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Kinetic theory and hydrodynamics of dense, reacting fluids far from equilibrium

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The kinetic theory for a fluid of hard spheres which undergo endothermic and/or exothermic reactions with mass transfer is developed. The exact balance equations for concentration, density, velocity, and temperature are derived. The Enskog approximation is discussed and used as the basis for the derivation, via the Chapman–Enskog procedure, of the Navier–Stokes reaction equations under various assumptions about the speed of the chemical reactions. It is shown that the phenomenological description consisting of a reaction–diffusion equation with a convective coupling to the Navier–Stokes equations is of limited applicability. [DOI: 10.1063/1.1648012]

I. INTRODUCTION

An understanding of chemically reactive flows is necessary in a wide range of disciplines including astrophysics, plasma physics, and applied chemistry. Recently, applications in aerospace engineering have led to a number of studies aimed at deriving phenomenological equations, the Navier–Stokes equations coupled to reactions, from the Boltzmann equation for increasingly complex systems including internal degrees of freedom and three-body interactions.[1,2] However, these investigations do not exhaust the range of interesting applications. A number of important applications arise in the physiochemistry of cavitating bubbles.[3] A side from obvious examples such as the study of flames and explosions, a recent area of interest is sonochemistry in which ultrasound is used to induce conditions of extreme temperature and pressure inside bubbles with the effect of dramatically increasing the rates of chemical reactions.[4] Closely related is the phenomena of somnoluminescence—in which a fluid irradiated with ultrasound emits light—which is believed to be caused by pressure waves acting on small bubbles of gas in the fluid (see, e.g., Ref. 5). The bubbles are subjected to such rapid compression that shock waves may develop and the concentrated energy drives many chemical reactions particularly when the shocks reach the center of the bubbles giving rise to high temperatures and densities. In fact, it has been suggested[6] that some (endothermic) reactions may play an important role in limiting the temperatures reached in the center of the bubble. It is therefore of interest for these applications, as well as some of the others mentioned above, to understand the phenomenological equations governing a reacting gas under extreme conditions and far from equilibrium. The Boltzmann equation cannot be considered an adequate basis for such a study due to the fact that it is only applicable at asymptotically low densities. In fact, the only simple fluid that is amenable to analytic investigation at finite densities is one composed of hard spheres. The purpose of this paper is therefore to review the kinetic theory of reacting hard-sphere systems and to use this as a basis for a hydrodynamic description of a reacting fluid far from equilibrium. In particular, the kinetic theory will be used to derive the exact balance equations describing the local concentration, density, velocity, and temperature fields from which the extension of the Navier–Stokes equations to include reactions is developed based on the Chapman–Enskog procedure applied to the Enskog approximation to the kinetic theory. A primary result will be to show that the usual phenomenological description consisting of the Navier–Stokes equations coupled to a reaction–diffusion–advection equation is only applicable if the chemical reactions take place on a time scale which is comparable to the dissipative time scale λk^2, where λ is a transport coefficient and k a typical wave vector. If the reactions are slower, then all hydrodynamic relaxation takes place before the chemistry gets started and chemistry and hydrodynamics are effectively decoupled. Faster reactions, with time scale comparable to ck, where c is the sound velocity, leads to additional couplings of the reactions to the hydrodynamic fields. Even faster reactions lead to the chemistry taking place so fast that hydrodynamics is irrelevant.

The hard-sphere interaction model has proven remarkably useful as models of single- and multiple-component simple fluids since, in many respects, the phenomenology of the hard-sphere systems and atoms interacting via more realistic pair potentials is qualitatively identical. For example, hard-sphere systems exhibit the full range of transport coefficients found in all simple fluids[7] and possess a freezing transition,[8] and the structure of hard-sphere fluids in equilibrium is not much different from that of any other fluid.[9] On the theoretical side, the equation of state of hard-sphere flu-

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ids is easily modeled.[9] Kinetic theory is simplified by the fact that only binary collisions are important and it is possible to formulate an extension of the Boltzmann equation—the so-called revised Enskog theory[10] (RET)—which not only describes the transport properties of multiple-component hard-sphere fluids at finite densities, but which also describes transport in the solid state.[11] More recently, inelastic hard spheres have been used as a model for driven granular fluids with similar success. The hard-sphere interaction is therefore an ideal model for understanding the extreme conditions occurring in sonochemical experiments.

The kinetic theory of chemically reacting hard spheres has in fact been discussed in the literature.[12–15] The principal aim of these studies was to investigate contributions to the reaction rates coming from dense fluid effects (e.g., ring kinetic theory leading to mode-coupling models) at equilibrium. In these studies, the atoms carry labels indicating their species (sometimes called their color) and all intrinsic properties like the atomic radius and mass is specific to the species. When the atoms collide, there is a probability that a reaction takes place in which the species labels and, hence, atomic properties change. The probability typically depends on the rest-frame energy of the colliding atoms: if the rest frame energy is greater than some specified activation energy, the reaction can take place with a probability that is, in general, a function of the relative energy. Energy may be gained or lost (exothermic or endothermic reactions), but the sizes of the atoms are generally invariant since, were they to also vary, a collision could result in one of the atoms overlapping a third atom. (Technically, there is no reason that atoms could not get smaller and most results would apply to such a model.) Besides being restricted to a chemistry consisting of color labels (and so excluding, e.g., the exchange of mass upon collision), a common assumption in earlier work is that the chemical reactions are slow compared to other transport processes. Since the rate of chemical reactions is generally determined by the ratio of the temperature to the activation energies and the difference in the concentrations, this implies that the results are only applicable near equilibrium or for low temperatures. One of the primary goals of the present work is to indicate how the phenomenological description (Navier–Stokes equations coupled to a set of advective–reaction–diffusion equations) must be modified to account for large deviations from equilibrium.

The organization of this paper is as follows: Section II develops the formal statistical description of the system. The discussion of possible collision rules is followed by the development of the Liouville equation and the exact balance laws describing the evolution of the local mass, energy, momentum, and partial densities. The Enskog approximation is also introduced. Section III discusses the Chapman–Enskog solution of the Enskog equation and, particularly, the difference between the assumptions of fast and slow chemical reactions. It is shown that, if the chemical reactions are sufficiently slow, the fluid may be described by the Navier–Stokes equations for the total mass, energy, and momentum densities and a reaction–diffusion–convection equation for the concentrations with the only coupling between the two being the convective term occurring in the latter (i.e., the "usual" description). However, under less restrictive assumptions, the reactions are shown to depend in a much more complicated way on the hydrodynamic fields. The paper concludes with a discussion of the physical meaning of the different assumptions.

II. STATISTICAL MECHANICS OF REACTING HARD SPHERES

Consider a system of N hard spheres of various species confined to a volume V with positions $\{\vec{q}_i\}_{i=1}^N$ and momenta $\{\vec{p}_i\}_{i=1}^N$. The combination of the position and the momentum of a given atom, i.e., its phase, will be denoted below by the letter x. Each atom will also be described by a set of discrete labels l_i for the ith atom, which fix its "chemical" properties (mass, hard-sphere diameter, and reaction parameters). When two atoms collide, both the mechanical variables and the species labels of the atoms change. The dynamical variables are altered according to some deterministic collision rule so that for collisions between the ith and jth atoms,

$$\begin{aligned} x_i &\to x_i' = \hat{b}_{l_i l_j}^{l_i' l_j'} x_i, \\ x_j &\to x_j' = \hat{b}_{l_i l_j}^{l_i' l_j'} x_j, \end{aligned} \tag{1}$$

where the collision operator $\hat{b}_{l_i l_j}^{l_i' l_j'}$ describes a collision involving the reaction $l_i + l_j \to l_i' + l_j'$ (i.e., the ith atom changes from species l_i to l_i', etc.) and, clearly, one expects that $\hat{b}_{l_i l_j}^{l_i' l_j'} = \hat{b}_{l_j l_i}^{l_j' l_i'}$. Because the species change instantaneously and randomly upon collision, the species labels must be viewed as discrete random variables. Attention here will be restricted to the model in which the probability of making a particular transition is given by some function of the relative phases of the two colliding atoms $K_{l_i l_j}^{l_i' l_j'}(x_{ij})$ where the notation indicates that this probability depends on the relative velocity $\vec{v}_{ij} = \vec{v}_i - \vec{v}_j$ and position $\vec{q}_{ij}$ [e.g., through the combination $(\vec{v}_{ij} \cdot \vec{q}_{ij})^2$].

A. Collision rules

The coupling between chemistry and hydrodynamics can be captured simply by considering atoms that carry a label (e.g., color) that can change during collisions. Allowing for the nonconservation of energy gives a relatively broad model that includes endothermic and exothermic reactions. However, in the interest of generality, the problem of modeling reactions that not only violate energy conservation, but that also allow for the exchange, or even loss, of mass will be considered.

The modeling of the collision rules in the case that mass is either exchanged or lost upon collision is somewhat problematic. To understand why, consider the usual arguments leading to specular collision rules in the case that mass is invariant. Defining the total and relative momenta, respectively, as

$$\begin{aligned} \vec{P} &= \vec{p}_1 + \vec{p}_2, \\ \vec{p} &= \vec{p}_1 - \vec{p}_2, \end{aligned} \tag{2}$$

the conservation of total momentum means that

$$\vec{P}\,' = \vec{P},$$
$$\vec{p}\,' = \vec{p} + \vec{\gamma}_{l_1 l_2}^{l_1' l_2'}, \tag{3}$$

where $\vec{\gamma}_{l_1 l_2}^{l_1' l_2'}(x_1, x_2) = -\vec{\gamma}_{l_2 l_1}^{l_2' l_1'}(x_2, x_1)$ is to be determined. Second, the energy balance equation can be written as

$$E(x_1', x_2') + \delta E_{l_1 l_2}^{l_1' l_2'}(x_1, x_2) = E(x_1', x_2'), \tag{4}$$

where $\delta E_{l_1 l_2}^{l_1' l_2'}(x_1, x_2)$ is the energy lost during the collision. Substitution of Eq. (3) gives

$$(\gamma_{l_1 l_2}^{l_1' l_2'})^2 + 2\left(\vec{p} + \frac{m_{l_2} - m_{l_1}}{m_{l_1} + m_{l_2}}\vec{P}\right)\cdot\vec{\gamma}_{l_1 l_2}^{l_1' l_2'} + 8\mu_{l_1 l_2}\delta E_{l_1 l_2}^{l_1' l_2'} = 0, \tag{5}$$

where the reduced mass is $\mu_{l_1 l_2} = m_{l_1} m_{l_2}/(m_{l_1} + m_{l_2})$. In D dimensions, this gives one constraint on the D independent components of $\vec{\gamma}_{l_1 l_2}^{l_1' l_2'}$ so, for example, it fixes the magnitude of $\vec{\gamma}_{l_1 l_2}^{l_1' l_2'}$ if its direction is known: In one dimension, the problem is therefore solved. In higher dimensions, the conservation of angular momentum gives the needed additional constraint. This reads

$$\vec{P}\,' \times \frac{\vec{q}_1 + \vec{q}_2}{2} + \frac{1}{2}\vec{p}\,'_{12} \times \vec{q}_{12} = \vec{P} \times \frac{\vec{q}_1 + \vec{q}_2}{2} + \frac{1}{2}\vec{p}_{12} \times \vec{q}_{12} \tag{6}$$

or, using the conservation of total momentum,

$$\vec{\gamma}_{l_1 l_2}^{l_1' l_2'} \times \vec{q}_{12} = 0, \tag{7}$$

thus fixing the direction of $\vec{\gamma}_{l_1 l_2}^{l_1' l_2'}$ as being along the line joining the centers of the atoms. In this case, Eq. (5) gives

$$\vec{\gamma}_{l_1 l_2}^{l_1' l_2'} = 2\mu_{l_1 l_2}\left(-\vec{v}_{12}\cdot\hat{q}_{12} - \sqrt{(\vec{v}_{12}\cdot\hat{q}_{12})^2 - \frac{2}{\mu_{l_1 l_2}}\delta E_{l_1 l_2}^{l_1' l_2'}}\right)\hat{q}_{12}. \tag{8}$$

Taking $\delta E_{l_1 l_2}^{l_1' l_2'} = 0$ gives the usual result for elastic hard spheres, whereas setting the loss to be a fixed fraction of the contribution to the rest-frame kinetic energy due to the velocity along the line joining the atoms, $\delta E_{l_1 l_2}^{l_1' l_2'} = \lambda_{l_1 l_2}^{l_1' l_2'}\frac{1}{2}\mu_{l_1 l_2}(\vec{v}_{12}\cdot\hat{q}_{12})^2$, is the model used for inelastic hard spheres (i.e., granular fluids) and gives a coefficient of restitution $\alpha_{l_1 l_2}^{l_1' l_2'} = \sqrt{1 - \lambda_{l_1 l_2}^{l_1' l_2'}}$.

When mass can be exchanged upon collision, it is useful to introduce the total mass $M_{l_1 l_2} = m_{l_1} + m_{l_2}$, the center of mass $\vec{Q} = (m_{l_1}\vec{q}_1 + m_{l_2}\vec{q}_2)/M_{l_1 l_2}$, and the center-of-mass velocity $\vec{V} = \vec{P}/M_{l_1 l_2}$. Notice that even with the conservation of total mass, the center of mass is not generally invariant if mass is exchanged and the positions are kept fixed. So the conservation of angular momentum gives

$$M_{l_1' l_2'}\vec{V}\,' \times \vec{Q}\,' + \mu_{l_1' l_2'} v\,' \times \vec{q}_{12} = M_{l_1 l_2}\vec{V} \times \vec{Q} + \mu_{l_1 l_2}\vec{v} \times \vec{q}_{12} \tag{9}$$

or, using the conservation of total momentum,

$$M_{l_1 l_2}\vec{V} \times (\vec{Q}\,' - \vec{Q}) + (\mu_{l_1' l_2'}\vec{v}\,' - \mu_{l_1 l_2}\vec{v}) \times \vec{q}_{12} = 0. \tag{10}$$

In general, this equation cannot be satisfied since it implies

$$[\vec{V} \times (\vec{Q}\,' - \vec{Q})]\cdot\vec{q}_{12} = 0, \tag{11}$$

which is not generally true. The conclusion is that any collision rule which does not leave invariant the center of mass will necessarily result in a violation of the conservation of angular momentum at the microscopic level. It is not possible to compensate by allowing the positions of the atoms to shift during the collision since this could lead to overlapping configurations involving a third atom. In fact, one would expect that the inclusion of internal degrees of freedom, in particular of rotation of the spherical atoms, would allow for a Galilean-invariant collision law and this will be explored at a later date. For present purposes, given that the collision rule cannot be uniquely fixed by appealing to general principles, the only recourse is to try to construct reasonable models. One possibility is to conserve the angular momentum in the center of mass (c.m.) rest frame since then $\vec{V} = 0$ and angular momentum can indeed be conserved. Another is to work in analogy to the case of invariant masses and to require that either all momentum transfer be along $\vec{q}_{12}$ (so $\vec{p}\,' = \vec{p} + 2\mu_{l_1 l_2}\gamma_{l_1 l_2}^{l_1' l_2'}\hat{q}_{12}$). However, since the former is not Galilean invariant when mass is transferred [since in a frame moving at velocity $\vec{u}$ the relative momentum is $\vec{p}_{\mathrm{boosted}} = \vec{p} + (m_{l_1} - m_{l_2})\vec{u}$], it is not clear how to uniquely apply it. In fact, if one tries to enforce this constraint in the c.m. frame, it gives the same result as fixing the angular momentum in the c.m. frame. A second possibility is to demand that all velocity change be along $\vec{q}_{12}$ (so $\vec{v}\,' = \vec{v} + \overline{\gamma}_{l_1 l_2}^{l_1' l_2'}\hat{q}_{12}$). For illustrative purposes, both options will be considered.

For the sake of generality, it is also interesting to consider the consequences when mass is not only exchanged, but is lost. It is clear that the previous considerations concerning the specification of the collision rule under mass exchange apply to this case as well so that, again, a model must be introduced in order to specify the relation between the lost mass and the total momentum and energy. Without considering specific applications, it is not clear that any unique conclusions can be drawn, so by way of illustration I will assume that the mass is carried away in such a way that the total momentum in the c.m. frame is conserved. This means in general that the law of conservation of momentum becomes

$$\vec{P}\,' = \vec{P} - \delta m_{l_1 l_2}^{l_1' l_2'}\vec{V}, \tag{12}$$

where $\delta m_{l_1 l_2}^{l_1' l_2'} = m_{l_1} + m_{l_2} - m_{l_1'} - m_{l_2'}$. The model adopted here is that the mass is carried away by $n_{l_1 l_2}^{l_1' l_2'}$ particles with masses m_i^0 so that $\delta m_{l_1 l_2}^{l_1' l_2'} = \Sigma_{i=1}^{n_{l_1 l_2}^{l_1' l_2'}} m_i^0$ and with rest-frame velocities $\vec{v}_i^0$ satisfying $\Sigma_{i=1}^{n_{l_1 l_2}^{l_1' l_2'}} \vec{v}_i^0 = 0$. For the case in which the angular momentum in the rest c.m. frame is held constant, it is natural to also require that these particles carry no net angular momentum.

