METHODS OF NONLINEAR KINETICS

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Contents

Summary

Nonequilibrium statistical physics studies the fast-slow decomposition for large systems. It is a collection of ideas and methods for the extraction of slow invariant manifolds. Most of these methods were developed initially for the Boltzmann equation. In this article, the main methods of nonlinear kinetics are described and illustrated on

this basic equation. General properties of the Boltzmann equation are presented. The Enskog, Vlasov, and Smoluchovski equations are outlined.

1. The Boltzmann Equation

1.1. The Equation

The **Boltzmann equation** is the first and most famous nonlinear kinetic equation introduced by the great Austrian physicist Ludwig Boltzmann in 1872. This equation describes the dynamics of a moderately rarefied gas, taking into account for the two processes, the free flight of the particles, and their collisions. In its original version, the Boltzmann equation has been formulated for particles represented by hard spheres. The physical condition of rarefaction means that only pair collisions are taken into account, a mathematical specification of which is given by the **Grad-Boltzmann limit:** if N is the number of particles, and σ is the diameter of the hard sphere, then the Boltzmann equation is expected to hold when N tends to infinity, σ tends to zero, $N\sigma^3$ (the volume occupied by the particles) tends to zero, while $N\sigma^2$ (the total collision cross section) remains constant. The microscopic state of the gas at time t is described by the one-body distribution function $P(\mathbf{x},\mathbf{v},t)$, where vector $\mathbf{x}$ is the position of the center of the particle, and vector $\mathbf{v}$ is the velocity of the particle. The distribution function P is the probability density of finding the particle at time t within the infinitesimal phase space volume $d\mathbf{x}\,d\mathbf{v}$ centered at the phase point $(\mathbf{x},\mathbf{v})$. The collision mechanism of two hard spheres is presented by a relation between the velocities of the particles before [$\mathbf{v}$ and $\mathbf{w}$] and after [$\mathbf{v}'$ and $\mathbf{w}'$] their impact:

$$\mathbf{v}' = \mathbf{v} - \mathbf{n}(\mathbf{n},\mathbf{v}-\mathbf{w}\},$$

$$\mathbf{w}' = \mathbf{w} + \mathbf{n}(\mathbf{n},\mathbf{v}-\mathbf{w}\},$$

where $\mathbf{n}$ is the unit vector along $\mathbf{v}-\mathbf{v}'$. Transformation of the velocities conserves the total momentum of the pair of colliding particles $(\mathbf{v}'+\mathbf{w}'=\mathbf{v}+\mathbf{w})$, and the total kinetic energy $\left(\mathbf{v}'^2+\mathbf{w}'^2=\mathbf{v}^2+\mathbf{w}^2\right)$. The Boltzmann equation reads:

$$\begin{aligned}&\frac{\partial P}{\partial t}+\left(\mathbf{v},\frac{\partial P}{\partial \mathbf{x}}\right)\\&=N\sigma^2\int_{R^3}\int_{B^-}\left(P(\mathbf{x},\mathbf{v}',t)P(\mathbf{x},\mathbf{w}',t)-P(\mathbf{x},\mathbf{v},t)P(\mathbf{x},\mathbf{w},t)\right)\left|\left(\mathbf{w}-\mathbf{v},\mathbf{n}\right)\right|\,d\mathbf{w}\,d\mathbf{n},\end{aligned} \tag{1}$$

where integration in $\mathbf{w}$ is carried over the space R^3, while integration in $\mathbf{n}$ goes over a hemisphere $B^-=\{\mathbf{n}|(\mathbf{w}-\mathbf{v},\mathbf{n})<0\}$. This hemisphere corresponds to the particles entering the collision. The nonlinear integral operator on the right of Eq. (1) is nonlocal in the velocity variable and local in space. The Boltzmann equation for arbitrary hard-core interaction is a generalization of the Boltzmann equation for hard spheres under the proviso that the true infinite-range interaction potential between the particles is cut-off at some distance. This generalization amounts to a replacement,

$$\sigma^2 \left|\left(\mathbf{w}-\mathbf{v},\mathbf{n}\right)\right| d\mathbf{n} \to B\left(\theta,\left|\mathbf{w}-\mathbf{v}\right|\right) d\theta\, d\varepsilon\,, \tag{2}$$

where function B is determined by the interaction potential, and vector $\mathbf{n}$ is identified with two angles, θ and ε. In particular, for potentials proportional to the nth inverse power of the distance, function B reads,

$$B\left(\theta,\left|\mathbf{v}-\mathbf{w}\right|\right) = \beta(\theta)\left|\mathbf{v}-\mathbf{w}\right|^{(n-5)/(n-1)}. \tag{3}$$

In the special case $n = 5$, function B is independent of the magnitude of the relative velocity (Maxwell molecules). Maxwell molecules occupy a distinct place in the theory of the Boltzmann equation, they provide exact results. Three most important findings for the Maxwell molecules are mentioned in the following:

1. The exact spectrum of the linearized Boltzmann collision integral, found by Truesdell and Muncaster.
2. Exact transport coefficients found by Maxwell even before the Boltzmann equation was formulated.
3. Exact solutions to the space-free model version of the nonlinear Boltzmann equation. Pivotal results in this domain belong to Galkin who has found the general solution to the system of moment equations in the form of a series expansion, to Bobylev, Krook and Wu who have found an exact solution of a particular elegant closed form, and to Bobylev who has demonstrated the complete integrability of this dynamic system.

