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Choosing Hydrodynamic Fields

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Abstract. Continuum mechanics (e.g., hydrodynamics, elasticity theory) is based on the assumption that a small set of fields provides a closed description on large space and time scales. Conditions governing the choice for these fields are discussed in the context of granular fluids and multi-component fluids. In the first case, the relevance of temperature or energy as a hydrodynamic field is justified. For mixtures, the use of a total temperature and single flow velocity is compared with the use of multiple species temperatures and velocities.

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1. Introduction

Continuum mechanics (e.g., hydrodynamics, elasticity theory) provides the macroscopic description for a wide class of physical systems and states in terms of a few space-time fields. The derivation and justification of the equations for these fields from the underlying Newtonian or quantum mechanics is a well-studied and open problem of non-equilibrium statistical mechanics [13, 22, 25, 26]. The central conceptual and practical problem is the reduction of the many degrees of freedom in the microscopic description to a closed description in terms of a few chosen macroscopic fields. Qualitatively, this is understood in terms of restrictions on the conditions for applicability of continuum mechanics. In particular, it is expected that such a reduced description can apply only for slowly varying fields that dominate the description on sufficiently long time

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scales. Under such conditions, all other fast degrees of freedom have decayed to zero leaving the possibility for a reduced description.

The choice of fields is therefore an important first step in any derivation of continuum mechanics. This in turn requires understanding relevant time scales active in the system. For a simple molecular fluid, there is a time independent uniform state, equilibrium, which is the reference state for the dynamics. The longest time scale for approach to equilibrium is set by the relative size of the spatial deviations of the relevant macroscopic fields y, $\mu \sim \Delta y/y_e$, where $\Delta y \sim y\left(\mathbf{r}+\mathbf{r}_0,t\right)-y\left(\mathbf{r},t\right)$, y_e is the equilibrium value of y, and $\mathbf{r}_0$ is a distance of the order of the mean free path. In the following, μ is referred to as the *uniformity parameter*. The local conserved fields of number, energy, and momentum densities obey balance equations expressing their time derivatives as gradients of fluxes. These derivatives are therefore proportional to the uniformity parameter, identifying a time scale that diverges as the system approaches equilibrium. A necessary condition for choosing a set of fields, therefore, is that they should include all local conserved densities. In the case of broken symmetries (e.g. solids, liquid crystals, superfluids) there are additional non-conserved fields whose time derivatives are proportional to the uniformity parameter, and therefore must also be included in the set of chosen fields [10, 21]. Finally, there are systems with internal processes on long time scales (polymers, plasmas) that remain finite in the uniform limit. Their associated fields can be included in the chosen set if these time scales are long compared to all other non-conserved excitations.

In the following, attention will be restricted to the fluid phase, for which the macroscopic description is hydrodynamics. Also it is assumed that there are no slow excitations associated with a broken symmetry. For reasons just noted, the hydrodynamic fields must include all conserved densities as a necessary condition to be complete on the longest time scale. The question addressed here is whether this minimal set can be extended to include additional fields, and if so, whether it is appropriate to do it. This issue has been discussed extensively in the context of extended irreversible thermodynamics (EIT) [17]. In EIT, additional fields, such as the fluxes in the balance equations for the conserved densities are included as independent hydrodynamic fields. One motivation there is to resolve paradoxes of Navier-Stokes hydrodynamics, usually associated with a misuse of those equations for conditions where they do not apply (e.g., initial slip, boundary layers, shock fronts). Another approach using additional fields is the moment method of Grad [19, 20]. Here, motivated by current applications of hydrodynamics to granular fluids [3, 12, 14, 18], related but different issues are addressed.

Section 2. outlines the basic ingredients for a derivation of hydrodynamic equations near a state of uniformity, from the underlying equations of nonequilibrium statistical mechanics [5, 6]. It relies on exact balance equations for the chosen fields, obtained from the Liouville equation, and on a special "normal" solution to that equation. Construction of a approximate normal solution is obtained by expansion in the uniformity parameter, leading to Navier-Stokes level hydrodynamics. The derivation does not make any explicit limitation on the chosen fields, other than the existence of a uniform reference state expressible in terms of those fields. However, it does not provide the context under which such a solution is applicable. It is argued that a necessary condition must be sufficiently long time scales.

In Sec. 3. the example of a simple granular fluid is considered. The uniform state in this case is not equilibrium, but one for which the temperature decreases monotonically due to inelastic collisions. The most significant differences from a molecular fluid are non-conservation of energy and a uniform state that is time dependent. The number and momentum densities are still conserved, so they are included in the set of hydrodynamic fields. The question of including the non-conserved energy density (or, equivalently, the granular temperature) is discussed. It is concluded that the minimal set of hydrodynamic fields must include the temperature.

In Sec. 4. binary mixtures are addressed, for both molecular and granular fluids. Two sets of fields are considered for hydrodynamic descriptions. One is the conserved number densities, flow velocity associated with the conserved total momentum, and the temperature associated with the total energy. The second one is an expanded set consisting of the conserved number densities, the species flow velocities associated with the non-conserved species momenta, and the species temperatures. It is argued that the second description, while more detailed, has no predictive value beyond the simpler hydrodynamic description on the relevant large space and time scales. The presentation is summarized in the last section with some concluding remarks.

2. Normal solutions, constitutive equations and hydrodynamics

The most general notion of a hydrodynamic description is a closed set of equations for a set of hydrodynamic fields, denoted by $\{y_\alpha\}$. The terminology "closed" means that they obey a set of equations of the form

$$\partial_t y_\alpha\left(\mathbf{r},t\right) = N_\alpha(\mathbf{r},t|\left\{y_\beta\right\}), \tag{2.1}$$

where the space, $\boldsymbol{r}$, and time, t, dependence of the right side is entirely determined from the fields themselves. In general, $N_\alpha(\mathbf{r},t|\left\{y_\beta\right\})$ is a nonlinear functional of the fields. The derivation of such equations procedes in two steps. First, balance equations for the fields are obtained directly from the Liouville equation,

$$\partial_t y_\alpha\left(\mathbf{r},t\right) + \nabla\cdot\mathbf{j}_\alpha\left(\mathbf{r},t\right) = s_\alpha(\mathbf{r},t). \tag{2.2}$$