Finally, some model must be specified for the energy lost (or gained), $\delta E_{l_1 l_2}^{l_1' l_2'}$, which might include contributions due to kinetic energy that is carried away by the lost mass and energy lost (or gained) through other mechanisms (excitation of internal degrees of freedom, radiation, exothermic, and endothermic chemical reactions, etc.). Suppressing the species indices for a moment, the energy differential can be written as the sum of two contributions, $\delta E = \delta E_m + \delta E_0$, where the first is the energy carried away with the lost mass, and the second is due to any other inelastic processes. In the c.m. rest frame, $\delta E_m = \Sigma_{i=1}^{n} \frac{1}{2} m_i (\vec{v}_i^0)^2 \equiv \overline{\delta E_m}$ so in the laboratory frame, $\delta E_m = \Sigma_{i=1}^{n} \frac{1}{2} m_i (\vec{v}_i^0 + \vec{V})^2 = \overline{\delta E_m} + \frac{1}{2} \delta m V^2$. Further, I assume, as is commonly done, that the remaining energy loss (or gain) is frame independent (which means in particular that it can only be a function of the relative velocity of the colliding atoms). The energy balance equation therefore reads

$$\frac{1}{2m_{l_1'}} p_1'^2 + \frac{1}{2m_{l_2'}} p_2'^2 + \overline{\delta E_{l_1 l_2}^{l_1' l_2'}} + \frac{1}{2} \delta m_{l_1 l_2}^{l_1' l_2'} V^2$$

$$= \frac{1}{2m_{l_1}} p_1^2 + \frac{1}{2m_{l_2}} p_2^2, \tag{13}$$

where it is understood that $\overline{\delta E_{l_1 l_2}^{l_1' l_2'}} = \overline{\delta E_{l_1 l_2}^{l_1' l_2'}}(x_1, x_2)$ is a Galilean-invariant function of the phases. This expression depends on the model for the lost mass (if any), but is independent of any other assumptions concerning the collision rule.

From Eq. (10), conservation of angular momentum in the rest frame then gives

$$\vec{v}_{12}' = \frac{\mu_{l_1 l_2}}{\mu_{l_1' l_2'}} (\vec{v}_{12} + \lambda_{l_1 l_2}^{l_1' l_2'} \hat{q}) \tag{14}$$

for some scalar $\lambda_{l_1 l_2}^{l_1' l_2'}(x_1, x_2)$. Substituting into Eq. (13) gives

$$\lambda_{l_1 l_2}^{l_1' l_2'} = -\vec{v} \cdot \hat{q} + \sqrt{(\vec{v} \cdot \hat{q})^2 - (1 - \mu_{l_1' l_2'} / \mu_{l_1 l_2}) v^2 - \frac{2\mu_{l_1' l_2'}}{\mu_{l_1 l_2}^2} \overline{\delta E_{l_1 l_2}^{l_1' l_2'}} - \frac{\mu_{l_1' l_2'}}{\mu_{l_1 l_2}^2} \delta m_{l_1 l_2}^{l_1' l_2'} V^2} \tag{15}$$

and one then finds that

$$\vec{\gamma}_{l_1 l_2}^{l_1' l_2'} = 2\mu_{l_1 l_2} \lambda_{l_1 l_2}^{l_1' l_2'} \hat{q}_{12} + \left(\frac{m_{l_1'} - m_{l_1}}{m_{l_1} + m_{l_2}} - \frac{m_{l_2'} - m_{l_2}}{m_{l_1} + m_{l_2}} \right) \vec{P}. \tag{16}$$

Demanding that the change in the relative velocity be along the line joining the atoms gives a very similar result

$$\vec{v}_{12}' = \vec{v}_{12} + \lambda_{l_1 l_2}^{l_1' l_2'} \hat{q}_{12}, \tag{17}$$

with

$$\lambda_{l_1 l_2}^{l_1' l_2'} = -\vec{v}_{12} \cdot \hat{q}_{12} + \sqrt{(\vec{v}_{12} \cdot \hat{q}_{12})^2 - (1 - \mu_{l_1 l_2} / \mu_{l_1' l_2'}) v_{12}^2 - \frac{2}{\mu_{l_1' l_2'}} \overline{\delta E_{l_1 l_2}^{l_1' l_2'}} - \frac{\delta m_{l_1 l_2}^{l_1' l_2'}}{\mu_{l_1' l_2'}} V^2} \tag{18}$$

and

$$\vec{\gamma}_{l_1 l_2}^{l_1' l_2'} = \left(\frac{\mu_{l_1' l_2'}}{\mu_{l_1 l_2}} - 1 \right) \vec{p}_{12} + 2\mu_{l_1' l_2'} \lambda_{l_1 l_2}^{l_1' l_2'} \hat{q}_{12} + \left[\frac{m_{l_1'} - m_{l_2'}}{m_{l_1} + m_{l_2}} - \frac{\mu_{l_1' l_2'}}{\mu_{l_1 l_2}} \left(\frac{m_{l_1} - m_{l_2}}{m_{l_1} + m_{l_2}} \right) \right] \vec{P}. \tag{19}$$

Note that these two models coincide in the special case that the reduced mass is invariant, which obtains in one of two circumstances: the atomic masses are invariant or if the atoms just exchange masses so that $m_{l_1'} = m_{l_2}$ and vice versa. In both cases, mass is necessarily conserved, $\delta m_{l_1 l_2}^{l_1' l_2'} = 0$, and all other conclusions are model-independent consequences of Galilean invariance.

B. Evolution of phase functions

The dynamics of any hard-sphere model consists of free streaming interrupted by binary collisions. In nonreacting fluids, the collisions lead to an instantaneous change of the velocities of the colliding atoms. The generalization to the reacting fluid only requires that the chemical species labels and, hence, the masses and any other species-specific properties to be viewed as dynamical variables as well and so as part of an enlarged phase space.

Two atoms—say, atoms *i* and *j*—collide at time τ_{ij} when their centers are separated by their relative hard-sphere diameter $\sigma_{l_i l_j}$:

$$|\vec{q}_i(\tau_{ij})-\vec{q}_j(\tau_{ij})|=q_{ij}^2(\tau_{ij})=\sigma_{l_i l_j}^2, \tag{20}$$

where—e.g., for additive models—the relative hard sphere diameter is simply the sum of the atom radii $\sigma_{l_i l_j}=\frac{1}{2}\sigma_{l_j}+\frac{1}{2}\sigma_{l_j}$. The atoms do not have to all have the same size (e.g., an acceptable possibility is that different species have different sizes, but chemical reactions always transform atoms from a species of a given size to other species of the same size). An exceptional possibility in which size could change is one in which atoms only get smaller upon collision: this might be useful to model certain granular materials that fragment upon collision (e.g., the ice composing the rings of Saturn) and could be handled within the present formalism as long as the position of the center of mass of each atom is invariant. From Eq. (20), one has that the time of the collision is

$$\tau_{ij}(\Gamma)=-\frac{1}{v_{ij}^2}\vec{v}_{ij}\cdot\vec{q}_{ij}-\frac{1}{v_{ij}^2}\sqrt{(\vec{v}_{ij}\cdot\vec{q}_{ij})^2-v_{ij}^2(q_{ij}^2-\sigma_{l_i l_j}^2)}, \tag{21}$$

where the sign has been chosen according to give the physical solution. If the right-hand side is imaginary, then no collision takes place for the given initial conditions. This aspect of the dynamics is independent of what actually happens after the collision and is the reason that the structure of the pseudo-Liouville equation is independent of the collision rule. The pseudo-Liouville equation describing the time evolution of an arbitrary phase function, $A(\Gamma;t)=A\,(x_1,l_1,\ldots,x_N,l_N;t)$, then follows immediately by analogy with the nonreacting fluid and is

$$\frac{d}{dt}A=\frac{\partial}{\partial t}A+\hat{\mathcal{L}}_+A,$$

$$\hat{\mathcal{L}}_+=\sum_i \dot{x}_i\frac{\partial}{\partial x_i}+\sum_{i<j}\hat{\mathcal{T}}_+(ij), \tag{22}$$

where the binary collision operators are

$$\hat{\mathcal{T}}_+(ij)=-\hat{q}_{ij}\cdot\vec{v}_{ij}\delta(q_{ij}-\sigma_{l_i l_j})\Theta(-\hat{q}_{ij}\cdot\vec{v}_{ij})\times\left(\sum_{l_1' l_j'}\mathcal{M}_{l_i l_j}^{l_i' l_j'}(x_{ij})\hat{b}_{l_i l_j}^{l_i' l_j'}-1\right). \tag{23}$$

As discussed in Appendix A, this can be derived directly for a system of two atoms by writing the exact solution to the two-body problem and differentiating; the generalization to *N* atoms follows immediately due to the fact that only binary collisions occur. Here $\mathcal{M}_{l_i l_j}^{l_i' l_j'}(x_{ij})$ is a random matrix which, in any realization, takes on the value 1 for some single combination of l_i', l_j' and is zero otherwise and which is distributed according to

$$\langle\mathcal{M}_{l_1 l_j}^{l_1' l_2'}(x_{ij})\rangle_{\text{react}}=K_{l_i l_j}^{l_i' l_j'}(x_{ij}). \tag{24}$$

(The notation used here indicates stochastic quantities by means of calligraphic type and uses carets to denote operators and averages over the stochastic process are denoted as $\langle\cdots\rangle_{\text{react}}$.) For a nonreacting system, it becomes $\mathcal{M}_{l_i l_j}^{l_i' l_j'}(x_{ij})=\delta_{l_i' l_i}\delta_{l_j' l_j}$. The only other formal difference from the nonreacting case is that the momentum transfer operator $\hat{b}_{l_i l_j}^{l_i' l_j'}$ has the effect of altering both the mechanical variables and the species labels. So just as this operator instantaneously changes the position in phase space of the *i*th atom from $x_i(t_-)$ before a collision at time *t* to $x_i(t_+)=x_i'(t_-)$, it also instantaneously alters the species labels from $l_i(t_-)$ to $l_i(t_+)=l_i'(t_-)$, the difference being that $x_i'(t_-)$ is a deterministic function of $x_i(t_-)$ and $x_j(t_-)$, whereas the evolution of $l_i'(t_-)$ is stochastic. For phase functions which have no explicit time dependence, the Liouville equation can be formally solved to get

$$\mathcal{A}(\Gamma,t)=\exp(\hat{\mathcal{L}}_+t)A(\Gamma), \tag{25}$$

which has the meaning that the system evolves from the initial phase Γ.

The most important difference from the nonreacting system appears in the evaluation of statistical averages. In the presence of reactions there are two statistical processes that must be considered: the distribution of initial conditions and the stochastic process that alters species labels at the collisions. For a given distribution of initial conditions $\rho^{(0)}(\Gamma)=\rho_{l_1 l_2\cdots l_N}^{(0)}(x_1,x_2,\ldots,x_N)$ (giving the probability that the first atom begins with species l_1 and phase x_1, and so on), one has

$$\begin{aligned}\langle A;t\rangle&=\int d\Gamma\,\rho^{(0)}(\Gamma)\langle\mathcal{A}(t)\rangle_{\text{react}}\\&=\int d\Gamma\,\rho^{(0)}(\Gamma)\langle\exp(\hat{\mathcal{L}}_+t)A(\Gamma)\rangle_{\text{react}}\end{aligned} \tag{26}$$

and the notation should be understood as implying a sum over the initial species labels

$$\begin{aligned}&\int d\Gamma\,\rho^{(0)}(\Gamma)\langle\exp(\hat{\mathcal{L}}_+t)A(\Gamma)\rangle_{\text{react}}\\&\quad\equiv\sum_{l_1\cdots l_N}\int dx_1\cdots dx_N\rho_{l_1\cdots l_N}^{(0)}(x_1,\ldots,x_N)\\&\quad\quad\times\langle\exp(\hat{\mathcal{L}}_+t)\rangle_{\text{react}}A(\Gamma),\end{aligned} \tag{27}$$

where $A(\Gamma)$ can be taken outside of the average over reactions since it depends only on the initial conditions. Now, since each collision involves an independent stochastic process, it follows that $\langle \exp(\hat{\mathcal{L}}_+ t)\rangle_{\mathrm{react}} = \exp(\langle \hat{\mathcal{L}}_+\rangle_{\mathrm{react}} t)$, which is evaluated using Eq. (24). Thus the time averages become

$$\langle A;t\rangle = \sum_{l_1\cdots l_N} \int dx_1\cdots dx_N \rho^{(0)}_{l_1\cdots l_N}(x_1,\ldots,x_N)\exp(\hat{L}_+ t)A(\Gamma), \tag{28}$$

with the deterministic operator

$$\hat{L}_+ = \sum_i \dot{x}_i \frac{\partial}{\partial x_i} + \sum_{i<j} \hat{T}_+(ij) \tag{29}$$

and the (reaction-averaged) collision operators are

$$\hat{T}_+(ij) = -\hat{q}_{ij}\cdot\vec{v}_{ij}\delta(q_{ij}-\sigma_{l_i l_j})\Theta(-\hat{q}_{ij}\cdot\vec{v}_{ij}) \times\left(\sum_{l_i' l_j'} K^{l_i' l_j'}_{l_i l_j}(x_{ij})\hat{b}^{l_i' l_j'}_{l_i l_j} - 1\right). \tag{30}$$

This shows that, from the point of view of evaluating the statistical averages, it suffices to work with the deterministic dynamics defined by $\hat{L}_+$, which no longer treats the species labels as discrete stochastic variables. Instead, the phase functions are at all times averaged over the reactions and so do not explicitly represent dynamical quantities as might be realized in a computer simulation. In fact, they correspond to the average result of an ensemble of simulations, all beginning with identical initial conditions, but differing in the realization of the reaction process $\mathcal{M}^{l_i' l_j'}_{l_i l_j}(x_{ij})$.

C. Evolution of the distribution function

The adjoint $\hat{L}^A_+$ of the Liouville operator $\hat{L}_+$ is defined as

$$\int d\Gamma\, B(\Gamma)\hat{L}_+ A(\Gamma) = \int d\Gamma[\hat{L}^A_+ B(\Gamma)]A(\Gamma), \tag{31}$$

from which one finds (see Appendix B)

$$\hat{L}^A_+ = -\sum_i \dot{x}_i \frac{\partial}{\partial x_i} + \sum_{i<j} \hat{T}^A_+(ij), \tag{32}$$

with the adjoint collision operator

$$\hat{T}^A_+(ij) = -\left[\sum_{a,b} J^{l_i l_j}_{ab}(x_i,x_j)(\hat{b}^{l_i l_j}_{ab})^{-1}K^{l_i l_j}_{ab}(x_{ij}) - 1\right] \times\Theta(-\vec{v}_{ij}\cdot\hat{q}_{ij})\,\delta(q_{ij}-\sigma_{l_i l_j})\vec{v}_{ij}\cdot\hat{q}_{ij}, \tag{33}$$

with

$$J^{l_1 l_2}_{ab}(x_i,x_j) = \left|\frac{\partial((\hat{b}^{l_i l_j}_{ab})^{-1}x_i,(\hat{b}^{l_i l_j}_{ab})^{-1}x_j)}{\partial(x_i,x_j)}\right|^{-1}. \tag{34}$$

Here the operator $(\hat{b}^{l_i l_j}_{ab})^{-1}$ is the inverse of $\hat{b}^{l_i l_j}_{ab}$ both in terms of the change of the mechanical variables as well as the species labels so that for an arbitrary function $(\hat{b}^{l_i l_j}_{ab})^{-1}\, B(x_i,l_i;x_j,l_j) = B\ ((\hat{b}^{l_i l_j}_{ab})^{-1}\ x_i,a;\ (\hat{b}^{l_i l_j}_{ab})^{-1}\ x_j,b)$. To illustrate the structure of this operator, consider the case of inelastic hard spheres used to model granular fluids. Specializing to a single species, one has

$$\vec{v}\,'_{ij} = \hat{b}\vec{v}_{ij} = \vec{v}_{ij} - (1+\alpha)\vec{v}_{ij}\cdot\hat{q}_{ij}, \tag{35}$$

where α is a constant, from which it follows that

$$\vec{v}_{ij} = \vec{b}^{-1}\vec{v}\,'_{ij} = \vec{v}\,'_{ij} - \left(\frac{1+\alpha}{\alpha}\right)\vec{v}\,'_{ij}\cdot\hat{q}_{ij}, \tag{36}$$

giving

$$\left|\frac{\partial(\hat{b}^{-1}x_i,\hat{b}^{-1}x_j)}{\partial(x_i,x_j)}\right| = \left|1-\left(\frac{1+\alpha}{\alpha}\right)\right| = \frac{1}{\alpha}, \tag{37}$$

so that

$$\hat{T}^A_+(ij)B(x_i,l_i;x_j,l_j) = -\left[\frac{1}{\alpha}\hat{b}^{-1}-1\right]\Theta(-\vec{v}_{ij}\cdot\hat{q}_{ij})\,\delta(q_{ij}-\sigma_{l_i l_j})\vec{v}_{ij} \cdot\hat{q}_{ij}B(x_i,l_i;x_j,l_j), \tag{38}$$

which is the usual result.[16]

An important generalization of this result concerns the case that the inverse transformation $\hat{b}^{l_i l_j}_{ab}x_i$ is not unique. This can happen even in the single-species, inelastic case if the coefficient of restitution depends on the velocities. For example, if $\alpha = \alpha(\vec{v}_{ij}\cdot\hat{q}_{ij})$, then the inverse collision rule is determined by solving

$$\vec{v}\,'_{ij}\cdot\hat{q}_{ij} = -\alpha(\vec{v}_{ij}\cdot\hat{q}_{ij})\vec{v}_{ij}\cdot\hat{q}_{ij}, \tag{39}$$

which may or may not have a unique solution. In the latter case, $\hat{T}^A_+$ must be written in terms of a sum over the various branches and must include step functions which restrict the domain of integration in Eq. (31) to the appropriate domain for each branch. In practical calculations, it is usually most convenient to recast integrals over $\hat{T}^A_+(ij)$ into integrals involving $\hat{T}_+(ij)$ so as to avoid this complication.

