pi - 2\sqrt{\cos(2\phi)} K(\sin\phi), \tag{B3}$$

$$F(\vartheta) = \frac{[2^{3/2}\sin\vartheta\,\sin(2\phi)]^{-1}\sqrt{\cos 2\phi}}{\cos^2(\phi)K(\sin\phi) - \cos(2\phi)E(\sin\phi)}, \tag{B4}$$

with the elliptic integrals $K(x)=\int_0^{\pi/2}(1-x^2\sin^2 y)^{-1/2}dy$, and $E(x)=\int_0^{\pi/2}(1-x^2\sin^2 y)^{1/2}dy$. Since the collision operator is spherically symmetric in the velocity space, the dependence of the eigenfunctions upon the direction of **c** is expected to be spherically harmonic. Indeed, the eigenvalue problem admits the following solutions:

$$L[\psi_{r,l}(c,z)] = \lambda_{r,l}\psi_{r,l}(c,z), \tag{B5}$$

$$\psi_{r,l}(c,z) = \sqrt{\frac{r!\left(l+\frac{1}{2}\right)\sqrt{\pi}}{\left(l+r+\frac{1}{2}\right)!}}\, c^l P_l(z) S^{(r)}_{l+1/2}(c^2), \tag{B6}$$

where $S^{(r)}_{l+1/2}(x)$ are Sonine polynomials, and $P_l(z)$ are Legendre polynomials which act on the azimuthal component of the peculiar velocity **c**. The Legendre and Sonine polynomials are each orthogonal sets,

$$\int_{-1}^{1} P_l(z)P_n(z)dz = \frac{2}{2l+1}\delta_{ln},$$

$$2\pi\int_0^\infty c^2 e^{-c^2} c^{2l} S^{(r)}_{l+1/2}(c^2) S^{(p)}_{l+1/2}(c^2) dc = \frac{\pi\left(l+\frac{1}{2}+r\right)!}{r!}\delta_{rp}.$$

Accordingly, the $\psi_{r,l}$ are normalized to unity with the weight factor $f_0(c)=\pi^{-3/2}\exp(-c^2)$ (as defined in Sec. II A),

$$\delta_{rr'}\delta_{ll'} = 2\pi^{-1/2}\int_{-1}^{1}\int_0^\infty c^2 e^{-c^2}\psi_{r,l}(c,z)\psi_{r',l'}(c,z)dcdz$$
$$\equiv \pi^{-3/2}\int e^{-c^2}\psi_{r,l}(\mathbf{c})\psi_{r',l'}(\mathbf{c})d^3c. \tag{B7}$$

The corresponding eigenvalues for Maxwell molecules are given by

$$\lambda_{r,l} = 2\pi\int \sin(\vartheta)F(\vartheta)T_{rl}(\vartheta)d\vartheta, \tag{B8}$$

$$T_{rl}(\vartheta) \equiv \cos^{2r+l}\left(\frac{\vartheta}{2}\right)P_l\left(\cos\frac{\vartheta}{2}\right) + \sin^{2r+l}\left(\frac{\vartheta}{2}\right)P_l\left(\sin\frac{\vartheta}{2}\right) - (1+\delta_{r0}\delta_{l0}), \tag{B9}$$

with $F(\vartheta)$ from Eq. (B4) with Eq. (B3). The collision operator is negative semidefinite, that is, all eigenvalues are negative except $\lambda_{0,0}$, $\lambda_{0,1}$, and $\lambda_{1,0}$ which are zero and correspond to the collision invariants. As it was shown in [9], there is no lower bound for the set of eigenvalues. Chang and Uhlenbeck's investigation [9] of the dispersion of sound in a Maxwell-molecules gas was based upon writing the deviation from the global equilibrium as: $(\varphi_0+\delta\varphi) = \Sigma_{\{r,l\}=0}^{\infty} a_{r,l}\Psi_{r,l}(\mathbf{c})$ so that the eigenvalue equation reduces to an algebraic equation for the coefficients $a_{r,l}$,

$$\omega a_{r,l} = -i\mathbf{k}\cdot\sum_{\{r',l'\}=0}^{\infty}\mathbf{\Omega}_{r,l,r',l'}a_{r',l'} + \lambda_{r,l}a_{r,l}, \tag{B10}$$

$$\mathbf{\Omega}_{r,l,r',l'} \equiv \langle f^{\mathrm{GM}}\Psi_{r,l}|\mathbf{c}|f^{\mathrm{GM}}\Psi_{r',l'}\rangle. \tag{B11}$$

The hydrodynamic modes for the Maxwell-molecules gas are found by setting to zero the determinant of the above system of linear equations. Within this approach, from the knowledge of the spectrum of $\hat{L}$, it is possible to solve eigenvalue problem (3) for an arbitrary number of modes, just by tuning the number of eigenfunctions taken into account in the *ansatz* for the nonequilibrium distribution function. The peculiarity of the Maxwell-molecules gas lies in the fact that at any stage of approximation the modes recover and extend those corresponding to lower order approximations. This method produces results which are found to be in agreement with the CE expansion.