Here, the fluxes $\mathbf{j}_\alpha\left(\mathbf{r},t\right)$ and sources $s_\alpha(\mathbf{r},t)$ are linear, time-independent functionals of the solution to the Liouville equation. In general, these functionals cannot be characterized entirely by the hydrodynamic fields, so although (2.2) are exact equations they do not constitute a closed set of equations for the fields in terms of themselves. This closure occurs for the special conditions of a "normal" state, defined as a solution to the Liouville equation of the form

$$\rho_n\left(\Gamma,t\right) = \rho_n\left(\Gamma|\left\{y_\alpha\right\}\right) = \rho_n\left(\left\{\mathbf{q}_{ij}\right\},\left\{\mathbf{v}_i\right\},\left\{y_\alpha\left(\mathbf{q}_i,t\right)\right\}\right), \tag{2.3}$$

where $\boldsymbol{q}_i$ and $\boldsymbol{v}_i$ are the position and velocity of particle i, and $\boldsymbol{q}_{ij}\equiv\boldsymbol{q}_i-\boldsymbol{q}_j$. For such solutions, all time dependence and the breaking of translational invariance occur only through the hydrodynamic fields. The notation in the second equality indicates that the *functional* of the fields $\rho_n\left(\Gamma\mid\left\{y_\alpha\right\}\right)$ is equivalent to a *function* of the fields at the particle positions of the specified Γ point. For a normal solution, the definitions of $\{\mathbf{j}_\alpha(\mathbf{r},t)\}$ and $\{s_\alpha(\mathbf{r},t)\}$ as linear functionals of this solution lead to "constitutive equations"

$$\mathbf{j}_\alpha(\mathbf{r},t)=\mathbf{j}_\alpha(\,\mathbf{r},t|\,\{y_\beta\}),\qquad s_\alpha(\mathbf{r},t)=s_\alpha(\mathbf{r},t|\,\{y_\beta\}). \tag{2.4}$$

With the fluxes and sources now determined by the fields, the balance equations (2.2) become closed hydrodynamic equations of the form (2.1).

Since the balance equations are exact consequences of the microscopic dynamics, questions about the existence of a hydrodynamic description turn on the necessary conditions for a normal solution (e.g., appropriate choice for the set of fields $\{y_\alpha\}$, restrictions on the space and time scale). Substitution of (2.3) into the Liouville equation gives the equation a normal solution must satisfy for a given choice of fields $\{y_\alpha\}$,

$$\int d\mathbf{r}\,\frac{\delta\rho_n}{\delta y_\alpha(\mathbf{r},t)}N_\alpha(\mathbf{r},t|\,\{y_\beta\})+L\rho_n=0, \tag{2.5}$$

where summation over repeated indices is implicit, L is the Liouville operator of the system, and $N_\alpha(\mathbf{r},t|\,\{y_\beta\})$ is the nonlinear functional in the hydrodynamic equations (2.1), defined in terms of the fluxes and sources. The latter in turn must be determined self-consistently in the form of constitutive equations (2.4), from the solution to (2.5). The resulting solution is implicit, being a function of the phase point Γ and a functional of the unknown fields. The space and time dependence of these fields is then obtained from a solution to the hydrodynamic equations for given initial and boundary conditions, completing specification of the normal solution.

Determination of a normal solution in this way is quite difficult, but its approximate construction can be carried out explicitly for states with small uniformity parameter μ (described above), by expansion in this parameter. This construction of the normal solution by expansion around the corresponding homogeneous solution will be referred to as the Chapman-Enskog method (the Chapman-Enskog method was originally developed to construct the normal solution to the Boltzmann equation. See for example, [8, 9]). This presumes the existence and determination of a reference homogeneous solution ρ_h to Eq. (2.5),

$$\frac{\partial\rho_h}{\partial y_\alpha(t)}s_\alpha(\{y_\beta(t)\})+L\rho_h=0, \tag{2.6}$$

together with the homogeneous hydrodynamic equations

$$\partial_t y_\alpha(t)=s_\alpha(\{y_\beta(t)\}). \tag{2.7}$$

The familiar example is a one component atomic fluid near spatially homogeneous equilibrium. If the fields chosen are all associated with local conserved densities, then the sources s_α vanish and (2.6) becomes the condition for a stationary equilibrium state. More generally, if the fields have sources, the homogeneous solution depends on the time dependence of these fields generated by the sources. Effects of small spatial gradients are described by returning to (2.5) and expanding the solution about ρ_h to linear order in μ,

$$\rho_n(\Gamma\mid\{y_\alpha\})=\rho_h(\Gamma;\{y_\alpha\})+\Delta_\alpha(\Gamma;\{y_\beta(\mathbf{r},t)\})\cdot\mu\nabla y_\alpha(\mathbf{r},t)+\ldots \tag{2.8}$$

The dots indicate terms of higher order in μ, and (2.5) provides a linear inhomogeneous equation for determination of Δ_{α}. With this result, the constitutive equations also are determined to first order in the gradients, providing N_{α} and the hydrodynamic equations to this order.

If the fields are chosen to be the local conserved densities of mass, energy, and momentum, then the sources $s_{\alpha}(\mathbf{r},t)$ all vanish, and the fluxes $\mathbf{j}_{\alpha}(\mathbf{r},t)$ are proportional to the uniformity parameter. Construction of the normal solution by the Chapman-Enskog method determines the time derivatives to be proportional to the uniformity parameter as well. The leading approximation yields the perfect fluid Euler equations, and the next order gives the usual Navier-Stokes equations. The derivation provides their context for applicability as well in this case: states must be near uniform equilibrium, with small fractional variations in the fields over a mean free path, and space and time scales large compared to the mean free path and mean free time, respectively.

It would appear that this approach is applicable for any choice of fields, leading to many forms for the macroscopic description of a system. However, the conditions under which a normal solution could be expected must be considered further. Consider first a normal fluid with elastic collisions in an initial non-equilibrium state with specified hydrodynamic fields $\{y_{\alpha}(\mathbf{r},t=0)\}$, whose values vary smoothly across the system. In each small region of dimension larger than a mean free path, the phase space density $\rho(\Gamma,t)$ approaches a Gibbs density characterized by the hydrodynamic fields at its central point $\mathbf{r}$. Subsequently, exchange of mass, energy, and momentum tends to equilibrate these fields to uniform values (or to steady values if the system is driven). The first stage, approach to a universal form for the velocity distribution, occurs after a few collisions. This establishes the normal form of the solution, where the hydrodynamic fields and their gradients characterize the state. Deviations from the equilibrium distribution are due to fluxes of mass, momentum, and energy across the cells. These fluxes are proportional to the differences in values of the fields (i.e., to their spatial gradients). The second stage is the slower evolution of the distribution through the changing values of the fields, according to the "usual" Navier-Stokes hydrodynamic equations. In this scenario, there is a characteristic microscopic time scale (mean free time) and a characteristic microscopic space scale (mean free path) that set the limits for validity of the normal solution. Beyond these limits, the dynamics is complex and not captured entirely by that of the hydrodynamic fields.