Given the adjoint operator $\hat{L}^A_+$, Eq. (28) can be written as

$$\langle A;t\rangle = \int d\Gamma[\exp(L^A t)\rho^{(0)}(\Gamma)]A(\Gamma) \equiv \int d\Gamma\rho(\Gamma;t)A(\Gamma), \tag{40}$$

where the second equality defines the time-dependent distribution function. Its time dependence is given by the pseudo-Liouville equation

$$\left(\frac{\partial}{\partial t} + \sum_i \dot{x}_i\frac{\partial}{\partial x_i} + \sum_{i<j}\overline{T}_-(ij)\right)\rho = 0, \tag{41}$$

where in the standard notation[7]

$$\overline{T}_-(ij) = -T^A_+(ij). \tag{42}$$

The Born–Bogoliubov–Green–Kirkwood–Yvon (BBGKY) hierarchy follows immediately from the Liouville equation. Defining the reduced distribution functions as

$$f_{l_1\cdots l_m}(x_1\cdots x_m) = \frac{N!}{(N-m)!}\sum_{l_{m+1}\cdots l_N}\int dx_{m+1}\cdots dx_N\rho(\Gamma), \tag{43}$$

integrating the pseudo-Liouville equation over $x_{m+1}\cdots x_N$, and summing over the corresponding species labels gives the mth equation of the hierarchy:

$$\left(\frac{\partial}{\partial t}+\sum_{i=1}^{m}\vec{v}_i\cdot\frac{\partial}{\partial\vec{q}_i}+\sum_{1\leqslant i<j\leqslant m}\overline{T}_-(ij)\right)f_{l_1\cdots l_m}(x_1\cdots x_m)$$
$$=-\sum_{i=1}^{m}\sum_{l_{m+1}}\int dx_{m+1}\overline{T}_-(im+1)f_{l_1\cdots l_{m+1}}(x_1\cdots x_{m+1}). \tag{44}$$

The first equation of the hierarchy is the starting point for the Enskog kinetic theory as described below.

III. EXACT BALANCE EQUATIONS

Now consider the phenomenology of the reacting fluid which is expressed in terms of the macroscopic hydrodynamic fields. The results presented here are derived using only the general form of the collision rule, Eq. (3), and the microscopic energy balance equation (13), so that the only assumptions made with respect to the collision model are those concerning the energy transported by any lost mass.

The local fields of interest are the number fractions

$$n_l(\vec{r},t)=\left\langle\sum_i\delta(\vec{r}-\vec{q}_i)\delta_{ll_i};t\right\rangle=\int d\vec{v}_1f_l(\vec{r},\vec{v}_1;t) \tag{45}$$

and the mass, momentum, and energy densities, defined, respectively, as

$$\rho(\vec{r},t)=\sum_l m_ln_l(\vec{r},t),$$
$$\rho(\vec{r},t)\vec{u}(\vec{r},t)=\left\langle\sum_i m_{l_i}\vec{v}_i\delta(\vec{r}-\vec{q}_i);t\right\rangle$$
$$=\sum_l m_l\int d\vec{v}_1\vec{v}_1f_l(\vec{r},\vec{v}_1;t),$$
$$\frac{D}{2}n(\vec{r},t)k_BT(\vec{r},t)=\left\langle\sum_i\frac{1}{2}m_{l_i}V_i^2\delta(\vec{r}-\vec{q}_i);t\right\rangle$$
$$=\sum_l\frac{1}{2}m_l\int d\vec{v}_1V_1^2f_l(\vec{r},\vec{v}_1;t), \tag{46}$$

where the excess velocity is $\vec{V}_i(t)=\vec{v}_i(t)-\vec{u}(\vec{q}_i,t)$ and the total number density is

$$n(\vec{r},t)=\sum_l n_l(\vec{r},t). \tag{47}$$

It is also convenient to introduce the number fractions, or concentrations, $x_l(\vec{r},t)=n_l(\vec{r},t)/n(\vec{r},t)$. The balance equations for these quantities follow directly from their definitions and the first equation of the BBGKY hierarchy. The details of the derivation are given in Appendix C and only the results summarized here.

A. Number, mass, and concentration

Integrating over the positions and velocities gives the balance equation for the local partial number density,

$$\frac{\partial}{\partial t}n_l+\vec{\nabla}\cdot(\vec{u}n_l)+\vec{\nabla}\cdot\vec{j}_l=S_l^{(n)}, \tag{48}$$

with the source

$$S_l^{(n)}(\vec{r},t)=-\tfrac{1}{2}\sum_{abl_1l_2}\int dx_1dx_2(\hat{q}_{12}\cdot\vec{v}_{12})\delta(q_{12}-\sigma_{l_1l_2})$$
$$\times\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})f_{l_1l_2}(x_1,x_2;t)$$
$$\times\delta(\vec{r}-\vec{q}_1)K_{l_1l_2}^{ab}(x_{12})(\delta_{al}+\delta_{bl}-\delta_{ll_1}-\delta_{ll_2}) \tag{49}$$

and the number current $\vec{j}_l=\vec{j}_l^K+\vec{j}_l^V$, with

$$\vec{j}_l^K(\vec{r},t)=\int d\vec{v}_1f_l(\vec{r},\vec{v}_1,t)\vec{V}_1 \tag{50}$$

and

$$\vec{j}_l^V(\vec{r},t)=-\tfrac{1}{2}\sum_{abl_1l_2}\int dx_1dx_2\vec{q}_{12}(\hat{q}_{12}\cdot\vec{v}_{12})\delta(q_{12}-\sigma_{l_1l_2})$$
$$\times\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})f_{l_1l_2}(x_1,x_2;t)$$
$$\times K_{l_1l_2}^{ab}(x_{12})(\delta_{al}-\delta_{bl}-\delta_{ll_1}+\delta_{ll_2})$$
$$\times\int_0^1dx\;\delta(\vec{r}-x\vec{q}_1-(1-x)\vec{q}_2). \tag{51}$$

The source term represents the gain or loss of atoms of type l due to chemical reactions. The kinetic part of the number current is familiar from the study of multiple-component, nonreacting systems[7] where it takes the form $\vec{j}_l^K=\Sigma_jD_{lj}\vec{\nabla}n_j+L_l\vec{\nabla}T+o(\nabla^2)$ and, e.g., gives rise to Fick's law when substituted into Eq. (48). Here it is seen that this diffusive current is enhanced by a second contribution, Eq. (51), that arises solely from the reactions (i.e., it vanishes if $K_{l_1l_2}^{ab}=\delta_{al_1}\delta_{bl_2}$). This is due to the transport of type-l atoms due to the reaction process. The conservation of total number density immediately follows by summing over the species label

$$\frac{\partial}{\partial t}n+\vec{\nabla}\cdot(\vec{u}n)+\vec{\nabla}\cdot\sum_l\vec{j}_l^K=0, \tag{52}$$

where the sum over the species of the collisional contributions to the number current vanishes. Similarly, multiplying by m_l and then summing gives the balance equation for the local mass density,

$$\frac{\partial}{\partial t}\rho+\vec{\nabla}\cdot(\vec{u}\rho)+\vec{\nabla}\cdot\vec{Q}=S^{(\rho)}, \tag{53}$$

where the mass flux is

$$\vec{Q}(\vec{r},t)=-\tfrac{1}{2}\sum_{abl_1l_2}\int dx_1dx_2\vec{q}_{12}(\hat{q}_{12}\cdot\vec{v}_{12})$$
$$\times\delta(q_{12}-\sigma_{l_1l_2})\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})f_{l_1l_2}(x_1,x_2;t)$$
$$\times K_{l_1l_2}^{ab}(x_{12})(m_a-m_b-m_{l_1}+m_{l_2})$$
$$\times\int_0^1dx\;\delta(\vec{r}-x\vec{q}_1-(1-x)\vec{q}_2), \tag{54}$$

which vanishes if no mass is transported during collisions, and the mass source term is

$$S_l^{(\rho)}(\vec{r},t)=\tfrac{1}{2}\sum_{abl_1l_2}\int dx_1dx_2(\hat{q}_{12}\cdot\vec{v}_{12})\delta(q_{12}-\sigma_{l_1l_2})\times\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})f_{l_1l_2}(x_1,x_2;t)\times\delta(\vec{r}-\vec{q}_1)K_{l_1l_2}^{ab}(x_{12})\delta m_{l_1l_2}^{ab},\tag{55}$$

which is only nonzero if the collisions do not conserve mass. Finally, using the definition of the concentrations, $x_l=n_l/n$, the reaction equation is found to be

$$\frac{\partial}{\partial t}x_l+\vec{u}\cdot\vec{\nabla}x_l+n^{-1}\left[\vec{\nabla}\cdot\vec{j}_l-x_l\vec{\nabla}\cdot\sum_l\vec{j}_l^K\right]=n^{-1}S_l^{(n)},\tag{56}$$

where the term on the right is now identified as the reaction rate.

B. Momentum and velocity fields

The balance equation for the local momentum, written in terms of the local velocity, is

$$\frac{\partial}{\partial t}\rho\vec{u}+\vec{\nabla}\cdot(\rho\vec{u}\vec{u})+\vec{\nabla}\cdot(\overleftrightarrow{P}+\vec{Q}\vec{u})=\overline{\vec{S}^{(p)}}+\vec{u}S_l^{(\rho)},\tag{57}$$

with the pressure tensor $\overleftrightarrow{P}=\overleftrightarrow{P}^K+\overleftrightarrow{P}^V+\overleftrightarrow{P}^M$, where the kinetic contribution is

$$\overleftrightarrow{P}^K(\vec{r},t)=\sum_l m_l\int d\vec{v}_1f_l(\vec{r},\vec{v}_1,t)\vec{V}_1\vec{V}_1\tag{58}$$

and the collisional contribution is

$$\overleftrightarrow{P}^V(\vec{r},t)=-\tfrac{1}{2}\sum_{l_1l_2l_1'l_2'}\int dx_1dx_2\vec{q}_{12}(\hat{q}_{12}\cdot\vec{v}_{12})\times\delta(q_{12}-\sigma_{l_1l_2})\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})f_{l_1l_2}(x_1,x_2;t)\times K_{l_1l_2}^{l_1'l_2'}(x_{12})\tilde{\vec{\gamma}}_{l_1l_2}^{l_1'l_2'}\int_0^1dx\ \delta(\vec{r}-x\vec{q}_1-(1-x)\vec{q}_2),\tag{59}$$

where $\tilde{\vec{\gamma}}_{l_1l_2}^{l_1'l_2'}$ is the change of momentum in the rest frame,

$$\vec{\gamma}_{l_1l_2}^{l_1'l_2'}=\tilde{\vec{\gamma}}_{l_1l_2}^{l_1'l_2'}+(m_{l_1'}-m_{l_1}+m_{l_2'}-m_{l_2'})\vec{V}_{12}.\tag{60}$$

Finally, the contribution from the instantaneous exchange of mass is

$$\overleftrightarrow{P}^M=-\tfrac{1}{2}\sum_{l_1l_2l_1'l_2'}\int dx_1dx_2\vec{q}_{12}(\hat{q}_{12}\cdot\vec{v}_{12})\delta(q_{12}-\sigma_{l_1l_2})\times\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})f_{l_1l_2}(x_1x_2)K_{l_1l_2}^{l_1'l_2'}(x_{12})(\vec{V}_{12}-\vec{u})\times(m_{l_1'}-m_{l_1}-m_{l_2'}-m_{l_2})\int_0^1dx\ \delta(\vec{r}-x\vec{q}_1-(1-x)\vec{q}_2).\tag{61}$$

The source terms arise due to momentum being carried away by the lost mass and the new term is given by

$$\overline{\vec{S}^{(p)}}(\vec{r},t)=\tfrac{1}{2}\sum_{l_1l_2l_1'l_2'}\int dx_1dx_2(\hat{q}_{12}\cdot\vec{v}_{12})\times\delta(q_{12}-\sigma_{l_1l_2})\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})(\vec{V}_{12}-\vec{u})\times f_{l_1l_2}(x_1,x_2;t)K_{l_1l_2}^{l_1'l_2'}(x_{12})\delta m_{l_1l_2}^{l_1'l_2'}(\vec{r}-\vec{q}_1).\tag{62}$$

By using the balance equation for the total mass density the equation of motion for the velocity field is found to be

$$\frac{\partial}{\partial t}\vec{u}+\vec{u}\cdot\vec{\nabla}\vec{u}+\rho^{-1}(\vec{\nabla}\cdot\overleftrightarrow{P}+\vec{Q}\cdot\vec{\nabla}\vec{u})=\rho^{-1}\overline{\vec{S}^{(p)}}.\tag{63}$$

C. Energy density and temperature

The balance equation for the total energy density is

$$\frac{\partial}{\partial t}E+\vec{\nabla}\cdot(\vec{u}E)+\vec{\nabla}\cdot\vec{q}+\vec{\nabla}\cdot(\vec{u}\cdot\overleftrightarrow{P})+\vec{\nabla}\cdot\left(\frac{1}{2}u^2\vec{Q}\right)=\xi+\vec{u}\cdot\overline{\vec{S}^{(p)}}+\frac{1}{2}u^2\overline{S^{(\rho)}},\tag{64}$$

where the new source term, arising if energy is not conserved by the collisions, is

$$\xi(\vec{r},t)=\frac{1}{2}\sum_{l_1l_2l_1'l_2'}\int dx_1dx_2(\hat{q}_{12}\cdot\vec{v}_{12})\delta(q_{12}-\sigma_{l_1l_2})\times\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})\left[\overline{\delta E_{l_1l_2}^{l_1'l_2'}}+\frac{1}{2}\delta m_{l_1l_2}^{l_1'l_2'}(\vec{V}-\vec{u})^2\right]\times f_{l_1l_2}(x_1,x_2;t)K_{l_1l_2}^{l_1'l_2'}(x_{12})\delta(\vec{r}-\vec{q}_1),\tag{65}$$

which is recognized as the generalization of the source term studied in the context of granular fluids. The heat flux is written as a sum of several contributions

$$\vec{q}=\vec{q}^K+\vec{q}^V+\vec{q}^m+\vec{q}^{\delta E},\tag{66}$$

where the kinetic part has the usual form

$$\vec{q}^K(\vec{r},t)=\sum_l\tfrac{1}{2}m_l\int d\vec{v}_1f_l(\vec{r},\vec{v}_1,t)\vec{V}_1V_1^2,$$

as does the first part of the collisional contribution,

$$\vec{q}^{V}(\vec{r},t)=-\tfrac{1}{2}\sum_{l_1l_2l_1'l_2'}\int dx_1dx_2\vec{q}_{12}(\hat{q}_{12}\cdot\vec{v}_{12})\times\delta(q_{12}-\sigma_{l_1l_2})\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})f_{l_1l_2}(x_1,x_2;t)\times K_{l_1l_2}^{l_1'l_2'}(x_{12})(\vec{V}-\vec{u}(\vec{q}_1))\cdot\tilde{\vec{\gamma}}_{l_1l_2}^{l_1'l_2'}\times\int_0^1 dx\;\delta(\vec{r}-x\vec{q}_1-(1-x)\vec{q}_2), \tag{67}$$

which is a measure of energy displacement during the collision (i.e., one atom experiences a net gain of energy, the other a net loss, and this represents an instantaneous movement of energy from the location of the second atom to the location of the first). Qualitatively new contributions arise from the instantaneous transfer of mass,

$$\vec{q}^{m}(\vec{r},t)=-\frac{1}{2}\sum_{l_1l_2l_1'l_2'}\frac{m_{l_2'}m_{l_1}-m_{l_1'}m_{l_2}}{(m_{l_2'}+m_{l_1'})(m_{l_2}+m_{l_1})}\times\int dx_1dx_2\vec{q}_{12}(\hat{q}_{12}\cdot\vec{v}_{12})\delta(q_{12}-\sigma_{l_1l_2})\times\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})f_{l_1l_2}(x_1,x_2;t)K_{l_1l_2}^{l_1'l_2'}(x_{12})\times\mu_{l_1l_2}v_{12}\int_0^1 dx\;\delta(\vec{r}-x\vec{q}_1-(1-x)\vec{q}_2), \tag{68}$$

and from the loss of energy,

$$\vec{q}^{\delta E}(\vec{r},t)=-\frac{1}{2}\sum_{l_1l_2l_1'l_2'}\frac{m_{l_1'}-m_{l_2'}}{m_{l_1'}+m_{l_2'}}\int dx_1dx_2\vec{q}_{12}(\hat{q}_{12}\cdot\vec{v}_{12})\times\delta(q_{12}-\sigma_{l_1l_2})\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})\times f_{l_1l_2}(x_1,x_2;t)K_{l_1l_2}^{l_1'l_2'}(x_{12})\overline{\delta E_{l_1l_2}^{l_1'l_2'}}\times\int_0^1 dx\;\delta(\vec{r}-x\vec{q}_1-(1-x)\vec{q}_2). \tag{69}$$

Alternatively, noting the relation between the total energy and the kinetic temperature,

$$E=\frac{D}{2}nk_BT+\frac{1}{2}\rho u^2, \tag{70}$$

the evolution of the kinetic temperature is found to be given by

$$\left(\frac{\partial}{\partial t}+\vec{u}\cdot\vec{\nabla}\right)T-\frac{T}{n}\vec{\nabla}\cdot\sum_l\vec{j}_l^K+\frac{2}{Dnk_B}[\vec{P}:\nabla\vec{u}+\vec{\nabla}\cdot\vec{q}]=\frac{2}{Dnk_B}\xi. \tag{71}$$

D. Enskog approximation

The expressions for the balance equations are exact. As a consequence, they depend on both the exact one-body and two-body distribution functions which are, in principle, determined by the BBGKY hierarchy. For example, the equation for the one-body distribution is explicitly

$$\left(\frac{\partial}{\partial t}+\vec{v}_1\cdot\frac{\partial}{\partial\vec{q}_1}\right)f_{l_1}(x_1;t)=-\sum_{a,b,l_2}\int d\vec{q}_2d\vec{v}_2\left[\left|\frac{\partial(\hat{b}_{ab}^{l_1l_2}x_1,\hat{b}_{ab}^{l_1l_2}x_2)}{\partial(x_1,x_2)}\right|^{-1}\times(\hat{b}_{ab}^{l_1l_2})^{-1}K_{ab}^{l_1l_2}(x_{12})-\delta_{l_1a}\delta_{l_2b}\right]\Theta(-\vec{v}_{12}\cdot\vec{q}_{12})\times\delta(q_{12}-\sigma_{l_1l_2})\vec{v}_{12}\cdot\hat{q}_{12}f_{l_1l_2}(\vec{q}_1,\vec{v}_1,\vec{q}_2,\vec{v}_2;t). \tag{72}$$