It is customary to write the Boltzmann equation using another normalization of the distribution function, $f\left(\mathbf{x},\mathbf{v},t\right) d\mathbf{x}\, d\mathbf{v}$, taken in such a way that function f is compliant with the definition of the hydrodynamic fields: **the mass density** ρ, **the momentum density** $\rho\mathbf{u}$, and **the energy density** ε:

$$\begin{aligned}
&\int f\left(\mathbf{x},\mathbf{v},t\right) m\, d\mathbf{v} = \rho\left(\mathbf{x},t\right),\\
&\int f\left(\mathbf{x},\mathbf{v},t\right) \mathbf{v}m\, d\mathbf{v} = \rho\mathbf{u}\left(\mathbf{x},t\right),\\
&\int f\left(\mathbf{x},\mathbf{v},t\right) m\frac{v^2}{2} d\mathbf{v} = \varepsilon\left(\mathbf{x},t\right).
\end{aligned} \tag{4}$$

Here m is the particle's mass.

The Boltzmann equation for the distribution function f is,

$$\frac{\partial f}{\partial t} + \left(\mathbf{v},\frac{\partial}{\partial \mathbf{x}} f\right) = Q\left(f,f\right), \tag{5}$$

where the nonlinear integral operator on the right is the Boltzmann **collision integral**,

$$Q = \int_{R^3} \int_{B^-} \left(f(\mathbf{v}') f(\mathbf{w}') - f(\mathbf{v}) f(\mathbf{w}) \right) B(\theta, \mathbf{v}) \, d\mathbf{w} \, d\theta \, d\varepsilon . \tag{6}$$

Finally, we mention the following form of the Boltzmann collision integral (sometimes referred to as the **scattering** or the **quasi-chemical** representation)

$$Q = \int W\left(\mathbf{v}, \mathbf{w} \middle| \mathbf{v}', \mathbf{w}'\right) \left[f(\mathbf{v}') f(\mathbf{w}') - f(\mathbf{v}) f(\mathbf{w}) \right] d\mathbf{v} \, d\mathbf{w}' d\mathbf{v}' , \tag{7}$$

where W is a generalized function which is called the probability density of the elementary event

$$W = w\left(\mathbf{v}, \mathbf{w} \middle| \mathbf{v}', \mathbf{w}'\right) \delta\left(\mathbf{v} + \mathbf{w} - \mathbf{v}' - \mathbf{w}'\right) \delta\left(v^2 + w^2 - v'^2 - w'^2\right) . \tag{8}$$

1.2. The Basic Properties of the Boltzmann Equation

Generalized function W has the following symmetries:

$$W\left(\mathbf{v}', \mathbf{w}' \middle| \mathbf{v}, \mathbf{w}\right) \equiv W\left(\mathbf{w}', \mathbf{v}' \middle| \mathbf{v}, \mathbf{w}\right) \equiv W\left(\mathbf{v}', \mathbf{w}' \middle| \mathbf{w}, \mathbf{v}\right) \equiv W\left(\mathbf{v}, \mathbf{w} \middle| \mathbf{v}', \mathbf{w}'\right) . \tag{9}$$

The first two identities reflect the symmetry of the collision process with respect to labeling the particles whereas the last identity is the celebrated **detailed balance** condition which is underpinned by the time-reversal symmetry of the microscopic (Newton's) equations of motion. The Boltzmann equation has the following basic properties.

1. **Additive invariants of collision operator**:

$$\int Q(f, f) \left\{ 1, \mathbf{v}, v^2 \right\} d\mathbf{v} = 0 \tag{10}$$

for any function f, assuming integrals exist. Equation (10) reflects the fact that the number of particles, the three components of particle's momentum, and the particle's energy are conserved in the collision. Conservation laws (10) imply that the local hydrodynamic fields (4) can change in time only due to redistribution in space.