Extending the hydrodynamic fields to include non-conserved fields necessarily introduces additional time scales in the hydrodynamic solutions, due to the sources s_{α} associated with the new fields. Thus the hydrodynamics of the second stage now has variations on the same time scale as the first stage. Furthermore, the additional fields give only a partial description of the short time scale dynamics, and therefore do not extend the domain of applicability for the hydrodynamic description. The qualitative initial stage described above for a general initial preparation of the system is still required for any reduction in the large number of degrees of freedom active in the system to decay. The hydrodynamics can be closed (Markovian) only after such a reduction. Even during the second stage, only the slower dynamical processess can be described by hydrodynamics, as there are continual fluctuations of the fast degrees of freedom that would prohibit isolation of the corresponding fast hydrodynamic modes. In summary, the choice of fields for hydrodynamic equations is somewhat arbitrary, but their dominance on some time scale is a central property for utility as a macroscopic description of the system. Predictions on shorter time scales are difficult to correlate with measurements, and potentially obscuring the simplicity of the larger time scale dynamics. On the common long time scale required for validity, it would appear that the normal solutions should be equivalent, with the more detailed fields becoming functionals of the simpler fields and being "slaved" to them.

Exceptions to this conclusion occur when the uniform reference state is not the equilibrium state, and may have an inherent dynamics of its own. This is the case for granular fluids. In the following, the hydrodynamic descriptions for two examples using non-conserved fields are discussed: a simple one-component granular fluid for which there is an energy source, and binary mixtures where non-conserved fields of individual species may be of interest. Attention is limited to states near a corresponding universal homogeneous state (homogeneous cooling or equilibrium state) for simplicity. The question addressed is "what are the appropriate Navier-Stokes hydrodynamic equations for these more complex conditions, and under what conditions do they apply?".

3. Granular fluid

A one-component granular fluid consists of "particles" (grains) of mass m with short ranged collisions that conserve number and momentum, but not energy. By analogy with a molecular fluid it is reasonable to expect a hydrodynamic description in terms of the local number, momentum, and energy densities. It is usual to replace the momentum by its associated flow velocity $\mathbf{u}$, and the energy by a granular temperature T. This is just a change of variables. The exact macroscopic balance equations for $n, \mathbf{u}$, and T are [1]

$$D_t n + n\nabla \cdot \mathbf{u} = 0, \tag{3.1}$$

$$D_t \mathbf{u} + \frac{1}{\rho}\nabla \cdot \mathsf{P} = 0, \tag{3.2}$$

$$D_t T + \frac{2}{3n}\left(\nabla \cdot \mathbf{q} + \mathsf{P} : \nabla \mathbf{u}\right) = -\zeta T. \tag{3.3}$$

where $D_t \equiv \partial_t + \mathbf{u} \cdot \nabla$ is the material derivative, and $\rho = nm$. For simplicity, the particles have been represented as hard spheres for which the temperature is defined in terms of the energy density e as $e = 3nT/2 + \rho u^2/2$. The heat flux $\mathbf{q}$ and pressure tensor P are defined as the energy and momentum fluxes in the local rest frame of a fluid element moving with velocity $\mathbf{u}$. They are related with the energy and momentum fluxes in the laboratory frame, s and T, by

$$\mathbf{q} = \mathbf{s} - e\mathbf{u} - \mathbf{u} \cdot \mathsf{P}, \qquad \mathsf{P} = \mathsf{T} - \rho \mathbf{u}\mathbf{u}. \tag{3.4}$$

These balance equations have the same form as for a molecular fluid, except for the presence of a source $-\zeta T$ in the temperature equation, resulting from the inelasticity of collisions among the particles. The parameter ζ will be referred to as the cooling rate. Application of the Chapman-Enskog method for a normal solution to first order in the uniformity parameter leads to constitutive equations for the heat and momentum fluxes, $\mathbf{q}$ and P, similar to Fourier's law and Newton's viscosity law [7]

$$\mathbf{q} = -\lambda\nabla T - \mu\nabla n, \qquad P_{ij} = p\delta_{ij} - \eta\left(\nabla_i u_j + \nabla_j u_i - \frac{2}{3}\delta_{ij}\nabla\cdot\mathbf{u}\right) - \kappa\delta_{ij}\nabla\cdot\mathbf{u}. \tag{3.5}$$

In addition, the constitutive equation for the cooling rate ζ up to first order in the gradients is given by

$$\zeta = \zeta_0 + \zeta_1\nabla\cdot\mathbf{u}. \tag{3.6}$$

The pressure p and the transport coefficients in these expressions, λ, μ, η, κ, ζ_0, and ζ_1, are also determined from the normal solution as functions of n and T.

Equations (3.1)-(3.6) constitute the Navier-Stokes order hydrodynamic equations for a simple granular fluid. In contrast to a molecular fluid, solutions to the granular hydrodynamic equations have two time scales, one set by the uniformity parameter and another set by the energy loss rate $\tau\sim\zeta_0^{-1}$. The former becomes large as the system approaches uniformity, while the latter remains finite in uniform systems. From the discussion of the last section, in order for the hydrodynamic description to dominate the complex microdynamics, both of these time scales should be large compared to the mean free time. In practice this appears to be the case, at least if the degree of inelasticity is not too large (since ζ_0 vanishes in the elastic limit).

As the system approaches uniformity, the two hydrodynamic time scales become very different and the question arises of whether the temperature is still a relevant hydrodynamic field. It is a "fast variable" on the time scale for the spatial variations, so perhaps there is a simpler description in terms of n and $\mathbf{u}$ alone. To see that this is not the case consider Eq. (2.6) for the reference homogeneous normal solution,

$$\left(-\zeta T\frac{\partial}{\partial T} + L\right)\rho_h = 0. \tag{3.7}$$

To exclude the temperature as a relevant variable, ρ_h should be independent of the temperature, i.e. T should represent a transient dynamics that vanishes or becomes constant on a sufficiently long time scale. Then (3.7) would become $L\rho_h = 0$ for the reference homogeneous normal solution on this time scale. However, there is no solution to this equation for finite inelasticity. This can be easily seen by considering the average rate of change in the energy E,

$$\partial_t\left\langle E\right\rangle = -\int d\Gamma\, EL\rho_h. \tag{3.8}$$

This can never vanish since the collisional cooling continues as the system evolves. Thus the temperature is an inherent property of all solutions and cannot be neglected on any time scale. Although ζ_0 characterizes a rapid variation relative to the spatial time scale, it persists as a modulation of that latter slow scale. The reference uniform state has a dynamics (cooling) that is inherited by spatial deviations from that state and the system continues to cool rapidly even after it has "aged" an arbitrarily long time.