However, since the latter cannot be solved exactly, except in the special case of equilibrium, it is necessary to introduce an approximation. The most common approximation is to assume that the velocities of two colliding atoms are uncorrelated prior to the collision (they are of course correlated after the collision since the collision itself generates correlations). That this approximation is sufficient to decouple the BBGKY hierarchy is seen from the right-hand side of Eq. (72) since the step function $\Theta(-\vec{v}_{12}\cdot\vec{q}_{12})$ is nonzero only for atoms approaching one another and the δ function restricts the domain to the instant of contact. Thus the assumption that atoms are uncorrelated just prior to a collision, Boltzmann's "assumption of molecular chaos," is precisely the statement that

$$\Theta(-\vec{v}_{12}\cdot\vec{q}_{12})\delta(q_{12}-\sigma_{l_1l_2})f_{l_1l_2}(\vec{q}_1,\vec{v}_1,\vec{q}_2,\vec{v}_2)\simeq\Theta(-\vec{v}_{12}\cdot\vec{q}_{12})\delta(q_{12}-\sigma_{l_1l_2})\times g(\vec{q}_1,\vec{q}_2;t)f_{l_1}(x_1;t)f_{l_2}(x_2;t), \tag{73}$$

which, when substituted into Eq. (72) gives the Enskog approximation to the one-body distribution function. The factor of $g(\vec{q}_1,\vec{q}_2;t)$, the spatial pair distribution function, allows for spatial correlations which always exist. In the revised Enskog theory, it is approximated by the equilibrium functional of the density evaluated for the local density field of the fluid.[10] The same approximation can be above to give the corresponding Enskog approximation to the balance equations. A final consequence follows from the second equation of the BBGKY hierarchy, which has the form

$$\left(\frac{\partial}{\partial t}+\vec{v}_1\cdot\frac{\partial}{\partial\vec{q}_1}+\vec{v}_2\cdot\frac{\partial}{\partial\vec{q}_2}+\overline{T}_-(12)\right)f_{l_1l_2}(x_1,x_2;t)=-n\int d3[\overline{T}_-(13)+\overline{T}_-(23)]f_{l_1l_2l_3}(x_1,x_2,x_3;t). \tag{74}$$

Since atoms cannot interpenetrate, the two-body distribution must have the form $f_{l_1l_2}(x_1,x_2;t)=\Theta(q_{12}-\sigma_{l_1l_2})\times y_{l_1l_2}(x_1,x_2;t)$ for some function $y_{l_1l_2}(x_1,x_2;t)$ which is continuous at $q_{12}=\sigma_{l_1l_2}$. Then one expects that the singular terms in Eq. (74), arising from the gradient acting on the step function and from the definition of $\overline{T}_-(12)$, must cancel, gives the constraint

$$\begin{aligned}&\vec{v}_{12}\cdot\hat{q}_{12}\delta(q_{12}-\sigma_{l_1l_2})f_{l_1l_2}(x_1,x_2;t)\\&\quad=-\overline{T}_-(12)f_{l_1l_2}(x_1,x_2;t)\end{aligned}\tag{75}$$

and some rearrangement, together with the approximation of Eq. (74) gives

$$\begin{aligned}&\delta(q_{12}-\sigma_{l_1l_2})f_{l_1l_2}(x_1,x_2;t)\\&\quad\simeq\delta(q_{12}-\sigma_{l_1l_2})g(\vec{q}_1,\vec{q}_2;t)f_{l_1}(x_1;t)f_{l_2}(x_2;t)\\&\qquad-(\vec{v}_{12}\cdot\hat{q}_{12})^{-1}\overline{T}_-(12)g(\vec{q}_1,\vec{q}_2;t)f_{l_1}(x_1;t)f_{l_2}(x_2;t),\end{aligned}\tag{76}$$

which expresses the two-body distribution function at contact in terms of a completely uncorrelated piece, the first term on the right, and a correction that takes into account velocity correlations generated by the collision, the second term on the right. This can be used to evaluate two-body correlations at the Enskog level of approximation.[17–19]

IV. CHAPMAN–ENSKOG SOLUTION

In the previous section, the exact balance equations were developed and the Enskog approximation introduced. Next, this framework is used to derive the explicit equations governing the evolution of the hydrodynamic fields by means of the Chapman–Enskog approximation. As noted in the Introduction, previous studies of the kinetic theory for reacting systems have often made the assumption that the chemical reactions are slow relative to the hydrodynamic time scales. The primary goal here is draw out, and make more precise, the meaning of this condition by outlining the Chapman–Enskog procedure under different assumptions about the speed of the chemical reactions.

Before beginning, note that the phrase ''hydrodynamic fields'' usually refers to those local fields which are conserved in the long-wavelength limit (which is to say that their sum over the entire system is conserved). For a nonreacting fluid of hard spheres, this means the local partial number densities and the momentum and energy densities. For a reacting fluid, the partial number densities are not conserved and for models of endothermic and exothermic reactions, even the energy is not be conserved. Following the practice developed in the study of granular fluids (which are nonreactive, but do not conserve energy) it seems natural to expand the definition of ''hydrodynamic'' fields to include those fields which would be conserved in the limit of vanishing reaction probabilities. A partial justification for this is that all of these fields are necessary to develop a meaningful description of the nonreacting fluid, so one expects that they must also be included in any description of the reacting fluid (i.e., a minimal-coupling argument based on continuity of the description with respect to the control parameters).

The Chapman–Enskog procedure attempts to construct a so-called normal solution of the Enskog equation, which is to say a solution which is a local functional of the (exact) hydrodynamic fields and for which all of the space and time dependence occurs implicitly through those fields.[7] This implies that the space and time derivatives of the distribution function can be written in terms of the corresponding derivatives of the fields and the functional derivative of the distribution with respect to the fields. In other words, one has

$$\begin{aligned}&f_a(\vec{q}_1,\vec{v}_1,t)\\&\quad=f_a[\vec{v}_1|x_i(\vec{q}_1,t),n(\vec{q}_1,t),\vec{u}(\vec{q}_1,t),T(\vec{q}_1,t)],\end{aligned}\tag{77}$$

so all of the dependence on $\vec{q}_1$ and t occur through the hydrodynamic fields so that the time derivative can be expressed as

$$\begin{aligned}\frac{\partial}{\partial t}f_a(\vec{q}_1,\vec{v}_1,t)=&\sum_i\frac{\partial x_i}{\partial t}\frac{\partial f_a}{\partial x_i}+\frac{\partial n}{\partial t}\frac{\partial f_a}{\partial n}\\&+\frac{\partial\vec{u}}{\partial t}\cdot\frac{\partial f_a}{\partial\vec{u}}+\frac{\partial T}{\partial t}\frac{\partial f_a}{\partial T}.\end{aligned}\tag{78}$$

Then the kinetic equation determines the functional dependence of the distribution on the fields and their derivatives, while the fields are in turn fixed self-consistently by the balance equations (in the Enskog approximation).

A further approximation which is made in practical calculations is to assume that spatial gradients are small so that the equations can be solved perturbatively via a gradient expansion. To order the terms, one introduces a uniformity parameter ϵ and replace $\vec{\nabla}$ with $\epsilon\vec{\nabla}$ and order terms in ϵ. Since the space and time derivatives are related by the balance equations, one also introduces an expansion of the time derivative $\partial/\partial t\equiv\partial_t=\partial_t^{(0)}+\epsilon\partial_t^{(1)}+\cdots$ as well as of the distribution itself:

$$f_a(\vec{q}_1,\vec{v}_1,t)=f_a^0[\vec{v}_1|x_i,n,\vec{u},T]+\epsilon f_a^1[\vec{v}_1|x_i,n,\vec{u},T]+\cdots,\tag{79}$$

where the notation indicates that the distribution is a functional of the hydrodynamic fields. These expansions are substituted into both the Enskog equation and the balance equations and an order-by-order solution is sought. Writing the Enskog equation as

$$\left(\frac{\partial}{\partial t}+\vec{v}_1\cdot\frac{\partial}{\partial\vec{q}_1}\right)f_a(x_1;t)=\sum_{bcd}J_{ab,cd}[f_c,f_d],\tag{80}$$

so that

$$\begin{aligned}&J_{ab,cd}[f_c,f_d]\\&\quad=\int d\vec{q}_2d\vec{v}_2\Bigg[\left|\frac{\partial(\hat{b}_{ab}^{cd}x_1,\hat{b}_{ab}^{cd}x_2)}{\partial(x_1,x_2)}\right|^{-1}\\&\qquad\times(\hat{b}_{ab}^{cd})^{-1}K_{ab}^{cd}(x_{12})-\delta_{ac}\delta_{bd}\Bigg]\Theta(-\vec{v}_{12}\cdot\vec{q}_{12})\\&\qquad\times\delta(q_{12}-\sigma_{cd})\vec{v}_{12}\cdot\hat{q}_{12}f_c(\vec{q}_1,\vec{v}_1;t)f_d(\vec{q}_2,\vec{v}_2;t),\end{aligned}\tag{81}$$

it is also necessary to expand the nonlocality of the collision operator which comes from the term $\delta(q_{12}-\sigma_{cd})=\delta(q_{12})+\epsilon\sigma_{cd}\delta'(q_{12})+\cdots$, where the derivatives of the δ function, which will give rise to spatial gradients of the distribution, are scaled with an appropriate factor of ϵ. In order to control the speed of the chemistry relative to the hydrodynamics, the nondiagonal part of the reaction probabilities is separated out as

$$K_{ab}^{cd} \rightarrow \delta_{ac}\delta_{bd} + \epsilon^{\alpha}(K_{ab}^{cd} - \delta_{ac}\delta_{bd}), \tag{82}$$

giving

$$\begin{aligned} J_{ab,cd}[f_c, f_d] = {} & \delta_{ac}\delta_{bd} J_{a,b}^{(\text{invariant})}[f_a, f_b] \\ & + \epsilon^{\alpha} J_{ab,cd}^{(\text{reactive})}[f_c, f_d], \end{aligned} \tag{83}$$

where the nonreactive, or invariant, part is the usual collision operator for nonreactive (but possible energy nonconserving) multiple-component fluids,

$$\begin{aligned} & J_{a,b}^{(\text{invariant})}[f_a, f_b] \\ & = \int d\vec{q}_2 d\vec{v}_2 \left[\left| \frac{\partial(\hat{b}_{ab}^{ab} x_1, \hat{b}_{ab}^{ab} x_2)}{\partial(x_1, x_2)} \right|^{-1} (\hat{b}_{ab}^{ab})^{-1} - 1 \right] \\ & \quad \times \Theta(-\vec{v}_{12} \cdot \vec{q}_{12}) \delta(q_{12} - \sigma_{ab}) \\ & \quad \times \vec{v}_{12} \cdot \hat{q}_{12} f_a(\vec{q}_1, \vec{v}_1; t) f_b(\vec{q}_2, \vec{v}_2; t), \end{aligned} \tag{84}$$

and, as indicated, the reactive part of the collision operator will be arbitrarily treated as being of order α in the gradient expansion. Thus the full expansion of the collision operator will take the form

$$\begin{aligned} J_{ab,cd}[f_c, f_d] = {} & \delta_{ac}\delta_{bd}(J_{a,b}^{(\text{invariant})0}[f_a, f_b] \\ & + \epsilon J_{a,b}^{(\text{invariant})1}[f_a, f_b] + \cdots) \\ & + \epsilon^{\alpha}(J_{ab,cd}^{(\text{reactive})0}[f_c, f_d] \\ & + \epsilon J_{ab,cd}^{(\text{reactive})1}[f_c, f_d] + \cdots). \end{aligned} \tag{85}$$

A. Zeroth order

The zeroth-order equation for the distribution is then

$$\partial_t^0 f_a^{(0)} = \sum_b J_{a,b}^{(\text{elastic})0}[f_a^0, f_b^0] + \delta_{\alpha 0} \sum_{bcd} J_{ab,cd}^{(\text{reactive})0}[f_c^0, f_d^0], \tag{86}$$

which must be supplemented by the corresponding equations for the fields expanded to zeroth order:

$$\begin{aligned} & \partial_t^0 x_l = \delta_{\alpha 0} n^{-1} S_l^{(n)(\text{reactive})0}, \\ & \partial_t^0 n = 0, \\ & \partial_t^0 \vec{u} = 0, \\ & \partial_t^0 T = \xi^{(\text{invariant})0} + \delta_{\alpha 0} \xi^{(\text{reactive})0}. \end{aligned} \tag{87}$$

These balance equations, together with the assumption of normality, Eq. (78), serve to define the meaning of the term $\partial_t^0 f_a^{(0)}$ in Eq. (86). Note that the fluxes do not enter, being of first order in the gradients, and that the sources are separated into a nonreactive and reactive part using Eq. (82). For the concentration, mass, and velocity fields, there are in general no nonreactive contributions to the sources, whereas for the temperature there is the possibility of such a contribution, in which case one recovers the inelastic hard-sphere system used to model granular fluids. Furthermore, use has been made of the fact that $f_a^{(0)}$ must be a function of $\vec{v}_1 - \vec{u}$, which implies that $\overline{\vec{S}}^{(p)(\text{reactive})0} = 0$ (since there are no other zeroth-order vectors) so that no source can appear in the velocity equation at this order. These zeroth-order equations illustrate a complication that occurs for fast reacting systems (e.g., $\alpha = 0$) compared to nonreacting multiple-component system s: namely, that the sources in the balance equations at order n require knowledge of the nth-order distribution. For nonreacting elastic systems, the nth-order balance equations generally require only the $(n-1)$, order distribution so that there is no coupling between the two. Nonreacting inelastic systems—i.e., granular fluids—share this complication as can be seen from the appearance of the source term $\xi^{(\text{non})0}$ in Eqs. (87).

For $\alpha > 0$, only the temperature can have a zeroth-order time dependence and so can contribute to the left side of Eq. (86). If this temperature source is zero, then the left-hand side of Eq. (86) is zero and the $f_a^{(0)}$ will simply be proportional to a Maxwellian. The solution of Eqs. (86) and (87) for the case $\alpha > 0$ and the nonreactive source in the temperature equation being nonzero corresponds to the so-called homogeneous cooling state in granular fluids and has been discussed in detail in the literature for single-component[20] and multiple-component systems.[21]

B. First order

At first order, one has

$$\begin{aligned} & \partial_t^0 f_a^{(1)} + (\partial_t^1 + \vec{v}_1 \cdot \vec{\nabla}) f_a^0 \\ & = \sum_b (J_{a,b}^{(\text{invariant})0}[f_a^0, f_b^1] + J_{a,b}^{(\text{invariant})0}[f_a^1, f_b^0] \\ & \quad + J_{a,b}^{(\text{invariant})1}[f_a^0, f_b^0]) + \delta_{\alpha 0} \sum_{bcd} (J_{ab,cd}^{(\text{reactive})0}[f_c^0, f_d^1] \\ & \quad + J_{ab,cd}^{(\text{reactive})0}[f_c^1, f_d^0] + J_{ab,cd}^{(\text{reactive})1}[f_c^0, f_d^0]) \\ & \quad + \delta_{\alpha 1} \sum_{bcd} J_{ab,cd}^{(\text{reactive})0}[f_c^0, f_d^0] \end{aligned} \tag{88}$$

and for the fields

$$\begin{aligned} & \partial_t^1 x_l + \vec{u} \cdot \vec{\nabla} x_l = \delta_{\alpha 0} n^{-1} S_l^{(n)(\text{reactive})1} + \delta_{\alpha 1} n^{-1} S_l^{(n)(\text{reactive})0}, \\ & \partial_t^1 n + \vec{\nabla} \cdot (\vec{u} n) = 0, \\ & \partial_t^1 \vec{u} + \vec{u} \cdot \vec{\nabla} \vec{u} + \rho^{-1} \vec{\nabla} p^{(0)} = \delta_{\alpha 0} \rho^{-1} \overline{\vec{S}}^{(p)(0)}, \\ & \partial_t^1 T + \vec{u} \cdot \vec{\nabla} T + \frac{2}{D n k_B} [p^{(0)} \vec{\nabla} \cdot \vec{u} + \vec{\nabla} \cdot (\vec{u} w^{(0)})] \\ & \quad = \xi^{(\text{invariant})1} + \delta_{\alpha 0} \xi^{(\text{reactive})1} + \delta_{\alpha 1} \xi^{(\text{reactive})0}, \end{aligned} \tag{89}$$

where we have used the fact that at zeroth order there are no velocity-independent vectors and only the unit tensor available so that we must have $\overleftrightarrow{P}^{(0)} = p^{(0)} \overleftrightarrow{1}$, $\overleftrightarrow{W}^{(0)} = w^{(0)} \overleftrightarrow{1}$, and all vector fluxes must vanish.