2. Zero point of the integral ($Q = 0$) satisfies the equation (which is also called the **detailed balance**): for almost all velocities,

$$f(\mathbf{v}', \mathbf{x}, t) \, f(\mathbf{w}', \mathbf{x}, t) = f(\mathbf{v}, \mathbf{x}, t) \, f(\mathbf{w}, \mathbf{x}, t) .$$

3. Boltzmann's **local entropy production inequality**:

$$\sigma(\mathbf{x}, t) = -k_{\mathrm{B}} \int Q(f, f) \ln f \, d\mathbf{v} \geq 0 \tag{11}$$

for any function f, assuming integrals exist. **Boltzmann's constant** ($k_{\mathrm{B}} \approx 1.38065 \cdot 10^{-23}\,\mathrm{JK}^{-1}$) in this expression is useful for a recalculation of the energy units into the absolute temperature units. Moreover, equality sign is applicable if $\ln f$ is a linear combination of the additive invariants of collision. Distribution functions f whose logarithm is a linear combination of additive collision invariants, with coefficients dependent on $\mathbf{x}$, are called **local Maxwell distribution functions** f_{LM},

$$f_{\mathrm{LM}} = \rho m^{-1} \left(\frac{2\pi k_{\mathrm{B}} T}{m} \right)^{-3/2} \exp\left\{ -\frac{m(\mathbf{v}-\mathbf{u})^2}{2k_{\mathrm{B}}T} \right\}. \tag{12}$$

Local Maxwellians are parameterized by values of five scalar functions, ρ, $\mathbf{u}$ and T. This parameterization is consistent with the definitions of the hydrodynamic fields (4) $\int f_{\mathrm{LM}} \left\{ m, m\mathbf{v}, mv^2/2 \right\} = \left\{ \rho, \rho\mathbf{u}, \varepsilon \right\}$ provided the relation between the energy and the kinetic temperature T holds, $\varepsilon = 3\rho/2mk_{\mathrm{B}}T$.

4. Boltzmann's ***H*** **theorem**: the function

$$S[f] = -k_{\mathrm{B}} \int f \ln f \, d\mathbf{v} \tag{13}$$

is called the **entropy density**. The **local** ***H*** **theorem** for distribution functions independent of space states that the rate of the entropy density increase is equal to the nonnegative entropy production,

$$\frac{dS}{dt} = \sigma \geq 0. \tag{14}$$

Thus, if space dependence is not of concern, the Boltzmann equation describes relaxation to the unique global Maxwellian (whose parameters are fixed by initial conditions), and the entropy density grows monotonically along the solutions. Mathematical specifications of this property have been initialized by Carleman, and many estimations of the entropy growth were obtained over the 1970s-1990s. In the case of space-dependent distribution functions, the local entropy density obeys the **entropy balance equation**:

$$\frac{\partial S(\mathbf{x},t)}{\partial t} + \left(\frac{\partial}{\partial \mathbf{x}}, \mathbf{J}_{\mathbf{S}}(\mathbf{x},t) \right) = \sigma(\mathbf{x},t) \geq 0 \tag{15}$$

where $\mathbf{J}_{\mathbf{S}}$ is the entropy flux, $\mathbf{J}_{\mathbf{S}}(\mathbf{x},t) = -k_{\mathrm{B}} \int \ln f(\mathbf{x},t) \mathbf{v} f(\mathbf{x},t) \, d\mathbf{v}$. For suitable boundary conditions, such as, specularly reflecting or at the infinity, the entropy flux gives no contribution to the equation for the **total entropy**, $S_{\mathrm{tot}} = \int S(\mathbf{x},t) \, d\mathbf{x}$ and its rate of changes is then equal to the total entropy production $\sigma_{\mathrm{tot}} = \int \sigma(\mathbf{x},t) \, d\mathbf{x}$ (the

global *H* theorem). For more general boundary conditions which maintain the entropy influx the global *H* theorem needs to be modified. A detailed discussion of this question is given by Cercignani.

The local Maxwellian is also specified as the maximizer of the Boltzmann entropy function (13), subject to fixed hydrodynamic constraints (4). For this reason, the local Maxwellian is also termed the local equilibrium distribution function.

1.3. Linearized Collision Integral

Linearization of the Boltzmann integral around the local equilibrium results in the linear integral operator,

$$
\begin{aligned}
&Lh(\mathbf{v}) \\
&= \int W(\mathbf{v},\mathbf{w}|\mathbf{v}',\mathbf{w}')\, f_{LM}(\mathbf{v})\, f(\mathbf{w}) \\
&\left[\frac{h(\mathbf{v}')}{f_{\mathrm{LM}}(\mathbf{v}')} + \frac{h(\mathbf{w}')}{f_{\mathrm{LM}}(\mathbf{w}')} - \frac{h(\mathbf{v})}{f_{\mathrm{LM}}(\mathbf{v})} - \frac{h(\mathbf{w})}{f_{\mathrm{LM}}(\mathbf{w})}\right] d\mathbf{w}'\,d\mathbf{v}'\,d\mathbf{w}.
\end{aligned}
$$