It might be argued that for special boundary conditions the hydrodynamic equations would support a solution with stationary temperature, such that variations of the temperature are indeed transient and rapidly approaching its stationary value. Subsequently, the residual relaxation of spatial variation might be described by n and $\mathbf{u}$ alone, and only parameterized by a constant temperature. While such a contrived description might be possible on a case-by-case basis, this does not constitute an alternative hydrodynamics. A hydrodynamic description is a set of closed equations for chosen fields that describes a class of states, e.g. Navier-Stokes equations for states near homogeneity, whose form is universal and independent of specific initial or boundary conditions.

The granular fluid with the source $-\zeta T$ can be contrasted with a molecular fluid including non-conserved fields. In the latter case, the sources vanish for the homogeneous (equilibrium) state so that solutions to $L\rho_e = 0$ do exist. There is then no restriction on the removal of the non-conserved fields in that case, for a simpler hydrodynamics. In contrast, the granular source discussed here does not vanish for its homogeneous state and hence the dynamics due to this source must be included in any set of hydrodynamic fields.

In summary, the Navier-Stokes hydrodynamics for a simple granular fluid is given in terms of $n, \mathbf{u}$, and T just as for a molecular fluid. Due to the inelasticity of collisions, there is a new time scale set by the cooling rate that does not increase as the system approaches spatial homogeneity. As for molecular fluids, the normal solution and hydrodynamics applies for times long compared to the mean free time when the transient dynamics of microscopic degrees of freedom has decayed and only that of the fields remains. However, the granular hydrodynamics retains a modulation of the spatial relaxation due to continual cooling of the system.

4. Binary mixtures

Consider next a granular or molecular fluid composed of two different species (e.g., different mass, size or collision law). If there are no reactions or fragmentation, the number of particles of each species is conserved and their local densities, n_i, are appropriate independent hydrodynamic fields. Other properties of interest might be the species temperatures, T_i, and the species flow velocities, $\mathbf{u}_i$. However, these are not associated with any conserved quantity even for a molecular fluid (there is continual energy and momentum exchange between species, even though the total energy and momentum are conserved). In this section, the possibility of including species properties, beyond their number densities, as hydrodynamic fields is discussed.

The species numbers and flow fields, $n_i, \boldsymbol{u}_i$, are related to the corresponding total fields n and $\mathbf{u}$ by

$$n = n_1 + n_2, \quad \rho\mathbf{u} = n_1 m_1 \mathbf{u}_1 + n_2 m_2 \mathbf{u}_2, \tag{4.1}$$

where the mass density is $\rho \equiv m_1 n_1 + m_2 n_2 = \rho_1 + \rho_2$. The temperature is determined from the total energies which are decomposed into their kinetic temperature and convective energies according to

$$e = \frac{3}{2}nT + \frac{1}{2}\rho u^2 = e_1 + e_2, \qquad e_i = \frac{3}{2}n_i T_i + \frac{1}{2}\rho_i u_i^2. \tag{4.2}$$

Two possible hydrodynamic descriptions are considered here, one for the six fields $\{n_i, \mathbf{u}, T\}$, and another for the ten fields $\{n_i, \mathbf{u}_i, T_i\}$.

4.1. Single temperature, single velocity balance equations

The exact macroscopic balance equations for $n_1, n_2, \mathbf{u}$, and T are

$$D_t n_i + n_i \nabla \cdot \mathbf{u} + \nabla \cdot \mathbf{j}_i = 0, \tag{4.3}$$

$$D_t \mathbf{u} + \frac{1}{\rho} \nabla \cdot \mathsf{P} = 0, \tag{4.4}$$

$$D_t T - \frac{T}{n} \nabla \cdot \sum_{i=1,2} \mathbf{j}_i + \frac{2}{3n} \left(\nabla \cdot \mathbf{q} + \mathsf{P} : \nabla \mathbf{u} \right) = -\zeta T \,, \tag{4.5}$$

where $\boldsymbol{j}_i$ is the number flow for species i relative to the local flow, $\mathbf{j}_i \equiv n_i \left(\mathbf{u}_i - \mathbf{u} \right)$. To obtain hydrodynamic equations for this choice of fields, constitutive equations must be obtained from the corresponding normal solution to give $\mathbf{j}_i$, $\mathbf{q}$, P, and ζ as functionals of these fields. As with the one component granular fluid, there are two time scales associated with this choice of hydrodynamic fields, that associated with the uniformity parameter and that associated with the cooling rate. Both should be larger than the mean free time.

4.2. Two temperatures, two velocities balance equations

The balance equations for the extended set of ten fields have the form

$$D_{it} n_i + n_i \nabla \cdot \mathbf{u}_i = 0, \tag{4.6}$$

$$\rho_i D_{it} \mathbf{u}_i + \nabla \cdot \mathsf{P}_i = -\boldsymbol{\lambda}_i. \tag{4.7}$$

$$D_{it} T_i + \frac{2}{3n_i} \left(\nabla \cdot \mathbf{q}_i + \mathsf{P}_i : \nabla \mathbf{u}_i \right) = -\zeta_i T_i + \frac{2}{3n_i} \mathbf{u}_i \cdot \boldsymbol{\lambda}_i, \tag{4.8}$$

where now $D_{it} \equiv \partial_t + \mathbf{u}_i \cdot \nabla$, and the heat flux $\mathbf{q}_i$ and pressure tensor P_i are now defined as the energy and momentum fluxes in the local rest frame of a fluid element moving with velocity $\mathbf{u}_i$ (compare with Eq. (3.4)). The sources $\boldsymbol{\lambda}_i$ and ζ_i depend on n_i, T_i, and $\mathbf{u}_i$. The normal solution for this choice of fields is needed to get the constitutive equations for $\mathbf{q}_i$, P_i, $\boldsymbol{\lambda}_i$, and ζ_i as functionals of these fields.

Note that $\mathbf{q} \neq \mathbf{q}_1 + \mathbf{q}_2$ and $\mathsf{P} \neq \mathsf{P}_1 + \mathsf{P}_2$, in general. The balance equations for $n_1, n_2, \mathbf{u}$, and T, Eqs. (4.3)-(4.5), follow from Eqs. (4.6)-(4.8) only if the sources have the properties

$$\zeta_1 n_1 T_1 + \zeta_2 n_2 T_2 = \zeta n T + \frac{2}{3} \nabla \cdot \left(\mathbf{s} - \mathbf{s}_1 - \mathbf{s}_2 \right), \tag{4.9}$$

$$\left(\boldsymbol{\lambda}_1 + \boldsymbol{\lambda}_2 \right) = \nabla \cdot \left(\mathsf{T} - \mathsf{T}_1 - \mathsf{T}_2 \right). \tag{4.10}$$

Here $\mathbf{s}_i$ and T_i are the energy and momentum fluxes of species i in the laboratory frame. These relations are proved in Appendix A, where explicit expressions for the sources are obtained.