In general, the first-order distribution must take the form

$$f_l^{(1)}(\vec{r},\vec{V};t)=nx_l\phi_l(\vec{V}) \times\left[\begin{array}{c} h_l(\vec{V})+\mathcal{A}_l(\vec{V})\vec{V}\cdot\vec{\nabla}n+\mathcal{B}_l\vec{V}\cdot\vec{\nabla}T \\ +\overleftrightarrow{\mathcal{C}}_l:\left(\vec{\nabla}\vec{V}-\frac{1}{D}\overleftrightarrow{1}\vec{\nabla}\cdot\vec{V}\right)+ \\ \mathcal{D}_l\vec{\nabla}\cdot\vec{V}+\sum_k\mathcal{E}_{lk}\vec{V}\cdot\vec{\nabla}x_k \end{array}\right], \tag{90}$$

where I have written the zeroth-order distribution in the form $f_l^{(0)}=nx_l\phi_l(V)$. Here the coefficients $\mathcal{A}_l$, $\mathcal{B}_l$,... are scalar functions of the velocity (and in general depend also on space and time through a dependence on the local hydrodynamic variables as does the zeroth-order distribution, although for the sake of conciseness this dependence has been suppressed). The function $h(V)$ represents the first-order correction to $\phi(V)$ due to the energy-dependent chemical reactions: for example, if the only allowed interaction were $A+A\rightarrow A+B$ and this only took place if the c.m. kinetic energy were greater than some threshold, E_{AB}, then starting with a system of all A-type atoms, one would expect to build up a preponderance of fast B atoms and a corresponding deficit of fast A atoms. It vanishes in the case that $\alpha>2$ and energy is conserved by the nonreactive dynamics. The consequences of different orderings of the reaction terms will be considered separately.

1. Ultraslow reactions: $\alpha>2$

In this case, there are no reactive terms in the first-order equations. The solution is therefore the same as for the equilibrium (or HCS) multiple-component system. The second-order balance equations will also have no reactive terms. Summing up to second order, the Navier–Stokes order balance equations are then

$$\frac{\partial}{\partial t}x_l+\vec{u}\cdot\vec{\nabla}x_l+n^{-1}\left[\vec{\nabla}\cdot\vec{j}_l-x_l\vec{\nabla}\cdot\sum_l\vec{j}_l^K\right]=0, \tag{91}$$

$$\frac{\partial}{\partial t}n+\vec{\nabla}\cdot\vec{u}n+\vec{\nabla}\cdot\sum_l\vec{j}_l^K=0,$$

$$\frac{\partial}{\partial t}\vec{u}+\vec{u}\cdot\vec{\nabla}\vec{u}+\rho^{-1}(\vec{\nabla}\cdot\overleftrightarrow{P}-\vec{u}\vec{\nabla}\cdot\vec{Q})=0,$$

$$\frac{\partial}{\partial t}T+\vec{u}\cdot\vec{\nabla}T-\frac{T}{n}\vec{\nabla}\cdot\sum_l\vec{j}_l^K+\frac{2}{Dnk_B}\times\left[\overleftrightarrow{P}:\vec{\nabla}\vec{u}+\vec{\nabla}\cdot\vec{q}+\vec{\nabla}\cdot(\vec{u}\cdot\overleftrightarrow{W})+\frac{1}{2}\vec{Q}\cdot\vec{\nabla}u^2\right]=\xi^{(\text{invariant})}, \tag{92}$$

where the fluxes are the sum of zeroth- and first-order contributions, $\overleftrightarrow{P}=\overleftrightarrow{P}^{(0)}+\overleftrightarrow{P}^{(1)}$, and the source ξ consists of (nonreactive) contributions summed through second order. This means that for the granular case $\xi^{(\text{invariant})}\neq 0$, the Navier–Stokes order balance equations require knowledge of the second-order (or Burnett order) distribution function. There is, at this order, no coupling between the hydrodynamic equations and the reaction equations. Inserted into Eq. (91), the result would be the Navier–Stokes equations for elastic hard spheres or their generalization for inelastic hard spheres. If this expansion is continued, the αth-order balance equation for the concentrations would be

$$\partial^{(\alpha)}x_l+n^{-1}\left[\vec{\nabla}\cdot\vec{j}_l^{(\alpha-1)}-x_l\vec{\nabla}\cdot\sum_l\vec{j}_l^{K(\alpha-1)}\right] =n^{-1}\dot{S}_l^{(n)(\text{reactive})0}. \tag{93}$$

Clearly, the reaction equation remains unknown in this case since one would need to consistently include the higher-order hydrodynamic contributions that would come from the number current, which, in turn, would bring in couplings to higher-order gradients of the hydrodynamic fields. Without knowledge of these higher-order terms (and they are not known for even the one-component fluid) the reaction equation can only be consistently studied in the absence of hydrodynamic gradients when the reactive terms are treated as of order $\alpha>2$.

2. Slow reactions: $\alpha=2$

In this case, the first-order solution is again the same as in the nonreacting case. However, the sources will have second-order contributions so that the Navier–Stokes equations take the form

$$\frac{\partial}{\partial t}x_l+\vec{u}\cdot\vec{\nabla}x_l+n^{-1}\left[\vec{\nabla}\cdot\vec{j}_l-x_l\vec{\nabla}\cdot\sum_l\vec{j}_l^K\right] =n^{-1}S_l^{(n)(\text{reactive})0}, \tag{94}$$

$$\frac{\partial}{\partial t}n+\vec{\nabla}\cdot\vec{u}n+\vec{\nabla}\cdot\sum_l\vec{j}_l^K=0,$$

$$\frac{\partial}{\partial t}\vec{u}+\vec{u}\cdot\vec{\nabla}\vec{u}+\rho^{-1}(\vec{\nabla}\cdot\overleftrightarrow{P}-\vec{u}\vec{\nabla}\cdot\vec{Q})=\rho^{-1}\overline{\vec{S}}^{(p)(\text{reactive})0},$$

$$\frac{\partial}{\partial t}T+\vec{u}\cdot\vec{\nabla}T-\frac{T}{n}\vec{\nabla}\cdot\sum_l\vec{j}_l^K+\frac{2}{Dnk_B}\times\left[\overleftrightarrow{P}:\vec{\nabla}\vec{u}+\vec{\nabla}\cdot\vec{q}+\vec{\nabla}\cdot(\vec{u}\cdot\overleftrightarrow{W})+\frac{1}{2}\vec{Q}\cdot\vec{\nabla}u^2\right] =\xi^{(\text{invariant})}+\xi^{(\text{reactive})0}. \tag{95}$$

For the simplest case that the reactions conserve energy and momentum, the reactions are governed by exactly the convective–reaction–diffusion equation that one might expect. The reaction rates are calculated using the local equilibrium distribution as in elementary treatments.[22] Except for the usual modification of the transport properties arising from the use of the Enskog equation, as opposed to the Boltzmann equation, there are no new dense-fluid effects.

3. Moderate reactions: $\alpha=1$

For moderately fast reactions, the situation becomes more interesting. Considering here only the case that mass and energy are conserved by all collisions, the first-order balance equations—the generalization of the Euler equations—are found to be

$$\begin{aligned}
&\left(\frac{\partial}{\partial t}+\vec{u}\cdot\vec{\nabla}\right)x_l=n^{-1}S_l^{(n)(\text{reactive})0},\\
&\frac{\partial}{\partial t}n+\vec{\nabla}\cdot\vec{u}n=0,\\
&\left(\frac{\partial}{\partial t}+\vec{u}\cdot\vec{\nabla}\right)\vec{u}+\rho^{-1}\vec{\nabla}p^{(0)}=0,\\
&\left(\frac{\partial}{\partial t}+\vec{u}\cdot\vec{\nabla}\right)T+\frac{2}{Dnk_B}p\vec{\nabla}\cdot\vec{u}=0,
\end{aligned}\tag{96}$$

so that the reactions, with reaction rates calculated from the local-equilibrium distribution function, enter into the Euler equations. The Navier–Stokes equations will involve the reaction rates calculated up to first order in the distribution. In general, the only nonzero coupling in the reaction source will take the form $S_l^{(n)(\text{reactive})1}=S_l^{(n)}\vec{\nabla}\cdot\vec{u}$, where $S_l^{(n)}$ is a scalar function of the concentrations, density, and temperature. The Navier–Stokes equations will therefore take the form

$$\begin{aligned}
&\left(\frac{\partial}{\partial t}+\vec{u}\cdot\vec{\nabla}\right)x_l+n^{-1}\left(\vec{\nabla}\cdot\vec{j}_l-x_l\vec{\nabla}\cdot\sum_l \vec{j}_l^K\right)\\
&\qquad=n^{-1}S_l^{(n)(\text{reactive})0}+n^{-1}S_l^{(n)(\text{reactive})1}+S_l^{(n)}\vec{\nabla}\cdot\vec{u},\\
&\frac{\partial}{\partial t}n+\vec{\nabla}\cdot\vec{u}n+\vec{\nabla}\cdot\sum_l \vec{j}_l^K=0,\\
&\left(\frac{\partial}{\partial t}+\vec{u}\cdot\vec{\nabla}\right)\vec{u}+\rho^{-1}\vec{\nabla}\cdot\overleftrightarrow{P}=0,\\
&\left(\frac{\partial}{\partial t}+\vec{u}\cdot\vec{\nabla}\right)T-\frac{T}{n}\vec{\nabla}\cdot\sum_l \vec{j}_l^K+\frac{2}{Dnk_B}(\overleftrightarrow{P}:\vec{\nabla}\vec{u}+\vec{\nabla}\cdot\vec{q})=0.
\end{aligned}\tag{97}$$

The source term for the reactions has three contributions: the zeroth-order reaction rate (calculated using the local-equilibrium distribution function), the first-order correction (due to deviations of the distribution from local equilibrium), and a new, dense-fluid effect which couples the reactions to the divergence of the velocity field with some field-dependent coefficient $S_l^{(n)}$. This coupling is a dense-fluid effect which does not exist in the Boltzmann approximation and, not surprisingly, its origin is closely related to that of the bulk viscosity, which is also zero in the Boltzmann theory, but not the Enskog theory. (The calculation of these terms will be discussed in detail in a future publication, but the fact that these are the only possible couplings is due to the fact that no other Galilean-invariant scalars, linear in the gradients of the fields, can be constructed.)

4. Fast reactions: $\alpha=0$

In the case of fast reactions, no *a priori* assumption is made about the speed of the reactions compared to the hydrodynamic time scales. The balance equations to first order—i.e., the Euler equations—are

$$\begin{aligned}
&\left(\frac{\partial}{\partial t}+\vec{u}\cdot\vec{\nabla}\right)x_l=n^{-1}S_l^{(n)(\text{reactive})0}+S_l^{(n)}\vec{\nabla}\cdot\vec{u},\\
&\left(\frac{\partial}{\partial t}+\vec{u}\cdot\vec{\nabla}\right)n+n\vec{\nabla}\cdot\vec{u}=0,\\
&\left(\frac{\partial}{\partial t}+\vec{u}\cdot\vec{\nabla}\right)\vec{u}+\rho^{-1}\vec{\nabla}p=0,\\
&\left(\frac{\partial}{\partial t}+\vec{u}\cdot\vec{\nabla}\right)T+\frac{2}{Dnk_B}[p\vec{\nabla}\cdot\vec{u}+\vec{\nabla}\cdot(w\vec{u})]\\
&\qquad=\xi^{(\text{invariant})0}+\xi^{(\text{reactive})0}+\xi^{(\text{invariant})1}+\xi^{(\text{reactive})1},
\end{aligned}\tag{98}$$

so that even the Euler equations show the dense-fluid correction to the reaction rates. The second-order, or Navier–Stokes, equations require evaluation of the source terms to second order, which in turn requires knowledge of the distribution function to second order (also called Burnett order). One then expects that even for mass and energy conserving interactions, the reaction equation will contain couplings to gradients of all of the hydrodynamic fields. However, since the complete Burnett-order Chapman–Enskog solution of the Enskog equation is not even known for the case of a single-component fluid, there is no practical value in continuing the analysis for this case.

V. CONCLUSION

In this paper, the kinetic theory of reactive hard-core systems has been extended to include the possibility of mass transfer and/or loss and energy gain and loss. When mass is not conserved, the collision rule becomes dependent on the model used to describe the lost mass. Nevertheless, quite general expressions for the dynamics of phase functions and the distribution function of the system can be given and used to derive equally general expressions for the exact balance laws for mass, momentum, energy, and concentration. For example, when mass is conserved but a fixed fraction of the rest-frame kinetic energy is lost during collisions, the usual inelastic hard-sphere kinetic theory, used as a model of granular fluids,[16] is recovered. The kinetic theory was used, within the Enskog approximation, to discuss the various phenomenological laws, extensions of the Navier–Stokes equations, that arise from different orderings of the reaction terms within the Chapman–Enskog procedure. It was noted that the intuitive model of the Navier–Stokes equations coupled to a reaction–diffusion equation through a convective term only arises when the “speed” of the chemical reactions is comparable to some hydrodynamic time scale and, even in this case, an additional coupling to the divergence of the velocity field can occur in dense fluids.

How fast do we expect the chemistry to be relative to the hydrodynamics? In the model considered here, chemical reactions cannot be faster than the collision time. In fact, a typical reaction rate would be something like $p(\delta x)e^{-E/k_BT}\nu_{\text{col}}$, where p is the probability of a reaction occurring if the colliding atoms have energy greater than the reaction energy barrier, E, δx is the difference between the concentration of the species and its equilibrium concentration, and ν_{col} is the collision frequency. On the other hand, the Chapman–Enskog procedure is based on a gradient expansion: the small parameter ϵ will generally be a measure of the ratio of the typical microscopic length scale, the mean free path l_{mfp}, to a typical length scale for hydrodynamic gradients L. (In Fourier space, where gradients $\vec{\nabla}$ correspond to wave vectors $\vec{k}$, this becomes $\epsilon \sim k l_{\mathrm{mfp}}$.) So setting $p e^{-E/k_B T} \nu_{\mathrm{col}} \sim (k l_{\mathrm{mfp}})^{\alpha} \nu_{\mathrm{col}} \sim (l_{\mathrm{mfp}}/L)^{\alpha} \nu_{\mathrm{col}}$ gives

$$\alpha \sim \frac{\ln p(\delta x) - \dfrac{E}{k_B T}}{\ln(l_{\mathrm{mfp}}/L)}. \tag{99}$$

For systems in which hydrodynamics is applicable, one has $l_{\mathrm{mfp}}/L \ll 1$ so that α ranges from a minimum of $\ln p(\delta x)/\ln(l_{\mathrm{mfp}}/L) \geqslant 0$, for $k_B T \gg E$, to very large values for low temperatures. Far from chemical equilibrium, $\delta x \sim 1$, the lower limit could be arbitrarily close to zero depending on the reaction probability so that ''moderate'' and ''fast'' reactions are possible at high temperatures. Indeed, if all of these parameters are fixed, then fast reactions will always occur in the hydodrynamic regime limit $l_{\mathrm{mfp}}/L \rightarrow 0$. The conclusion is that, unless the concentrations are close to their equilibrium values, the reaction probabilities are very small or the temperature is extremely low, the concept of slow chemical reactions may be of limited applicability and so the correct phenomenological description, from the standpoint of kinetic theory, may be more complex than the reaction–diffusion–advection model.

In summary, if chemical reactions are slow compared to the rate of dissipation in the fluid, then hydrodynamics and chemistry are not meaningfully coupled. If the reaction rate is comparable to the rate of dissipation in the fluid—i.e., λk^2 for some transport coefficient λ and wave vector k—then the usual reaction–diffusion–advection equation results. For faster reactions, additional couplings occur and the chemistry and hydrodynamics become more interdependent. The detailed solution of the Enskog and the resulting phenomenological equations for particular reaction models will be the subject of a future publication where the importance for sonochemistry of additional terms, such as those occurring in Eq. (97), will be investigated.

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APPENDIX A: THE HARD-CORE LIOUVILLE OPERATOR

The goal in this Appendix is to provide motivation for the statement in the text that the form of the pseudo-Liouville operator is independent of the collision rule. To start with, restrict attention to a system of two atoms. Let $X(\Gamma;t)$ be the characteristic function for collisions after at time t beginning with the phase Γ at time 0 so that if the two atoms do not collide between during the interval $[0,t]$, then $X(\Gamma;t)=0$, whereas if they do collide, $X(\Gamma;t)=1$. Then the time evolution of the phase function $A_{\Gamma}(t)=A(\Gamma(t),t)$ is given by

$$A_{\Gamma}(t)=[1-X(\Gamma;t)]A(\Gamma_0(t),t)+X(\Gamma;t)A(\Gamma'(t),t), \tag{A1}$$

where $\Gamma_0(t)$ is just the phase of the system propagated a time t into the future in the absence of interactions and is explicitly $\Gamma_0(t)=(\vec{q}_1+\vec{v}_1 t,\vec{v}_1,\hat{l}_1,\vec{q}_2+\vec{v}_2 t,\vec{v}_2,\hat{l}_2)$. (Note that attention is restricted to the case that velocities are constant during free streaming: generalization to include one-body forces is straightforward.) The phase point $\Gamma'(t)$ is the position the system would reach in phase space if a collision occurred at some time $\tau(\Gamma) \in [0,t]$. Explicit expressions can also be given for its components such as $\vec{q}_1'(t)=\vec{q}_1+\vec{v}_1\tau+\vec{v}_1'(t-\tau)$, etc. Direct differentiation then gives

$$\begin{aligned}\frac{dA_{\Gamma}(t)}{dt} &= \frac{\partial A}{\partial t}+[1-X(\Gamma;t)]\frac{\partial q(t)}{\partial t}\cdot\frac{\partial}{\partial q(t)}A(\Gamma_0(t),t)\\ &\quad +X(\Gamma;t)\frac{\partial q(t)}{\partial t}\cdot\frac{\partial}{\partial q(t)}A(\Gamma'(t),t)\\ &\quad +\frac{dX(\Gamma;t)}{dt}[A(\Gamma'(t),t)-A(\Gamma_0(t),t)].\end{aligned} \tag{A2}$$