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[30] Adopting the notation in [27,28] the distribution function is written as a sum over n-fold contracted products of nth rank tensors, $f(\mathbf{c})=f_0(c)\Sigma_{k,n=0}^{\infty}\langle\phi_k^n\rangle\odot^n\phi_k^n(\mathbf{c})$ with $\langle\phi_k^n\rangle=\int f(\mathbf{c})\phi_k^n d^3c$ and base functions $\phi_k^n(\mathbf{c})=l_k^n L_k^{n+1/2}(c^2)\overline{\otimes^n\mathbf{c}}$, where L_k^n are the associated Laguerre (kth order) polynomials [29], $\otimes^n\mathbf{c}$ denotes the n-fold tensor product, and $\overline{\mathbf{a}}$ denotes the irreducible part of a tensor $\mathbf{a}$. For the explicit construction of nth rank irreducible tensors $\overline{\otimes^n\mathbf{c}}$ see page 160 of [28]. The normalization coefficients evaluate as $l_k^n=(\sqrt{\pi}k!(1+2n)!!/[2(k+n+1/2)!n!])^{1/2}$. The base function $\phi_k^n(\mathbf{c})$ is thus a $(2k+n)$th order polynomial in c. The lowest-order base functions read $\phi_0^0=1$, $\phi_0^1=\sqrt{2}\mathbf{c}$, $\phi_1^0=\sqrt{2/3}(3/2-c^2)$, $\phi_1^1=(2/\sqrt{5})(5/2-c^2)\mathbf{c}$, and $\phi_0^2=\sqrt{2}\overline{\mathbf{cc}}$. Density, velocity, temperature, heat flux, and stress tensor are related to the moments as follows: $\tilde{n}=\langle\phi_0^0\rangle$, $\tilde{\mathbf{u}}=\langle\phi_0^1\rangle/\sqrt{2}$, $\tilde{T}=\langle\phi_1^0\rangle\sqrt{3/2}$, $\mathbf{q}=\langle\phi_1^1\rangle$, and $\boldsymbol{\sigma}=\langle\phi_0^2\rangle/\sqrt{2}$. The distribution function is then split into (orthogonal) parts as $f(\mathbf{c})=f^{\mathrm{LM}}(\mathbf{c})+\delta f^{\mathrm{Grad}}(\mathbf{c})+\delta f^{\mathrm{rest}}(\mathbf{c})$ with $f^{\mathrm{LM}}(\mathbf{c})\equiv f_0(c)(\langle\phi_0^0\rangle\phi_0^0+\langle\phi_0^1\rangle\phi_0^1+\langle\phi_1^0\rangle\phi_1^0)$ and $\delta f^{\mathrm{Grad}}(\mathbf{c})\equiv f_0(c)(\langle\phi_1^1\rangle\phi_1^1+\langle\phi_0^2\rangle\phi_0^2)$, while the sum in $\delta f^{\mathrm{rest}}(\mathbf{c})=\Sigma_{k,n}\langle\phi_k^n\rangle\odot^n\phi_k^n(\mathbf{c})$ extends over the remaining (k,n)–pairs. Density, velocity, and temperature are therefore determined by f^{LM} alone, and δf automatically obeys constrains such as orthogonality requirement $\int\delta f(\mathbf{c})\phi_1^0 d^3c=0$ and also $\int\delta f(\mathbf{c})\xi(\mathbf{c})d^3c=0$, as mentioned in the text part. These conditions become redundant ones calculations are performed using the particular basis ϕ_k^n. For Maxwell molecules, the dependence on the polar angle ϕ can be included by replacing $P_l(z)$ by $e^{im\phi}P_l^m(z)$ involving the associated Legendre polynomials [29], and the eigenvalues are independent of m. Then, these base function reduce to the eigenfunctions $\Psi_{r,l}(c,z)$ [Eq. (B6)] of the Maxwell gas.

[31] The integrals listed in Table II obey the following decoupling rules,

$$\int\left(c_\parallel^2-\frac{1}{3}c^2\right)\delta X_n d^3c \propto 1-\delta_{n,4},$$

$$\int c_\parallel c_\perp \delta X_n d^3c \propto \delta_{n,4},$$

$$\int c_\parallel\left(c^2-\frac{5}{2}\right)\delta X_n d^3c \propto 1-\delta_{n,4},$$

$$\int c_\perp\left(c^2-\frac{5}{2}\right)\delta X_n d^3c \propto \delta_{n,4}.$$