The coefficients $\boldsymbol{\lambda}_i$ are proportional to the collision frequency, and hence introduce dynamics on the short mean free time scale. The rates ζ_i have two contributions. One is positive and proportional to the degree of dissipation, like ζ in Eq. (4.5). However, there is an additional contribution of indefinite sign and which does not vanish in the elastic limit. It represents the collisional transfer of energy between different species. This latter contribution is of the order of the collision rate and consequently generates dynamics on the mean free time scale. There are now three hydrodynamic time scales: the largest one set by the uniformity parameter, that set by the cooling rate, and the fastest one defined on the mean free time scale. This last time scale is the central difference between the two hydrodynamic descriptions being discussed here.

4.3. Comparison of hydrodynamic descriptions

To compare and contrast the above two hydrodynamic descriptions, it is sufficient to consider the homogeneous limit, for which the details of the constitutive equations are not required. Consider first the case of zero flow velocities, in which case Eq. (4.2) gives

$$nT = n_1 T_1 + n_2 T_2. \tag{4.11}$$

Equations (4.3)-(4.5) reduce to constant species densities, and a time dependent temperature obtained from

$$\partial_t T = -\zeta\left(T\right) T, \tag{4.12}$$

while the two temperature description, Eqs. (4.6)-(4.8), gives also constant species densities and

$$\partial_t T_1 = -\zeta_1\left(T_1, T_2\right) T_1, \qquad \partial_t T_2 = -\zeta_2\left(T_1, T_2\right) T_2. \tag{4.13}$$

Equation (4.12) follows from Eqs. (4.13) via the exact relationships (4.9) and (4.11) for the uniform case. In this respect, the two temperature description is more complete. However, it is also more complex and masks the simplicity of the long time dynamics of (4.12) by superposing on it a higher frequency dynamics, as described in the following.

An approximate representation for the cooling rates is given in Appendix B in the form [24, 11]

$$\zeta_i = \nu\left(T_2\right) \xi_i(\phi), \tag{4.14}$$

where

$$\phi \equiv \frac{m_2 T_1}{m_1 T_2} \tag{4.15}$$

is a measure of the temperature ratio, and $\nu > 0$ is some average collision frequency. The explicit expressions for ν, ξ_1, and ξ_2 are given in Appendix B. Equations (4.13) lead to an equation for ϕ,

$$\partial_t \ln \phi = -\nu\left(T_2\right)\left(\xi_1\left(\phi\right) - \xi_2\left(\phi\right)\right). \tag{4.16}$$

There is a stationary solution ϕ_h determined by

$$\xi_1\left(\phi_h\right) = \xi_2\left(\phi_h\right). \tag{4.17}$$

It follows from Eqs. (B2) and (B3) in Appendix B that $\xi_1\left(\phi\right) - \xi_2\left(\phi\right) > 0$ for $\phi > \phi_h$ and $\xi_1\left(\phi\right) - \xi_2\left(\phi\right) < 0$ for $\phi < \phi_h$, so the stationary solution is approached in general for times greater than the mean free time. This solution is the homogeneous cooling state for a granular mixture.

Stationarity of ϕ implies that the cooling rates of each species are the same,

$$\frac{\partial_t T_1}{T_1} = \frac{\partial_t T_2}{T_2} \Rightarrow \zeta_1 = \zeta_2 = \zeta.$$

The equivalence to ζ follows from the relationship $nT = n_1T_1 + n_2T_2$. Thus all three temperatures are different in general but their cooling rates are the same. The equivalence of the cooling rates means only one temperature field is needed to describe the dynamics on this time scale, for arbitrary initial preparation. For example, in the two temperature case considered above, the homogeneous solution corresponding to (3.7) is

$$\left(- \left(\zeta_1 - \zeta_2\right) \phi \frac{\partial}{\partial \phi} - \zeta T \frac{\partial}{\partial T} + L \right) \rho_h = 0, \tag{4.18}$$

where a change of variables has been made from $\{T_1, T_2\}$ to $\{T, \phi\}$. The solution of this equation depends on two time dependent fields, $\rho_h = \rho_h(\Gamma, T(t), \phi(t))$. But on the mean free time scale $\phi(t) \rightarrow \phi_h$, $\zeta_1\left(\phi_h\right) = \zeta_2\left(\phi_h\right)$, and so $\rho_h(\Gamma, T(t), \phi(t)) \rightarrow \rho_h(\Gamma, T(t), \phi_h)$. The latter is the homogeneous solution to (3.7), the normal solution for the single temperature case.

This analysis of the homogeneous state illustrates the behavior for more general inhomogeneous states as well. The slow dynamics on the scale of the uniformity parameter in (4.3)-(4.5) is present as well in the two temperature formulation (4.6)-(4.8), but the latter superposes on that either initial transients or a continual modulation at the collision frequency. Since it is only the slow dynamics that is relevant experimentally, and for justification of the normal solution, the two temperature formulation is unnecessarily complex. This does not mean that the slow components of the species temperatures are irrelevant. These are provided by the single temperature formulation and the normal solution that gives these species temperatures as functions of the slow global temperature, $T_i(t) = T_i(T(t))$. This picture has been confirmed by molecular dynamics simulations in the homogeneous case [4, 23] where the rapid approach of T_1/T_2 to a constant different from unity is observed on the scale of the mean free time. Similar results have been seen for an inhomogeneous vibrated mixture of inelastic hard disks [2], showing that the two species temperatures in the steady state are determined by the densities and global temperature profiles, being independent from the details of the heating mechanism, aside from a boundary layer next to the vibrating wall.

Finally, consider the species velocities, described by (4.7). It is clear that the source in these equations drives the species velocities towards the common flow field $\mathbf{u}$, on the mean free time scale. This is similar to the equilibration of the species temperatures, and is the same for both molecular and granular systems. As with the species temperatures, this extended description yields transients and modulation of the slow dynamics. Instead the single flow hydrodynamics describes only the relevant slow components of the species flow fields, through the normal solution, in the form $\mathbf{u}_i = \mathbf{u}_i(T(t), \mathbf{u}(t))$.