Now, from the definitions above

$$\begin{aligned}&[1-X(\Gamma;t)]\frac{\partial q(t)}{\partial t}\cdot\frac{\partial}{\partial q(t)}A(\Gamma_0(t),t)+X(\Gamma;t)\frac{\partial q(t)}{\partial t}\\ &\quad\cdot\frac{\partial}{\partial q(t)}A(\Gamma'(t),t)\\ &\quad=[1-X(\Gamma;t)]\sum_{i=1,2}\vec{v}_i\cdot\frac{\partial}{\partial\vec{q}_i(t)}A(\Gamma_0(t),t)\\ &\qquad+X(\Gamma;t)\sum_{i=1,2}\vec{v}_i^{IH}\cdot\frac{\partial}{\partial\vec{q}_i(t)}A(\Gamma'(t),t)\\ &\quad=\sum_{i=1,2}\vec{v}_i(t)\cdot\frac{\partial}{\partial\vec{q}_i(t)}A(\Gamma(t),t),\end{aligned} \tag{A3}$$

giving

$$\begin{aligned}\frac{dA_{\Gamma}(t)}{dt} &= \frac{\partial A}{\partial t}+\sum_{i=1,2}\vec{v}_i(t)\cdot\frac{\partial}{\partial\vec{q}_i(t)}A_{\Gamma}(t)\\ &\quad+\frac{dX(\Gamma;t)}{dt}(A(\Gamma'(t),t)-A(\Gamma_0(t),t)).\end{aligned} \tag{A4}$$

Now, since $X(\Gamma;t)$ has the form of a step function [it is zero if $t<\tau(\Gamma)$ and one otherwise], we must have

$$\frac{dX(\Gamma;t)}{dt}=\delta(t-\tau(\Gamma)), \tag{A5}$$

and this also gives the correct result (zero) if $\tau(\Gamma)$ is imaginary (indicating that no collision ever occurs starting from the given state). Then, using

$$\begin{aligned}\delta(t-\tau(\Gamma))[A(\Gamma'(t),t)-A(\Gamma_0(t),t))]\\ &= \delta(t-\tau(\Gamma)),[A(\Gamma'(\tau(\Gamma)),\tau(\Gamma))\\ &\quad -A(\Gamma_0(\tau(\Gamma)),\tau(\Gamma))]\\ &= \delta(t-\tau(\Gamma))\left(\sum_{l_1'l_2'}\hat{M}_{l_1l_2}^{l_1'l_2'}\hat{b}_{l_1l_2}^{l_1'l_2'}-1\right)A_\Gamma(\tau(\Gamma))\\ &= \delta(t-\tau(\Gamma))\left(\sum_{l_1'l_2'}\hat{M}_{l_1l_2}^{l_1'l_2'}\hat{b}_{l_1l_2}^{l_1'l_2'}-1\right)A_\Gamma(t) \qquad \text{(A6)}\end{aligned}$$

gives

$$\begin{aligned}\frac{dA_\Gamma(t)}{dt} &= \left[\frac{\partial}{\partial t}+\sum_{i=1,2}\vec{v}_i(t)\cdot\frac{\partial}{\partial\vec{q}_i(t)}+\delta(t-\tau(\Gamma))\right.\\ &\quad\left.\times\left(\sum_{l_1'}\hat{M}_{l_1l_2}^{l_1'l_2'}\hat{b}_{l_1l_2}^{l_1'l_2'}-1\right)\right]A_\Gamma(t). \qquad \text{(A7)}\end{aligned}$$

In order to express the right-hand side entirely in terms of $\Gamma(t)$ rather than the initial condition Γ, the temporal δ function is rewritten using

$$\delta(q_{12}(t)-\sigma_{l_1,l_2})=\sum_i\frac{\delta(t-\tau_i(\Gamma))}{\left|\frac{\partial}{\partial t}q_{12}(t)\right|_{t=\tau_i(\Gamma)}}, \qquad \text{(A8)}$$

where $\tau_i(\Gamma)$ are the roots of $q_{12}^2(\tau_i)-\sigma_{l_1l_2}^2=0$. They correspond to the time at which the two atoms are first in contact—i.e., the physical collision time which is denoted as $\tau(\Gamma)$—and the time at which they are last in contact if they are allowed to pass through one another (which is not physical). One picks out the correct root by noting that at the physical collision time $\vec{q}_{12}(\tau)\cdot\vec{v}_{12}(\tau)<0$, while the sign is reversed at the unphysical collision time so that

$$\begin{aligned}\delta(q_{12}(t)-\sigma_{l_1l_2})\Theta(-\vec{q}_{12}(t)\cdot\vec{v}_{12}(t))\\ &= \frac{\delta(t-\tau(\Gamma))}{\left|\frac{\partial}{\partial t}q_{12}(t)\right|_{t=\tau(\Gamma)}}\\ &= \frac{\delta(t-\tau(\Gamma))}{|\hat{q}_{12}(\tau)\cdot\vec{v}_{12}(\tau)|}=\frac{\delta(t-\tau(\Gamma))}{|\hat{q}_{12}(t)\cdot\vec{v}_{12}(t)|}, \qquad \text{(A9)}\end{aligned}$$

or

$$\begin{aligned}\delta(t-\tau(\Gamma)) &= \delta(q_{12}(t)-\sigma_{l_1l_2})\Theta(-\vec{q}_{12}(t)\cdot\vec{v}_{12}(t))\\ &\quad\times|\hat{q}_{12}(t)\cdot\vec{v}_{12}(t)|, \qquad \text{(A10)}\end{aligned}$$

giving finally

$$\frac{dA_\Gamma(t)}{dt}=\left[\frac{\partial}{\partial t}+\hat{L}(t)\right]A_\Gamma(t), \qquad \text{(A11)}$$

with

$$\hat{L}(t)=\sum_{1\leqslant i\leqslant 2}\vec{v}_i(t)\cdot\frac{\partial}{\partial\vec{q}_i(t)}+\sum_{1\leqslant i<j\leqslant 2}\hat{T}_+(12;t), \qquad \text{(A12)}$$

where, for arbitrary phase function $B(\Gamma,t)$,

$$\begin{aligned}\hat{T}_+(12;t)B(\Gamma(t),t)\\ &= \delta(q_{12}(t)-\sigma_{l_1l_2})\Theta(-\vec{q}_{12}(t)\cdot\vec{v}_{12}(t))|\hat{q}_{12}(t)\cdot\vec{v}_{12}(t)|\\ &\quad\times\left(\sum_{l_1'l_2'}\hat{M}_{l_1l_2}^{l_1'l_2'}\hat{b}_{l_1l_2}^{l_1'l_2'}-1\right)B(\Gamma(t),t). \qquad \text{(A13)}\end{aligned}$$

For more than two atoms, one simply extends the sums in Eq. (A12) since, in a finite system, only binary collisions can occur.

Starting with an initial condition $A_\Gamma(t)=A(\Gamma)$, iteration of Eq. (A11) immediately gives

$$\left.\frac{d^nA_\Gamma(t)}{dt^n}\right|_{t=0}=\hat{L}^nA(\Gamma), \qquad \text{(A14)}$$

with $\hat{L}=\hat{L}(0)$, which implies that

$$A_\Gamma(t)=\exp(\hat{L}t)A(\Gamma) \qquad \text{(A15)}$$

and

$$\frac{d}{dt}A_\Gamma(t)=\hat{L}\exp(\hat{L}t)A(\Gamma)=\hat{L}A_\Gamma(t), \qquad \text{(A16)}$$

as claimed in the text.

APPENDIX B: THE ADJOINT LIOUVILLE OPERATOR

To derive the adjoint operator, begin with its definition

$$\int d\Gamma\,B(\Gamma)L_+A(\Gamma)=\int d\Gamma[L_+^AB(\Gamma)]A(\Gamma) \qquad \text{(B1)}$$

or, more explicitly,

$$\begin{aligned}\sum_{l_1,l_2,\ldots}\int dx_1dx_2\cdots B(\Gamma)L_+A(\Gamma)\\ &= \sum_{l_1,l_2}\int dx_1dx_2[L_+^AB(\Gamma)]A(\Gamma). \qquad \text{(B2)}\end{aligned}$$

Now,

$$L_+=L_+^{(0)}+\sum_{i<j}T_+(ij) \qquad \text{(B3)}$$

and it is obvious that, neglecting surface terms,

$$\int d\Gamma\,B(\Gamma)L_+^{(0)}A(\Gamma)=\int d\Gamma[-L_+^{(0)}B(\Gamma)]A(\Gamma), \qquad \text{(B4)}$$

so

$$L_+^{(0)A}=-L_+^{(0)}. \qquad \text{(B5)}$$

Next, consider one of the collision operators and restrict attention to a system of two atoms. Then,

$$\sum_{l_1,l_2}\int dx_1dx_2B(x_1,l_1;x_2,l_2)[T_+(12)A(x_1,l_1;x_2,l_2)]$$
$$=-\sum_{l_1,l_2,a,b}\int dx_1dx_2B(x_1,l_1;x_2,l_2)\Theta(-\vec{v}_{12}\cdot\hat{q}_{12})$$
$$\times\delta(q_{12}-\sigma_{12})\vec{v}_{12}\cdot\hat{q}_{12}[K^{ab}_{l_1l_2}(x_1,l_1;x_2,l_2)$$
$$\times A(\hat{b}^{ab}_{l_1l_2}x_1,a;\hat{b}^{ab}_{l_1l_2}x_2,b)-\delta_{al_1}\delta_{bl_2}A(x_1,l_1;x_2,l_2)]. \tag{B6}$$

Consider the first term. Relabeling the species in the sum gives

$$-\sum_{l_1,l_2,a,b}\int dx_1dx_2B(x_1,l_1;x_2,l_2)\Theta(-\vec{v}_{12}\cdot\hat{q}_{12})$$
$$\times\delta(q_{12}-\sigma_{l_1l_2})\vec{v}_{12}\cdot\hat{q}_{12}K^{ab}_{l_1l_2}(x_1,l_1;x_2,l_2)$$
$$\times A(\hat{b}^{ab}_{l_1l_2}x_1,a;\hat{b}^{ab}_{l_1l_2}x_2,b)$$
$$=-\sum_{l_1,l_2,a,b}\int dx_1dx_2B(x_1,a;x_2,b)$$
$$\times\Theta(-\vec{v}_{12}\cdot\hat{q}_{12})\delta(q_{12}-\sigma_{ab})\vec{v}_{12}$$
$$\cdot\hat{q}_{12}K^{l_1l_2}_{ab}(x_1,a;x_2,b)A(\hat{b}^{l_1l_2}_{ab}x_1,l_1;\hat{b}^{l_1l_2}_{ab}x_2,l_2). \tag{B7}$$

Assuming that the collision operator is invertible, then introducing new integration variables $y_i=\hat{b}^{l_1l_2}_{ab}x_i$ and the corresponding Jacobian

$$J^{l_1l_2}_{ab}(y_1,y_2)=\left|\frac{\partial((\hat{b}^{l_1l_2}_{ab})^{-1}y_1,(\hat{b}^{l_1l_2}_{ab})^{-1}y_2)}{\partial(y_1,y_2)}\right| \tag{B8}$$

gives

$$-\sum_{l_1,l_2,a,b}\int dx_1dx_2B(x_1,l_1;x_2,l_2)\Theta(-\vec{v}_{12}\cdot\hat{q}_{12})\delta(q_{12}-\sigma_{l_1l_2})\vec{v}_{12}\cdot\hat{q}_{12}K^{ab}_{l_1l_2}(x_1,l_1;x_2,l_2)A(\hat{b}^{ab}_{l_1l_2}x_1,a;\hat{b}^{ab}_{l_1l_2},b)$$
$$=-\sum_{l_1,l_2,a,b}\int dy_1dy_2J^{l_1l_2}_{ab}(y_1,y_2)B((\hat{b}^{l_1l_2}_{ab})^{-1}y_1,a;(\hat{b}^{l_1l_2}_{ab})^{-1}y_2;b)\Theta(-(\hat{b}^{l_1l_2}_{ab})^{-1}\vec{v}_{12}\cdot\vec{q}_{12})\delta(q_{12}-\sigma_{ab})[(\hat{b}^{l_1l_2}_{ab})^{-1}\vec{v}_{12}]$$
$$\cdot\vec{q}_{12}K^{l_1l_2}_{ab}((\hat{b}^{l_1l_2}_{ab})^{-1}y_1,a;(\hat{b}^{l_1l_2}_{ab})^{-1}y_2,b)A(y_1,l_1;y_2,l_2)$$
$$=-\sum_{l_1,l_2,a,b}\int dy_1dy_2A(y_1,l_1;y_2,l_2)[J^{l_1l_2}_{ab}(y_1,y_2)(\hat{b}^{l_1l_2}_{ab})^{-1}\Theta(-\vec{v}_{12}\cdot\hat{q}_{12})\delta(q_{12}-\sigma_{l_1l_2})\vec{v}_{12}$$
$$\cdot\hat{q}_{12}K^{l_1l_2}_{ab}(y_1,l_1;y_2,l_1)]B(x_1,l_1;x_2,l_2), \tag{B9}$$

where the operator $(\hat{b}^{l_1l_2}_{ab})^{-1}$ has the effect of changing the species from l_1, l_2 to *a, b*. One can then write

$$T^A_+(12)B(x_1,l_1;x_2,l_2)$$
$$=-\sum_{ab}[J^{l_1l_2}_{ab}(x_1,x_2)(\hat{b}^{l_1l_2}_{ab})^{-1}K^{l_1l_2}_{ab}(x_1,l_1;x_2,l_2)-1]\Theta(-\vec{v}_{12}\cdot\hat{q}_{12})\delta(q_{12}-\sigma_{l_1l_2})\vec{v}_{12}\cdot\hat{q}_{12}B(x_1,l_1;x_2,l_2). \tag{B10}$$

In some cases of interest, the collision dynamics may not be invertible. For example, suppose that collisions with total rest frame energy less than some threshold, *E*, are elastic while those with energy greater than this are inelastic. Then a pair of atoms with rest frame energy after collision of $\frac{1}{2}\mu_{12}v'^2_{12}<E$ might have resulted from either (a) a collision between two atoms with rest-frame energy below the threshold or (b) a collision between two atoms that had energy above the threshold, but that lost part of this due to the inelastic process. In this case, it is necessary in the definition of the adjoint operator to include an additional sum over the various branches of the inverse collision dynamics. Even when it occurs, such a complication may not be of practical importance since it is often the case that expressions involving the adjoint operator T^A_+ can be rewritten in terms of the original operator T_+.

APPENDIX C: DERIVATION OF THE BALANCE EQUATIONS

In this section, the general form of the local balance equations is derive and then specialized to the partial density, momentum and energy fields.

1. General form of the balance equations

Consider any one-body phase function of the form

$$\hat{\Psi}_l(\vec{r})=\sum_i\psi_{l_i}(\vec{v}_i)\delta(\vec{r}-\vec{q}_i)\delta_{l_il} \tag{C1}$$

and its average

$$\begin{aligned}\Psi_l(\vec{r},t) &= \langle\hat{\Psi}_l(\vec{r});t\rangle \\ &= \frac{N}{V}\sum_{l_1}\int dx_1 f_{l_i}(x_1,t)\,\psi_{l_i}(\vec{v}_1)\,\delta(r-\vec{q}_1)\,\delta_{l_1 l} \\ &= n\int d\vec{v}_1 f_l(\vec{r},\vec{v}_1,t)\,\psi_l(\vec{v}_1).\end{aligned} \tag{C2}$$

The balance equation for this follows from the first BBGKY equation

$$\left(\frac{d}{dt}+\vec{v}_1\cdot\frac{\partial}{\partial\vec{q}_1}\right)f_{l_1}(x_1)=\sum_{l_2}\int dx_2\,\overline{T}_-(12)\,f_{l_1l_2}(x_1x_2) \tag{C3}$$

and is

$$\begin{aligned}&\frac{d}{dt}\Psi_l(\vec{r},t)+\vec{\nabla}\cdot\int d\vec{v}_1 f_l(\vec{r},\vec{v}_1,t)\vec{v}_1\psi_l(\vec{v}_1) \\ &\quad=\sum_{l_1l_2}\int dx_1\,\delta_{ll_1}\psi_{l_1}(\vec{v}_1)\,\delta(r-\vec{q}_1) \\ &\quad\quad\times\int dx_2\,\overline{T}_-(12)\,f_{ll_2}(x_1x_2).\end{aligned} \tag{C4}$$

Introducing the specific velocity $\vec{V}_1(\vec{r},t)=\vec{v}_1-\vec{u}\ (\vec{r},t)$, the second term on the left becomes

$$\begin{aligned}&\int d\vec{v}_1 f_l(\vec{r},\vec{v}_1,t)\vec{v}_1\psi_l(\vec{v}_1) \\ &\quad=\vec{u}(\vec{r},t)\Psi_l(\vec{r},t)+\int d\vec{v}_1 f_l(\vec{r},\vec{v}_1,t)\vec{V}_1(\vec{r},t)\,\psi_l(\vec{v}_1),\end{aligned} \tag{C5}$$

while it proves more convenient to rewrite the right-hand side in terms of the $\hat{T}_+$ collision operator

$$\begin{aligned}&\sum_{l_1l_2}\int dx_1\,\delta_{ll_1}\psi_{l_1}(\vec{v}_1)\,\delta(r-\vec{q}_1)\int dx_2\,\overline{T}_-(12)\,f_{ll_2}(x_1x_2) \\ &\quad=\sum_{l_1l_2}\int dx_1dx_2 f_{ll_2}(x_1x_2)T_+(12)\,\delta_{ll_1}\psi_{l_1}(\vec{v}_1)\,\delta(r-\vec{q}_1),\end{aligned} \tag{C6}$$

so that the balance equation becomes

$$\begin{aligned}&\frac{d}{dt}\Psi_l(\vec{r},t)+\vec{\nabla}\cdot\vec{u}(\vec{r},t)\Psi_l(\vec{r},t)+\vec{\nabla} \\ &\quad\cdot\int d\vec{v}_1 f_l(\vec{r},\vec{v}_1,t)\vec{V}_1\psi_l(\vec{v}_1) \\ &\quad=\sum_{l_1l_2}\int dx_1dx_2 f_{l_1l_2}(x_1x_2)\,\delta(r-\vec{q}_1)T_+(12)\,\delta_{ll_1}\psi_{l_1}(\vec{v}_1),\end{aligned} \tag{C7}$$

with

$$\begin{aligned}&T_+(12)\,\delta_{ll_1}\psi_{l_1}(\vec{v}_1) \\ &\quad=-\hat{q}_{12}\cdot\vec{v}_{12}\delta(q_{12}-\sigma_{l_1l_2})\Theta(-\hat{q}_{12}\cdot\vec{v}_{12}) \\ &\quad\quad\times\left(\sum_{l_1'l_2'}K_{l_1l_2}^{l_1'l_2'}(x_{12})b_{l_1l_2}^{l_1'l_2'}-1\right)\delta_{ll_1}\psi_{l_1}(\vec{v}_1) \\ &\quad=-\hat{q}_{12}\cdot\vec{v}_{12}\delta(q_{12}-\sigma_{l_1l_2})\Theta(-\hat{q}_{12}\cdot\vec{v}_{12}) \\ &\quad\quad\times\sum_{l_1'l_2'}[K_{l_1l_2}^{l_1'l_2'}(x_{12})b_{l_1l_2}^{l_1'l_2'}-\delta_{l_1l_1'}\delta_{l_2l_2'}]\delta_{ll_1}\psi_{l_1}(\vec{v}_1).\end{aligned} \tag{C8}$$