Linearized collision integral is symmetric with respect to scalar product defined by the second derivative of the entropy functional,

$$\int f_{\mathrm{LM}}^{-1}(\mathbf{v})\, g(\mathbf{v})\, Lh(\mathbf{v})\, d\mathbf{v} = \int f_{\mathrm{LM}}^{-1}(\mathbf{v})\, h(\mathbf{v})\, Lg(\mathbf{v})\, d\mathbf{v},$$

it is nonpositively definite

$$\int f_{\mathrm{LM}}^{-1}(\mathbf{v})\, h(\mathbf{v})\, Lh(\mathbf{v})\, d\mathbf{v} \le 0,$$

where equality sign takes place if the function hf_{LM}^{-1} is a linear combination of collision invariants, which characterize the null-space of the operator L. Spectrum of the linearized collision integral is well studied in the case of small angle cut-off.

2. Phenomenology and Quasi-chemical Representation of the Boltzmann Equation

Boltzmann's original derivation of his collision integral was based on a phenomenological "bookkeeping" of the **gain** and of the **loss** of probability density in the collision process. This derivation postulates that the rate of gain G equals

$$G = \int W^{+}(\mathbf{v},\mathbf{w}|\mathbf{v}',\mathbf{w}')\, f(\mathbf{v}')\, f(\mathbf{w}')\, d\mathbf{v}'d\mathbf{w}'d\mathbf{w}$$

while the rate of loss is

$$L = \int W^{-}(\mathbf{v},\mathbf{w}|\mathbf{v}',\mathbf{w}')\, f(\mathbf{v})\, f(\mathbf{w})\, d\mathbf{v}'d\mathbf{w}'d\mathbf{w}.$$

The form of the gain and of the loss, containing products of one-body distribution functions in place of the two-body distribution, constitutes the famous Stosszahlansatz (the collision frequency formula). The Boltzmann collision integral follows now as ($G - L$), subject to the detailed balance for the rates of individual collisions,
$W^{+}\left(\mathbf{v},\mathbf{w}\middle|\mathbf{v}',\mathbf{w}'\right)=W^{-}\left(\mathbf{v}',\mathbf{w}'\middle|\mathbf{v},\mathbf{w}\right)$.

This representation for interactions different from hard spheres requires also the cut-off of functions β in (3) at small angles. The gain-loss form of the collision integral makes it evident that the detailed balance for the rates of individual collisions is sufficient to prove the local H theorem. A weaker condition which is also sufficient to establish the H theorem was first derived by Stueckelberg (so-called **semi-detailed balance**), and later generalized **to inequalities of concordance**:

$$\int d\mathbf{v}'\int d\mathbf{w}'\left(W^{+}\left(\mathbf{v},\mathbf{w}\middle|\mathbf{v}',\mathbf{w}'\right)-W^{-}\left(\mathbf{v},\mathbf{w}\middle|\mathbf{v}',\mathbf{w}'\right)\right)\geq 0,$$

$$\int d\mathbf{v}\int d\mathbf{w}\left(W^{+}\left(\mathbf{v},\mathbf{w}\middle|\mathbf{v}',\mathbf{w}'\right)-W^{-}\left(\mathbf{v},\mathbf{w}\middle|\mathbf{v}',\mathbf{w}'\right)\right)\leq 0.$$

The semi-detailed balance follows from these expressions if the inequality signs are replaced by equalities.

The pattern of Boltzmann's phenomenological approach is often used in order to construct nonlinear kinetic models. In particular, **nonlinear equations of chemical kinetics** are based on this idea: if n chemical species A_i participate in a complex chemical reaction,

$$\sum_i \alpha_{si}A_i \leftrightarrow \sum_i \beta_{si}A_i,$$

where α_{si} and β_{si} are nonnegative integers (stoichiometric coefficients) then equations of chemical kinetics for the concentrations of species c_j are written

$$\frac{dc_i}{dt}=\sum_{s=1}^{n}(\beta_{si}-\alpha_{si})\left[\varphi_s^{+}\exp\left(\sum_{j=1}^{n}\frac{\partial G}{\partial c_j}\alpha_{sj}\right)-\varphi_s^{-}\exp\left(\sum_{j=1}^{n}\frac{\partial G}{\partial c_j}\beta_{sj}\right)\right]$$

Functions φ_s^{+} and φ_s^{-} are interpreted as constants of the direct and of the inverse reactions, while the function G is an analog of the Boltzmann's H-function.

Modern derivation of the Boltzmann equation, initialized by the seminal work of N.N. Bogoliubov, seeks a replacement condition, and which would be more closely related to many-particle dynamics. Such conditions are applied to the N-particle Liouville equation should factorize in the remote past, as well as in the remote infinity (the hypothesis of weakening of correlations). Different conditions have been formulated by D.N. Zubarev, J. Lewis and others. The advantage of these formulations is the possibility to systematically find corrections not included in the collision frequency formula.

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