In summary, the two temperature, two velocity hydrodynamic description of a binary mixture subsumes the one temperature, one velocity formulation by providing a more detailed description of the fluid. However, the additional details are on the short time scale of the mean free time where the dynamics is entangled with many other microscopic degrees of freedom, and for which the underlying normal solution is not expected to apply. Of course, it has the additional computational difficulty of requiring the determination of many more transport coefficients in the constitutive equations (approximate calculations have been made based on the Enskog kinetic theory, but the results remain incomplete; see [15, 16]), and solving for ten coupled fields in contrast to six fields in the simple hydrodynamic description.

5. Discussion

The hydrodynamic fields should include all those fields with the longest time scale, fixed by the uniformity parameter. In addition, fields with shorter times scales may need to be included. For example, systems with long internal relaxation times (viscoelastic liquids) can be described by non-local in time constitutive equations or, equivalently, by local equations with additional fields. For some non-equilibrium states with inherent dynamics persisting in the homogeneous state, such as for granular fluids, non-conserved fields may be essential. Non-conserved species fields may be useful for cases where their equilibration times in the homogeneous state are long, such as for electron-ion two temperature plasmas.

A more difficult question is whether to include non-conserved fields whose time scales include the mean free time, since many other non-hydrodynamic degrees of freedom are also active on this time scale. There does not seem to be any formal objection to including such fields, since the Chapman-Enskog construction of a corresponding normal solution, outlined in Sec. 2., can be implemented. However, the normal solution in such cases is still restricted to apply only for time scales large compared to the mean free time. Consequently, the new short time scale component in the hydrodynamics is not relevant and can obscure the relevant slow dynamics inherent in all fields.

To make this point in a different way, let $\{\widehat{y}_\alpha\}$ be the phase functions whose average values in some nonequilibrium state are the fields $\{y_\alpha\}$. It is possible to write the equations of motion for $\{\widehat{y}_\alpha\}$ as formally exact Langevin equations [13, 25, 26], generalizing Eq. (2.1)

$$\partial_t \widehat{y}_\alpha(\mathbf{r},t) - M_\alpha(\mathbf{r},t| \{\widehat{y}_\beta\}) = \widehat{f}_\alpha(\mathbf{r},t). \tag{5.1}$$

The functional M_α is similar to N_α in (2.1), except the former is a time dependent functional, depending on time explicitly as well as through its functional argument. The sources $\widehat{f}_\alpha(\mathbf{r},t)$ represent the dynamics of all other degrees of freedom, beyond the set $\{\widehat{y}_\alpha\}$. The solution to (5.1) is equivalent to that from Newton's equations, but the dynamics now has been separated into two parts that are supposed to be distinct: a slow dynamics associated with the homogeneous equation, modulated by a fast dynamics due to $\widehat{f}_\alpha(\mathbf{r},t)$. The average of these sources vanish, so the average of Eq. (5.1) resembles a hydrodynamic description,

$$\partial_t y_\alpha(\mathbf{r},t) - M_\alpha(\mathbf{r},t \mid \{y_\beta\})\ldots = 0. \tag{5.2}$$

The dots denote additional terms due to fluctuations in the fields, for instance proportional to $\left\langle (\widehat{y}_\alpha - y_\alpha)^2 \right\rangle$, which occur since M_α is a nonlinear functional. Although the sources no longer appear their effects are still present in the explicit time dependence of M_α. Only after taking time scales long compared to that of the sources does this time dependence become negligible, and a hydrodynamic description obtained. This shows that general sets of fields can be chosen, but their hydrodynamics is restricted to long times when a simpler description may be available in terms of fewer fields.

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A Momentum and energy sources

The sources in the momentum and energy balance equations are determined in this Appendix, and properties (4.9) and (4.10) are verified. It is assumed that the particles are hard spheres, although the analysis applies as well for general pairwise additive forces. The Liouville operator of the system has the form

$$L=\sum_{i=1}^{N_1}\frac{\boldsymbol{p}_{i1}}{m_1}\cdot\frac{\partial}{\partial\boldsymbol{q}_{i1}}+\sum_{i=1}^{N_2}\frac{\boldsymbol{p}_{i2}}{m_2}\cdot\frac{\partial}{\partial\boldsymbol{q}_{i2}}+\frac{1}{2}\sum_{j\neq i}^{N_1}\sum_{i=1}^{N_1}T_{i1j1}+\frac{1}{2}\sum_{j\neq i}^{N_2}\sum_{i=1}^{N_2}T_{i2j2}+\sum_{i=1}^{N_1}\sum_{j=1}^{N_2}T_{i1j2}\,, \qquad \text{(A1)}$$

where $\boldsymbol{q}_{i1}$ ($\boldsymbol{q}_{i2}$) and $\boldsymbol{p}_{i1}$ ($\boldsymbol{p}_{i2}$) are the position and momentum of particle i of species 1 (2), and N_1 and N_2 are the total number of particles of each species. The operators $T_{ikjl}=T_{jlik}$ describe the binary collision between particle i of species k and particle j of species l, $k,l=1,2$.

A1. Momentum balance equation

The average momentum density for species 1 is

$$\mathbf{p}_1(\mathbf{r})=\left\langle\sum_{i=1}^{N_1}\mathbf{p}_{i1}\delta\left(\mathbf{r}-\mathbf{q}_{\alpha 1}\right)\right\rangle, \qquad \text{(A2)}$$

where the brackets denote ensemble average. The time derivative is

$$\begin{aligned}\partial_t\mathbf{p}_1(\mathbf{r}) &= -m_1^{-1}\boldsymbol{\nabla}\cdot\left\langle\sum_{i=1}^{N_1}\mathbf{p}_{i1}\mathbf{p}_{i1}\delta\left(\mathbf{r}-\mathbf{q}_{i1}\right)\right\rangle+\left\langle\sum_{j\neq i}^{N_1}\sum_{i=1}^{N_1}T_{i1j1}\delta\left(\mathbf{r}-\mathbf{q}_{i1}\right)\mathbf{p}_{i1}\right\rangle\\ &\quad+\left\langle\sum_{i=1}^{N_1}\sum_{j=1}^{N_2}T_{i1j2}\delta\left(\mathbf{r}-\mathbf{q}_{i1}\right)\mathbf{p}_{i1}\right\rangle. \qquad \text{(A3)}\end{aligned}$$