In general, the right-hand side can be separated into a sum of a flux and a source term. Let

$$B_{l_1l_2,l_1'l_2';l}(x_1,x_2)=[K_{l_1l_2}^{l_1'l_2'}(x_{12})b_{l_1l_2}^{l_1'l_2'}-\delta_{l_1l_1'}\delta_{l_2l_2'}]\delta_{ll_1}\psi_{l_1}(\vec{v}_1) \tag{C9}$$

and define its even and odd components as

$$\begin{aligned}&F_{l_1l_2,l_1'l_2';l}(x_1,x_2) \\ &\quad=\tfrac{1}{2}[B_{l_1l_2,l_1'l_2';l}(x_1,x_2)-B_{l_1l_2,l_1'l_2';l}(x_2,x_1)] \\ &\quad=\tfrac{1}{2}[K_{l_1l_2}^{l_1'l_2'}(x_{12})b_{l_1l_2}^{l_1'l_2'}-\delta_{l_1l_1'}\delta_{l_2l_2'}] \\ &\quad\quad\times[\delta_{ll_1}\psi_{l_1}(\vec{v}_1)-\delta_{ll_2}\psi_{l_2}(\vec{v}_2)],\end{aligned}$$

$$\begin{aligned}&S_{l_1l_2,l_1'l_2';l}(x_1,x_2) \\ &\quad=\tfrac{1}{2}[B_{l_1,l_2,l_1'l_2';l}(x_1,x_2)+B_{l_1l_2,l_1'l_2';l}(x_2,x_1)] \\ &\quad=\tfrac{1}{2}[K_{l_1l_2}^{l_1'l_2'}(x_{12})b_{l_1l_2}^{l_1'l_2'}-\delta_{l_1l_1'}\delta_{l_2l_2'}] \\ &\quad\quad\times[\delta_{ll_1}\psi_{l_1}(\vec{v}_1)+\delta_{ll_2}\psi_{l_2}(\vec{v}_2)],\end{aligned} \tag{C10}$$

so that

$$\begin{aligned}&\frac{d}{dt}\Psi_l(\vec{r},t)+\vec{\nabla}\cdot\vec{u}(\vec{r},t)\Psi_l(\vec{r},t) \\ &\quad+\vec{\nabla}\cdot\sum_l\int d\vec{v}_1 f_l(\vec{r},\vec{v}_1,t)\vec{V}_1\psi_l(\vec{v}_1) \\ &\quad=-\sum_{l_1l_2l_1'l_2'}\int dx_1dx_2 f_{l_1l_2}(x_1x_2)\,\delta(\vec{r}-\vec{q}_1)\hat{q}_{12}\cdot\vec{v}_{12}\delta \\ &\quad\quad\times(q_{12}-\sigma_{l_1l_2})\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})[F_{l_1l_2,l_1'l_2';l}(x_1,x_2) \\ &\quad\quad+S_{l_1l_2,l_1'l_2';l}(x_1,x_2)].\end{aligned} \tag{C11}$$

Then relabel the dummy variables to give

$$\begin{aligned}
&\sum_{l_1l_2l_1'l_2'}\int dx_1dx_2 f_{l_1l_2}(x_1x_2)\,\delta(\vec r-\vec q_1)\vec q_{12}\cdot\vec v_{12}\delta(q_{12}-\sigma_{l_1l_2})\\
&\quad\times\Theta(-\hat q_{12}\cdot\vec v_{12})F_{l_1l_2,l_1'l_2';l}(x_1,x_2)\\
&\quad=\frac{1}{2}\sum_{l_1l_2l_1'l_2'}\int dx_1dx_2\vec q_{12}\cdot\vec v_{12}\delta(q_{12}-\sigma_{l_1l_2})\\
&\qquad\times\Theta(-\hat q_{12}\cdot\vec v_{12})F_{l_1l_2,l_1'l_2';l}(x_1,x_2)f_{l_1l_2}(x_1x_2)\\
&\qquad\times[\delta(\vec r-\vec q_1)-\delta(\vec r-\vec q_2)],
\end{aligned}\tag{C12}$$

where use has been made of the asymmetry of $F_{l_1l_2,l_1'l_2';l}(x_1,x_2)$ and of the symmetry of the distribution under an interchange of atoms. Finally, write

$$\begin{aligned}
&\delta(\vec r-\vec q_1)-\delta(\vec r-\vec q_2)\\
&\quad=\int_0^1 dx\,\frac{d}{dx}\,\delta(\vec r-x\vec q_1-(1-x)\vec q_2)\\
&\quad=-\vec\nabla\cdot\vec q_{12}\int_0^1 dx\;\delta(\vec r-x\vec q_1-(1-x)\vec q_2),
\end{aligned}\tag{C13}$$

so that the balance equation becomes

$$\frac{d}{dt}\Psi_l(\vec r,t)+\vec\nabla\cdot\vec u(\vec r,t)\Psi_l(\vec r,t)+\vec\nabla\cdot\vec F_l(\vec r,t)=S_l(\vec r,t),\tag{C14}$$

with the flux written as $\vec F_l(\vec r,t)=\vec F_l^K(\vec r,t)+\vec F_l^V(\vec r,t)$, where the kinetic contribution is

$$\vec F^K(\vec r,t)=\int d\vec v_1 f_l(\vec r,\vec v_1,t)\vec V_1\psi_l(\vec v_1)\tag{C15}$$

and the collisional contribution is

$$\begin{aligned}
\vec F^V(\vec r,t)=&-\sum_{l_1l_2l_1'l_2'}\int dx_1dx_2\vec q_{12}(\vec q_{12}\cdot\vec v_{12})\\
&\times\delta(q_{12}-\sigma_{l_1l_2})\Theta(-\hat q_{12}\cdot\vec v_{12})\\
&\times f_{l_1l_2}(x_1x_2)F_{l_1l_2,l_1'l_2';l}(x_1,x_2)\\
&\times\int_0^1 dx\;\delta(\vec r-x\vec q_1-(1-x)\vec q_2)
\end{aligned}\tag{C16}$$

and the source is

$$\begin{aligned}
S_l(\vec r,t)=&-\sum_{l_1l_2l_1'l_2'}\int dx_1dx_2(\vec q_{12}\cdot\vec v_{12})\delta(q_{12}-\sigma_{l_1l_2})\\
&\times\Theta(-\hat q_{12}\cdot\vec v_{12})f_{l_1l_2}(x_1x_2)S_{l_1l_2,l_1'l_2';l}(x_1,x_2)\\
&\times\delta(\vec r-\vec q_1).
\end{aligned}\tag{C17}$$

2. Local number density

Setting $\psi_l(\vec v_1)=1$, one has that

$$\begin{aligned}
&F_{l_1l_2,l_1'l_2';l}(x_1,x_2)\\
&\quad=\tfrac{1}{2}[K_{l_1l_2}^{l_1'l_2'}(x_{12})(\delta_{ll_1'}-\delta_{ll_2'})-\delta_{l_1l_1'}\delta_{l_2l_2'}(\delta_{ll_1}-\delta_{ll_2})],
\end{aligned}$$

$$\begin{aligned}
&S_{l_1l_2,l_1'l_2';l}(x_1,x_2)\\
&\quad=\tfrac{1}{2}[K_{l_1l_2}^{l_1'l_2'}(x_{12})(\delta_{ll_1'}+\delta_{ll_2'})-\delta_{l_1l_1'}\delta_{l_2l_2'}(\delta_{ll_1}+\delta_{ll_2})].
\end{aligned}\tag{C18}$$

From the normalization condition

$$1=\sum_{lb}K_{l_1l_2}^{lb},\tag{C19}$$

one has that

$$\begin{aligned}
&\sum_{l_1'l_2'}F_{l_1l_2,l_1'l_2';l}(x_1,x_2)\\
&\quad=\tfrac{1}{2}\sum_{l_1'l_2'}K_{l_1l_2}^{l_1'l_2'}(x_{12})(\delta_{ll_1'}-\delta_{ll_2'}-\delta_{ll_1}+\delta_{ll_2}),
\end{aligned}$$

$$\begin{aligned}
&\sum_{l_1'l_2'}S_{l_1l_2,l_1'l_2';l}(x_1,x_2)\\
&\quad=\tfrac{1}{2}\sum_{l_1'l_2'}K_{l_1l_2}^{l_1'l_2'}(x_{12})(\delta_{ll_1'}-\delta_{ll_2'}+\delta_{ll_1}-\delta_{ll_2}),
\end{aligned}\tag{C20}$$

so that the balance equation becomes

$$\frac{d}{dt}n_l+\vec\nabla\cdot(\vec u n_l)+\vec\nabla\cdot\vec j_l=S_l^{(n)},\tag{C21}$$

with the source

$$\begin{aligned}
S_l^{(n)}=&-\tfrac{1}{2}\sum_{abl_1l_2}\int dx_1dx_2(\hat q_{12}\cdot\vec v_{12})\delta(q_{12}-\sigma_{l_1l_2})\\
&\times\Theta(-\hat q_{12}\cdot\vec v_{12})f_{l_1l_2}(x_1x_2)\delta(\vec r-\vec q_1)K_{l_1l_2}^{ab}(x_{12})\\
&\times(\delta_{al}+\delta_{bl}-\delta_{ll_1}-\delta_{ll_2})
\end{aligned}\tag{C22}$$

and the number current $\vec j_l=\vec j_l^K+\vec j_l^V$ with

$$\vec j_l^K=\int d\vec v_1 f_l(\vec r,\vec v_1,t)\vec V_1\tag{C23}$$

and

$$\begin{aligned}
\vec j_l^V=&-\tfrac{1}{2}\sum_{abl_1l_2}\int dx_1dx_2\vec q_{12}(\hat q_{12}\cdot\vec v_{12})\delta(q_{12}-\sigma_{l_1l_2})\\
&\times\Theta(-\hat q_{12}\cdot\vec v_{12})f_{l_1l_2}(x_1x_2)K_{l_1l_2}^{ab}(x_{12})\\
&\times(\delta_{al}-\delta_{bl}-\delta_{ll_1}+\delta_{ll_2})\\
&\times\int_0^1 dx\;\delta(\vec r-x\vec q_1-(1-x)\vec q_2).
\end{aligned}\tag{C24}$$

The balance equations for total number and mass density follow immediately. Summing over l gives

$$\frac{d}{dt}n(\vec r,t)+\vec\nabla\cdot\vec u(\vec r,t)n(\vec r,t)+\vec\nabla\cdot\sum_l\vec j_l^K=0,\tag{C25}$$

since the sum of the collisional contributions to the number current vanishes. Similarly, multiplying by m_l and then summing gives the balance equation for local mass density:

$$\frac{d}{dt}\rho(\vec{r},t)+\vec{\nabla}\cdot\vec{u}(\vec{r},t)\rho(\vec{r},t)+\vec{\nabla}\cdot\vec{Q}=S^{(\rho)}. \tag{C26}$$

Here the anomalous mass flux is

$$\begin{aligned}\vec{Q}=&-\tfrac{1}{2}\sum_{abl_1l_2}\int dx_1dx_2\vec{q}_{12}(\hat{q}_{12}\cdot\vec{v}_{12})\,\delta(q_{12}-\sigma_{l_1l_2})\\&\times\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})f_{l_1l_2}(x_1x_2)K^{ab}_{l_1l_2}(x_{12})\\&\times(m_a-m_b-m_{l_1}+m_{l_2})\\&\times\int_0^1 dx\;\delta(\vec{r}-x\vec{q}_1-(1-x)\vec{q}_2)\end{aligned} \tag{C27}$$

and the mass source term is

$$\begin{aligned}S^{(\rho)}_l=&\tfrac{1}{2}\sum_{abl_1l_2}\int dx_1dx_2(\hat{q}_{12}\cdot\vec{v}_{12})\,\delta(q_{12}-\sigma_{l_1l_2})\\&\times\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})f_{l_1l_2}(x_1x_2)\,\delta(\vec{r}-\vec{q}_1)K^{ab}_{l_1l_2}(x_{12})\,\delta m^{ab}_{l_1l_2},\end{aligned} \tag{C28}$$

which is only nonzero if the collisions do not conserve mass.

3. Momentum density

Taking $\psi_l(\vec{v}_1)=m_l\vec{v}_1=\vec{p}_1$ in Eq. (C14) and summing over l gives

$$\frac{\partial}{\partial t}\rho\vec{u}+\vec{\nabla}\cdot(\rho\vec{u}\vec{u})+\vec{\nabla}\cdot(\overleftrightarrow{P}+\vec{Q}\vec{u})=\vec{S}^{(p)}, \tag{C29}$$

with $\overleftrightarrow{P}=\overleftrightarrow{P}^K+\overleftrightarrow{P}^V+\overleftrightarrow{P}^M$, where the kinetic contribution is

$$\overleftrightarrow{P}^K=\sum_l m_l\int d\vec{v}_1f_l(\vec{r},\vec{v}_1,t)\vec{V}_1\vec{V}_1. \tag{C30}$$

To explicitly write the remaining flux and source terms, we need

$$(b^{l_1'l_2'}_{l_1l_2}\vec{p}_1-\vec{p}_1)=\tfrac{1}{2}(\vec{\gamma}^{l_1'l_2'}_{l_1l_2}-\delta m^{l_1'l_2'}_{l_1l_2}\vec{V}_{12}), \tag{C31}$$

giving

$$\begin{aligned}S^{l_1'l_2'}_{l_1l_2}&=-\tfrac{1}{2}\,\delta m^{l_1'l_2'}_{l_1l_2}(\vec{V}_{12}-\vec{u})-\tfrac{1}{2}\,\delta m^{l_1'l_2'}_{l_1l_2}\vec{u},\\F^{l_1'l_2'}_{l_1l_2}&=\tfrac{1}{2}\,\vec{\gamma}^{l_1'l_2'}_{l_1l_2}.\end{aligned} \tag{C32}$$

At this point, it is useful to separate $\vec{\gamma}^{l_1'l_2'}_{l_1l_2}$ into two parts: its value in the local rest frame of the colliding atoms, $\tilde{\vec{\gamma}}^{l_1'l_2'}_{l_1l_2}$, and the part coming from the Galilean transformation to the laboratory frame,

$$\vec{\gamma}^{l_1'l_2'}_{l_1l_2}=\tilde{\vec{\gamma}}^{l_1'l_2'}_{l_1l_2}+(m_{l_1'}-m_{l_1}-m_{l_2'}-m_{l_2})\vec{V}_{12},$$

so that we have that the collisional part of the flux is

$$\begin{aligned}\overleftrightarrow{P}^V=&-\tfrac{1}{2}\sum_{l_1l_2l_1'l_2'}\int dx_1dx_2\vec{q}_{12}(\hat{q}_{12}\cdot\vec{v}_{12})\,\delta(q_{12}-\sigma_{l_1l_2})\\&\times\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})f_{l_1l_2}(x_1x_2)K^{l_1'l_2'}_{l_1l_2}(x_{12})\,\tilde{\vec{\gamma}}^{l_1'l_2'}_{l_1l_2}\\&\times\int_0^1 dx\;\delta(\vec{r}-x\vec{q}_1-(1-x)\vec{q}_2)\end{aligned} \tag{C33}$$

and the contribution from the instantaneous exchange of mass is

$$\begin{aligned}\overleftrightarrow{P}^M=&-\tfrac{1}{2}\sum_{l_1l_2l_1'l_2'}\int dx_1dx_2\vec{q}_{12}(\hat{q}_{12}\cdot\vec{v}_{12})\,\delta(q_{12}-\sigma_{l_1l_2})\\&\times\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})f_{l_1l_2}(x_1x_2)K^{l_1'l_2'}_{l_1l_2}(x_{12})(\hat{V}_{12}-\vec{u})\\&\times(m_{l_1'}-m_{l_1}-m_{l_2'}-m_{l_2})\int_0^1 dx\;\delta(\vec{r}-x\vec{q}_1-(1-x)\vec{q}_2)\end{aligned} \tag{C34}$$

and the source can be written as

$$\begin{aligned}\vec{S}^{(p)}=&\vec{u}S^{(\rho)}+\overline{\vec{S}^{(p)}},\\\overline{\vec{S}^{(p)}}=&\tfrac{1}{2}\sum_{l_1l_2l_1'l_2'}\int dx_1dx_2(\hat{q}_{12}\cdot\vec{v}_{12})\,\delta(q_{12}-\sigma_{l_1l_2})\\&\times\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})(\vec{V}-\vec{u})f_{l_1l_2}(x_1x_2)K^{l_1'l_2'}_{l_1l_2}(x_{12})\\&\times\delta m^{l_1'l_2'}_{l_1l_2}\delta(\vec{r}-\vec{q}_1).\end{aligned} \tag{C35}$$

By using the balance equation for the total mass density,

$$\frac{d}{dt}\rho\vec{u}+\vec{\nabla}\cdot(\vec{u}\rho\vec{u})=\rho\frac{d}{dt}\vec{u}+\rho\vec{u}\cdot\vec{\nabla}\vec{u}-\vec{u}\vec{\nabla}\cdot\vec{Q}+\vec{u}S^{(\rho)}, \tag{C36}$$

we can write

$$\frac{\partial}{\partial t}\vec{u}+\vec{u}\cdot\vec{\nabla}\vec{u}+\rho^{-1}(\vec{\nabla}\cdot\overleftrightarrow{P}+\vec{Q}\cdot\vec{\nabla}\vec{u})=\rho^{-1}\overline{\vec{S}^{(p)}}. \tag{C37}$$

4. Energy

Taking $\psi_l(\vec{v}_1)=\frac{1}{2}m_lv_1^2$ in Eq. (C14) and summing over l gives

$$\frac{d}{dt}E+\vec{\nabla}\cdot(\vec{u}E)+\vec{\nabla}\cdot\vec{F}=S^{(E)}, \tag{C38}$$

where the kinetic part of the flux is

$$\vec{F}^K=\sum_l\tfrac{1}{2}m_l\int d\vec{v}_1f_l(\vec{r},\vec{v}_1,t)\vec{V}_1v_1^2 \tag{C39}$$

$$\begin{aligned}&=\sum_l\tfrac{1}{2}m_l\int d\vec{v}_1f_l(\vec{r},\vec{v}_1,t)\vec{V}_1(\vec{V}_1+\vec{u})^2\\&=\vec{q}^K+\vec{u}\cdot\overleftrightarrow{P}^K,\end{aligned} \tag{C40}$$

with the kinetic contribution to the heat flux being defined as

$$\vec{q}^{K}\equiv\sum_{l}\ \tfrac{1}{2}m_l\int d\vec{v}_1 f_l(\vec{r},\vec{v}_1,t)\vec{V}_1V_1^2. \tag{C41}$$

The source term comes from the even part of the collision kernel,

$$\begin{aligned}S_{l_1l_2}^{l_1'l_2'}&=\frac{1}{2}(b_{l_1l_2}^{l_1'l_2'}-1)\left(\frac{1}{2m_{l_1}}p_1^2+\frac{1}{2m_{l_2}}p_2^2\right)\\&=\frac{1}{2}\left[\frac{1}{2m_{l_1'}}p_1'^2+\frac{1}{2m_{l_2'}}p_2'^2-\frac{1}{2m_{l_1}}p_1^2-\frac{1}{2m_{l_2}}p_2^2\right]\\&=-\frac{1}{2}\left[\overline{\delta E_{l_1l_2}^{l_1'l_2'}}+\frac{1}{2}\delta m_{l_1l_2}^{l_1'l_2'}V^2\right]\\&=-\frac{1}{2}\left[\overline{\delta E_{l_1l_2}^{l_1'l_2'}}+\frac{1}{2}\delta m_{l_1l_2}^{l_1'l_2'}(\vec{V}-\vec{u})^2\right]\\&\quad-\frac{1}{2}\delta m_{l_1l_2}^{l_1'l_2'}(\vec{V}-\vec{u})\cdot\vec{u}-\frac{1}{4}\delta m_{l_1l_2}^{l_1'l_2'}u^2,\end{aligned} \tag{C42}$$

so that

$$S^{(E)}=\xi+\vec{u}\cdot\overline{\vec{S}^{(p)}}+\tfrac{1}{2}u^2\overline{S^{(\rho)}}, \tag{C43}$$

with the (rest-frame) source term

$$\begin{aligned}\xi=\tfrac{1}{2}\sum_{l_1l_2l_1'l_2'}&\int dx_1dx_2(\hat{q}_{12}\cdot\vec{v}_{12})\delta(q_{12}-\sigma_{l_1l_2})\\&\times\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})[\overline{\delta E_{l_1l_2}^{l_1'l_2'}}+\tfrac{1}{2}\delta m_{l_1l_2}^{l_1'l_2'}(\vec{V}-\vec{u})^2]\\&\times f_{l_1l_2}(x_1x_2)K_{l_1l_2}^{l_1'l_2'}(x_{12})\delta(\vec{r}-\vec{q}_1).\end{aligned} \tag{C44}$$

The flux comes from the odd part of the collision kernel,

$$\begin{aligned}F_{l_1l_2}^{l_1'l_2'}&=\frac{1}{2}(b_{l_1l_2}^{l_1'l_2'}-1)\left(\frac{1}{2m_{l_1}}p_1^2-\frac{1}{2m_{l_2}}p_2^2\right)\\&=\frac{1}{2}(b_{l_1l_2}^{l_1'l_2'}-1)\left[\frac{1}{m_{l_1}+m_{l_2}}(p_1^2-p_2^2)\right.\\&\quad\left.-\frac{m_{l_1}-m_{l_2}}{m_{l_1}+m_{l_2}}\left(\frac{1}{2m_{l_1}}p_1^2+\frac{1}{2m_{l_2}}p_2^2\right)\right].\end{aligned} \tag{C45}$$

The first term gives

$$\begin{aligned}&(b_{l_1l_2}^{l_1'l_2'}-1)\frac{1}{m_{l_1}+m_{l_2}}(p_1^2-p_2^2)\\&\quad=\frac{1}{m_{l_1'}+m_{l_2'}}\left[\left(\vec{p}_1+\frac{1}{2}\vec{\gamma}_{l_1l_2}^{l_1'l_2'}-\frac{1}{2}\delta m_{l_1l_2}^{l_1'l_2'}\vec{V}\right)^2\right.\\&\qquad\left.-\left(\vec{p}_2-\frac{1}{2}\vec{\gamma}_{l_1l_2}^{l_1'l_2'}-\frac{1}{2}\delta m_{l_1l_2}^{l_1'l_2'}\vec{V}\right)^2\right]-\frac{1}{m_{l_1}+m_{l_2}}(p_1^2-p_2^2)\\&\quad=\vec{V}\cdot\vec{\gamma}_{l_1l_2}^{l_1'l_2'}+\frac{\delta m_{l_1l_2}^{l_1'l_2'}}{m_{l_1'}+m_{l_2'}}\vec{p}_{12}\cdot\vec{V}\\&\qquad+\left(\frac{1}{m_{l_1'}+m_{l_2'}}-\frac{1}{m_{l_1}+m_{l_2}}\right)(p_1^2-p_2^2),\end{aligned} \tag{C46}$$

while the second is

$$\begin{aligned}&(b_{l_1l_2}^{l_1'l_2'}-1)\frac{m_{l_1}-m_{l_2}}{m_{l_1}+m_{l_2}}\left(\frac{1}{2m_{l_1}}p_1^2+\frac{1}{2m_{l_2}}p_2^2\right)\\&\quad=-\frac{m_{l_1'}-m_{l_2'}}{m_{l_1'}+m_{l_2'}}\left(\overline{\delta E_{l_1l_2}^{l_1'l_2'}}+\frac{1}{2}\delta m_{l_1l_2}^{l_1'l_2'}V^2\right)\\&\qquad+\left(\frac{m_{l_1'}-m_{l_2'}}{m_{l_1'}+m_{l_2'}}-\frac{m_{l_1}-m_{l_2}}{m_{l_1}+m_{l_2}}\right)\left(\frac{1}{2m_{l_1}}p_1^2+\frac{1}{2m_{l_2}}p_2^2\right)\\&\quad=-\frac{m_{l_1'}-m_{l_2'}}{m_{l_1'}+m_{l_2'}}\left(\overline{\delta E_{l_1l_2}^{l_1'l_2'}}+\frac{1}{2}\delta m_{l_1l_2}^{l_1'l_2'}V^2\right)\\&\qquad+\left(\frac{1}{m_{l_1'}+m_{l_2'}}\right)\left(\frac{m_{l_1'}}{m_{l_1}}p_1^2-\frac{m_{l_2'}}{m_{l_2}}p_2^2\right)-\left(\frac{1}{m_{l_1}+m_{l_2}}\right)(p_1^2-p_2^2),\end{aligned} \tag{C47}$$

so

$$\begin{aligned}2F_{l_1l_2}^{l_1'l_2'}&=\vec{V}_{12}\cdot\vec{\gamma}_{l_1l_2}^{l_1'l_2'}+\frac{\delta m_{l_1l_2}^{l_1'l_2'}}{m_{l_1'}+m_{l_2'}}\vec{p}_{12}\cdot\vec{V}_{12}\\&\quad+\frac{m_{l_1'}-m_{l_2'}}{m_{l_1'}+m_{l_2'}}\left(\overline{\delta E_{l_1l_2}^{l_1'l_2'}}+\frac{1}{2}\delta m_{l_1l_2}^{l_1'l_2'}V_{12}^2\right)\\&\quad+\left(\frac{m_{l_1}-m_{l_1'}}{m_{l_1'}+m_{l_2'}}\right)\frac{1}{m_{l_1}}p_1^2+\left(\frac{m_{l_2'}-m_{l_2}}{m_{l_1'}+m_{l_2'}}\right)\frac{1}{m_{l_2}}p_2^2,\end{aligned} \tag{C48}$$

which gives, after some algebra,

$$\begin{aligned}2F_{l_1l_2}^{l_1'l_2'}&=\vec{V}_{12}\cdot\tilde{\vec{\gamma}}_{l_1l_2}^{l_1'l_2'}+\frac{1}{m_{l_1}+m_{l_2}}\left(\frac{m_{l_1}m_{l_2'}-m_{l_2}m_{l_1'}}{m_{l_1'}+m_{l_2'}}\right)\\&\quad\times\mu_{l_1l_2}v^2+\frac{m_{l_1'}-m_{l_2'}}{m_{l_1'}+m_{l_2'}}\overline{\delta E_{l_1l_2}^{l_1'l_2'}}\\&\quad-\frac{1}{2}-(-m_{l_1'}+m_{l_2'}-m_{l_2}+m_{l_1})V_{12}^2.\end{aligned} \tag{C49}$$

This can also be written as

$$\begin{aligned}2F_{l_1l_2}^{l_1'l_2'}&=(\vec{V}_{12}-\vec{u})\cdot\tilde{\vec{\gamma}}_{l_1l_2}^{l_1'l_2'}+\frac{m_{l_2'}m_{l_1}-m_{l_1'}m_{l_2}}{(m_{l_2'}+m_{l_1'})(m_{l_2}+m_{l_1})}\\&\quad\times\mu_{l_1l_2}v^2+\frac{m_{l_1'}-m_{l_2'}}{m_{l_1'}+m_{l_2'}}\overline{\delta E_{l_1l_2}^{l_1'l_2'}}\\&\quad-\frac{1}{2}(-m_{l_1'}+m_{l_2'}-m_{l_2}+m_{l_1})(\vec{V}_{12}-\vec{u})^2\\&\quad+(m_{l_1'}-m_{l_1}-m_{l_2'}+m_{l_2})[(\vec{V}_{12}-\vec{u})\cdot\vec{u}]\\&\quad+\frac{1}{2}(m_{l_1'}-m_{l_1}-m_{l_2'}+m_{l_2})u^2,\end{aligned} \tag{C50}$$

$$+\vec{u}\cdot\tilde{\vec{\gamma}}_{l_1l_2}^{l_1'l_2'}, \tag{C51}$$

so that

$$\vec{F}^{(V)}=\vec{q}^{V}+\vec{q}^{m}+\vec{q}^{\delta E}+\vec{u}\cdot(\vec{P}^{V}+\vec{P}^{M})+\tfrac{1}{2}u^{2}\vec{Q}, \tag{C52}$$

where the different pieces of the heat flux vector are the usual collisional contribution

$$\begin{aligned}\vec{q}^{V}=&-\tfrac{1}{2}\sum_{l_1l_2l_1'l_2'}\int dx_1dx_2\vec{q}_{12}(\hat{q}_{12}\cdot\vec{v}_{12})\,\delta(q_{12}-\sigma_{l_1l_2})\\&\times\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})f_{l_1l_2}(x_1x_2)K_{l_1l_2}^{l_1'l_2'}(x_{12})(\vec{V}_{12}-\vec{u})\\&\cdot\tilde{\vec{\gamma}}_{l_1l_2}^{l_1'l_2'}\int_0^1dx\;\delta(\vec{r}-x\vec{q}_1-(1-x)\vec{q}_2),\end{aligned} \tag{C53}$$

a part arising from the instantaneous transfer of mass,

$$\begin{aligned}\vec{q}^{m}=&-\frac{1}{2}\sum_{l_1l_2l_1'l_2'}\frac{m_{l_2'}m_{l_1}-m_{l_1'}m_{l_2}}{(m_{l_2'}+m_{l_1'})(m_{l_2}+m_{l_1})}\\&\times\int dx_1dx_2\vec{q}_{12}(\hat{q}_{12}\cdot\vec{v}_{12})\,\delta(q_{12}-\sigma_{l_1l_2})\\&\times\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})f_{l_1l_2}(x_1x_2)K_{l_1l_2}^{l_1'l_2'}(x_{12})\mu_{l_1l_2}v^{2}\\&\times\int_0^1dx\;\delta(\vec{r}-x\vec{q}_1-(1-x)\vec{q}_2),\end{aligned} \tag{C54}$$

and a part arising from the loss of energy,

$$\begin{aligned}\vec{q}^{\delta E}=&-\frac{1}{2}\sum_{l_1l_2l_1'l_2'}\frac{m_{l_1'}-m_{l_2'}}{m_{l_1'}+m_{l_2'}}\int dx_1dx_2\vec{q}_{12}(\hat{q}_{12}\cdot\vec{v}_{12})\\&\times\delta(q_{12}-\sigma_{l_1l_2})\Theta(-\hat{q}_{12}\cdot\vec{v}_{12})f_{l_1l_2}(x_1x_2)K_{l_1l_2}^{l_1'l_2'}(x_{12})\\&\times\overline{\delta E_{l_1l_2}^{l_1'l_2'}}\int_0^1dx\;\delta(\vec{r}-x\vec{q}_1-(1-x)\vec{q}_2).\end{aligned} \tag{C55}$$

A little rearrangement allows us to write the energy balance equation as

$$\begin{aligned}&\frac{\partial}{\partial t}E+\vec{\nabla}\cdot(\vec{u}E)+\vec{\nabla}\cdot\vec{q}+\vec{\nabla}\cdot(\vec{u}\cdot\vec{P})+\vec{\nabla}\cdot\left(\frac{1}{2}u^{2}\vec{Q}\right)\\&\quad=\xi+\vec{u}\cdot\overline{\vec{S}^{(p)}}+\frac{1}{2}u^{2}\overline{S^{(\rho)}}.\end{aligned} \tag{C56}$$

Alternatively, noting the relation between the total energy and the kinetic temperature,

$$E=\frac{D}{2}nk_BT+\frac{1}{2}\rho u^{2}, \tag{C57}$$

gives an equation for the evolution of the kinetic temperature:

$$\left(\frac{\partial}{\partial t}+\vec{u}\cdot\vec{\nabla}\right)T-\frac{T}{n}\vec{\nabla}\cdot\sum_{l}\vec{j}_l^{K}+\frac{2}{Dnk_B}[\vec{P}:\vec{\nabla}\vec{u}+\vec{\nabla}\cdot\vec{q}]=\xi. \tag{C58}$$

[1] B. V. Alexeev, A. Chikhaoui, and I. T. Grushin, Phys. Rev. E **49**, 2809 (1994).

[2] A. Chikhaoui, J. P. Dudon, S. Genieys, E. V. Kustova, and E. A. Nagnibeda, Phys. Fluids **12**, 220 (2000).

[3] D. Lohse, Phys. Today **56(X)**, 36 (2004).

[4] K. S. Suslick, Science **247**, 1439 (1990).

[5] M. P. Brenner, S. Higenfeldt, and D. Lohse, Rev. Mod. Phys. **74**, 425 (2002).

[6] Y. T. Didenko and K. S. Suslick, Nature (London) **418**, 394 (2002).

[7] J. A. McLennan, *Introduction to Nonequilibrium Statistical Mechanics* (Prentice-Hall, Englewood Cliffs, NJ, 1989).

[8] D. J. Evans and G. P. Morriss, Phys. Rev. Lett. **56**, 2172 (1986).

[9] J.-P. Hansen and I. McDonald, *Theory of Simple Liquids* (Academic, San Diego, CA, 1986).

[10] H. van Beijeren and M. H. Ernst, Physica (Amsterdam) **68**, 437 (1973).

[11] T. R. Kirkpatrick, S. P. Das, M. H. Ernst, and J. Piasecki, J. Chem. Phys. **92**, 3768 (1990).

[12] R. Kapral, J. Chem. Phys. **68**, 1903 (1978).

[13] S. Bose and P. Ortoleva, J. Chem. Phys. **70**, 3041 (1979).

[14] R. I. Cukier, R. Kapral, J. R. Mehaffey, and K. J. Shin, J. Chem. Phys. **72**, 1830 (1980).

[15] R. Kapral, *Advances in Chemical Physics* (Wiley, New York, 1981), Vol. XLVIII, Chap. 2.

[16] J. J. Brey, J. W. Dufty, and A. Santos, J. Stat. Phys. **87**, 1051 (1997).

[17] J. F. Lutsko, Phys. Rev. Lett. **77**, 2225 (1996).

[18] J. F. Lutsko, Phys. Rev. Lett. **86**, 3344 (2001).

[19] J. F. Lutsko, Phys. Rev. E **63**, 061211 (2001).

[20] T. P. C. van Noije and M. H. Ernst, Granular Matter **1**, 57 (1998).

[21] V. Garzo and J. Dufty, Phys. Rev. E **60**, 5706 (1999).

[22] D. A. McQuarry and J. D. Simon, *Physical Chemistry: A molecular approach* (University Science Books, Sausalito, 1997).