The first term on the right hand side of Eq. (A3) gives the gradient of the kinetic part of the momentum flux for species 1, while the second term describes collisions among particles of species 1. Finally, the last term represents collisions between pairs of particles of different species. The second term can be written as the gradient of a flux,

$$\begin{aligned}\left\langle \sum_{j\neq i}^{N_1}\sum_{i=1}^{N_1} T_{i1j1}\delta\left(\mathbf{r}-\mathbf{q}_{i1}\right)\mathbf{p}_{i1}\right\rangle &= \frac{1}{2}\left\langle \sum_{j\neq i}^{N_1}\sum_{i=1}^{N_1}\left(\delta\left(\mathbf{r}-\mathbf{q}_{i1}\right)T_{i1j1}\mathbf{p}_{i1}+\delta\left(\mathbf{r}-\mathbf{q}_{j1}\right)T_{j1i1}\mathbf{p}_{j1}\right)\right\rangle \\ &= \frac{1}{2}\left\langle \sum_{j\neq i}^{N_1}\sum_{i=1}^{N_1}\left(\delta\left(\mathbf{r}-\mathbf{q}_{i1}\right)-\delta\left(\mathbf{r}-\mathbf{q}_{j1}\right)\right)T_{i1j1}\mathbf{p}_{i1}\right\rangle . \qquad \text{(A4)}\end{aligned}$$

In the last line use has been made of $T_{i1j1}\mathbf{p}_{j1} = -T_{i1j1}\mathbf{p}_{i1}$ (Newton's third law). Finally, the difference of the delta functions can be written as a divergence using the identity

$$\begin{aligned}\delta\left(\mathbf{r}-\mathbf{q}_{i1}\right)-\delta\left(\mathbf{r}-\mathbf{q}_{j1}\right) &= \int_0^1 dx\,\frac{\partial}{\partial x}\delta\left(\mathbf{r}-x\mathbf{q}_{i1}-(1-x)\mathbf{q}_{j1}\right) \\ &= -\boldsymbol{\nabla}\cdot\left(\mathbf{q}_{i1}-\mathbf{q}_{j1}\right)\int_0^1 dx\,\delta\left(\mathbf{r}-x\mathbf{q}_{i1}-(1-x)\mathbf{q}_{j1}\right). \qquad \text{(A5)}\end{aligned}$$

Use of Eq. (A5) into Eq. (A4) identifies the second term of (A3) as minus the gradient of the momentum flux tensor for species 1.

A similar analysis of the third term does not lead to a gradient because exchanging i, j in the sums leads to two different pairs, for which Newton's third law does not apply. Hence this last term is the momentum source in Eq. (4.7),

$$\boldsymbol{\lambda}_1\left(\mathbf{r}\right) = -\left\langle \sum_{i=1}^{N_1}\delta\left(\mathbf{r}-\mathbf{q}_{i1}\right)\boldsymbol{F}_{i1;2}\right\rangle, \qquad \boldsymbol{F}_{i1;2} = \sum_{j=1}^{N_2} T_{i1j2}\mathbf{p}_{i1}. \qquad \text{(A6)}$$

The property (4.10) follows directly from this result since

$$\begin{aligned}\boldsymbol{\lambda}_1\left(\mathbf{r}\right)+\boldsymbol{\lambda}_2\left(\mathbf{r}\right) &= -\left\langle \sum_{i=1}^{N_1}\sum_{j=1}^{N_2}\left(\delta\left(\mathbf{r}-\mathbf{q}_{i1}\right)T_{i1j2}\mathbf{p}_{i1}+\delta\left(\mathbf{r}-\mathbf{q}_{j2}\right)T_{j2i1}\mathbf{p}_{j2}\right)\right\rangle \\ &= -\left\langle \sum_{i=1}^{N_1}\sum_{j=1}^{N_2}\left(\delta\left(\mathbf{r}-\mathbf{q}_{i1}\right)-\delta\left(\mathbf{r}-\mathbf{q}_{j2}\right)\right)T_{i1j2}\mathbf{p}_{i1}\right\rangle . \qquad \text{(A7)}\end{aligned}$$

where momentum conservation, $T_{i1j2}\mathbf{p}_{j2} = -T_{i1j2}\mathbf{p}_{i1}$, has been used. Using again the identity (A5) this becomes the gradient of the momentum flux tensor due to collisions between particles of different species. This confirms Eq. (4.10).

A2. Energy balance equation

The average energy density for species 1 is

$$e_1\left(\mathbf{r}\right) = \left\langle \sum_{i=1}^{N_1}\frac{p_{i1}^2}{2m_1}\delta\left(\mathbf{r}-\mathbf{q}_{i1}\right)\right\rangle . \qquad \text{(A8)}$$

Its time derivative is given by

$$\begin{aligned}\partial_t e_1(\mathbf{r}) &= -m_1^{-1}\nabla\cdot\left\langle\sum_{i=1}^{N_1}\frac{p_{i1}^2}{2m_1}\mathbf{p}_{i1}\delta(\mathbf{r}-\mathbf{q}_{i1})\right\rangle+\left\langle\sum_{j\neq i}^{N_1}\sum_{i=1}^{N_1}T_{i1j1}\frac{p_{i1}^2}{2m_1}\delta(\mathbf{r}-\mathbf{q}_{i1})\right\rangle\\ &\quad+\left\langle\sum_{i=1}^{N_1}\sum_{j=1}^{N_2}T_{i1j2}\frac{p_{i1}^2}{2m_1}\delta(\mathbf{r}-\mathbf{q}_{i1})\right\rangle.\end{aligned}\tag{A9}$$

The first term on the right is the divergence of the kinetic part of the energy flux for species 1. The second term is due to collisions among species 1 particles while the last term is due to collisions between species 1 and 2. The second term can be analyzed as above for the momentum density,

$$\begin{aligned}&\left\langle\sum_{j\neq i}^{N_1}\sum_{i=1}^{N_1}T_{i1j1}\frac{p_{i1}^2}{2m_1}\delta(\mathbf{r}-\mathbf{q}_{i1})\right\rangle=\frac{1}{2}\left\langle\sum_{j\neq i}^{N_1}\sum_{i=1}^{N_1}\left(\delta(\mathbf{r}-\mathbf{q}_{i1})T_{i1j1}\frac{p_{i1}^2}{2m_1}+\delta(\mathbf{r}-\mathbf{q}_{j1})T_{j1i1}\frac{p_{j1}^2}{2m_1}\right)\right\rangle\\ &=-\frac{1}{2}\left\langle\sum_{j\neq i}^{N_1}\sum_{i=1}^{N_1}\delta(\mathbf{r}-\mathbf{q}_{i1})\Delta_{i1j1}\right\rangle+\frac{1}{2}\left\langle\sum_{j\neq i}^{N_1}\sum_{i=1}^{N_1}\left[(\delta(\mathbf{r}-\mathbf{q}_{j1})-\delta(\mathbf{r}-\mathbf{q}_{i1}))T_{j1i1}\frac{p_{j1}^2}{2m_1}\right]\right\rangle.\end{aligned}\tag{A10}$$

In the second equality, use has been made again of $T_{i1j1}=T_{j1i1}$ and also of

$$T_{i1j1}\left(\frac{p_{i1}^2}{2m_1}+\frac{p_{j1}^2}{2m_1}\right)=-\Delta_{i1j1},\tag{A11}$$

where Δ_{i1j1} is the energy loss by the pair of particles i,j in the collision. The difference between the delta functions in the last term of Eq. (A10) can be transformed to the divergence of the energy flux using again Eq. (A5). Therefore, the second term on the right side of (A9) is the sum of the energy loss due to inelasticity and the energy flux for particles of species 1 alone.

The last term of (A9) cannot be represented as the divergence of a flux since interchanging i and j in the summation introduces a different pair. The total energy source for species 1 is then identified as

$$w_1(\mathbf{r})\equiv-\frac{1}{2}\left\langle\sum_{j\neq i}^{N_1}\sum_{i=1}^{N_1}\delta(\mathbf{r}-\mathbf{q}_{i1})\Delta_{i1j1}\right\rangle+\left\langle\sum_{i=1}^{N_1}\delta(\mathbf{r}-\mathbf{q}_{i1})G_{i1;2}\right\rangle,\quad G_{i1;2}=\sum_{j=1}^{N_2}T_{i1j2}\frac{p_{i1}^2}{2m_1}.\tag{A12}$$

The cooling rates in the temperature equation are proportional to $w_i,(\mathbf{r})$

$$\zeta_1T_1=-\frac{2}{3n_1}w_1.\tag{A13}$$

The sum of the two sources is

$$w_1(\mathbf{r})+w_2(\mathbf{r})=-\frac{1}{2}\left\langle\sum_{j\neq i}^{N_1}\sum_{i=1}^{N_1}\delta(\mathbf{r}-\mathbf{q}_{i1})\Delta_{i1j1}+\sum_{j\neq i}^{N_2}\sum_{i=1}^{N_2}\delta(\mathbf{r}-\mathbf{q}_{j2})\Delta_{i2j2}\right\rangle$$

$$+\left\langle \sum_{i=1}^{N_1}\sum_{j=1}^{N_2}\left(\delta\left(\mathbf{r}-\mathbf{q}_{i1}\right)T_{i1j2}\frac{p_{i1}^2}{2m_1}+\delta\left(\mathbf{r}-\mathbf{q}_{j2}\right)T_{j2i1}\frac{p_{j2}^2}{2m_2}\right)\right\rangle . \tag{A14}$$

Using (A11) this becomes

$$\begin{aligned} w_1(\mathbf{r})+w_2(\mathbf{r}) \;=\; & -\left\langle \frac{1}{2}\sum_{j\neq i}^{N_1}\sum_{i=1}^{N_1}\delta\left(\mathbf{r}-\mathbf{q}_{j1}\right)\Delta_{i1j1}+\frac{1}{2}\sum_{j\neq i}^{N_2}\sum_{i=1}^{N_2}\delta\left(\mathbf{r}-\mathbf{q}_{j2}\right)\Delta_{i2j2} \right. \\ & \left. +\sum_{i=1}^{N_1}\sum_{j=1}^{N_2}\delta\left(\mathbf{r}-\mathbf{q}_{j2}\right)\Delta_{i1j2}\right\rangle \\ & +\left\langle \sum_{i=1}^{N_1}\sum_{j=1}^{N_2}\left(\delta\left(\mathbf{r}-\mathbf{q}_{i1}\right)-\delta\left(\mathbf{r}-\mathbf{q}_{j2}\right)\right)T_{i1j2}\frac{p_{i1}^2}{2m_1}\right\rangle . \end{aligned} \tag{A15}$$

The first term is the total energy loss due to all inelastic collisions, while the last term becomes (using (A5)) the contribution to the divergence of the energy flux from collisions between particles of different species. This confirms Eq. (4.9).

B Energy exchange rates

The "cooling" rates for a binary mixture, ζ_i, appearing in (4.13) have been estimated from an approximate two particle reduced distribution function (local equilibrium or information entropy distribution), to give their dependence on the fields n_i, T_i and the mechanical properties of the particles. It is assumed that the particles are hard, smooth, inelastic spheres with masses, diameters, and densities m_i, σ_i, and n_i respectively. The inelasticity is measured by restitution coefficients α_{ij} for collisions between particles of type i and j, with $0<\alpha_{ij}\leq 1$ and $\alpha_{ij}=1$ representing elastic collisions. The cooling rates are proportional to an average collision frequency ν with the approximate results [24, 11]

$$\zeta_i=\nu\xi_i,\quad \nu=\frac{4\pi m_2}{3m}\chi_{21}n\sigma_{21}^2\sqrt{\frac{8T_2}{\pi m_2}}\left(1+\alpha_{21}\right), \tag{B1}$$

$$\xi_1=(1-\alpha_{11}^2)x_1\beta_1\sqrt{\phi}+x_2\frac{\sqrt{1+\phi}}{1+\phi_0}\left(1-\mu+\phi_0-\frac{\mu}{\phi}\right), \tag{B2}$$

$$\xi_2=\left(1-\alpha_{22}^2\right)x_2\beta_2+x_1\frac{\sqrt{1+\phi}}{1+\phi_0}\left(1+\frac{\phi_0-\phi}{\mu}+\phi\right)(1-\mu). \tag{B3}$$

The variable ϕ is a measure of the temperature ratio defined in Eq. (4.15), $\sigma_{21}\equiv(\sigma_1+\sigma_2)/2$, $mequivm_1+m_2$, χ_{ij} is the pair correlation function at contact of a particle of species i and a particle of species j, $x_i=n_i/n$, and the constants β_1,β_2,ϕ_0, and μ are given by

$$\beta_1=\frac{1+\phi_0}{4\sqrt{2}\mu}\frac{\chi_{11}}{\chi_{21}}\left(\frac{\sigma_1}{\sigma_{21}}\right)^2,\quad \beta_2=\frac{1+\phi_0}{4\sqrt{2}\mu}\frac{\chi_{22}}{\chi_{21}}\left(\frac{\sigma_2}{\sigma_{21}}\right)^2, \tag{B4}$$

$$\phi_0 = \frac{1-\alpha_{21}}{1+\alpha_{21}}, \quad \mu = \frac{m_2}{m}\,. \tag{B5}$$

As noted in the text, ζ_i has two contributions, one that is positive and vanishes as $(1-\alpha_{ii}^2)$ in the elastic limit, and another that remains finite in that limit.

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