Chapter 3

The derivation of the balance equations

In this chapter we present the derivation of the balance equations for an arbitrary physical quantity which starts from the Liouville equation. We follow, with small modifications, the derivation of the hydrodynamic equations from [27]. A similar derivation can be found in [51]. In comparison with the usual method from the kinetic theory (for example [1], [4], [12], [21]), Irving and Kirkwood's derivation is more general from two points of view. First, one does not use the Boltzmann equation which is obtained by projecting the Liouville equation on the one-particle phase space. Besides, the derivation in [27] is valid for an arbitrary physical quantity, whereas Boltzmann's method is applicable only to so called collisional invariants, that is to the physical quantities which are conserved when two molecules collide (mass, momentum, and energy). Since the collision invariants provide a complete description for the most continuums and the constitutive relations can be determined only by their means, the more general method from [27] is less used.

We consider a Hamiltonian corpuscular system as the one described at the end of the chapter 2. In statistical mechanics one uses the probability density which is a positive, smooth, and real function $P = P(\mathbf{R}, \mathbf{P}, t)$ proportional with the probability to find the system state within a infinitesimal domain in the phases space. The probability that at the moment t the system state should be within the finite domain D in the phases space is given by the integral of P on D. For the entire phase space we have

$$\int P(\mathbf{R}, \mathbf{P}, t)\, d\mathbf{R}\, d\mathbf{P} = 1\,. \tag{3.1}$$

The Liouville equation reads

$$\partial_t P + \sum_{i=1}^{N} (\boldsymbol{\xi}_i \cdot \nabla_{\mathbf{r}_i} P + \dot{\mathbf{p}}_i \cdot \nabla_{\mathbf{p}_i} P) = 0, \tag{3.2}$$

and usually one assumes that the force $\dot{\mathbf{p}}_i$ on the particle i does not depend but on the particles position not on their momentum One notices that (3.2) is of the form (1.1) with $\mathbf{\Phi} = 0$, $p = 0$ and $s = 0$, hence it corresponds to the probability conservation in the phase space of the Hamiltonian dynamic systems. The Liouville equation can be also generalized in the case in which the phase space is an orientable differentiable manifold [62].

Let f_i be a function corresponding to a physical quantity f associated to the particle i. The quantity $f_i(\mathbf{R}, \mathbf{P}, t)$ may depend on the position and momentum of the particle i, but also of all the other particles. It can be, for example, the kinetic energy or the potential energy of the particle. The mean value of f for the entire corpuscular system is obtained by averaging on the phase space with a weight equal with the probability distribution P and summing up the contribution of all the particles.

$$\bar{f}(t) = \sum_{i=1}^{N} \int \int f_i(\mathbf{R}, \mathbf{P}, t) P(\mathbf{R}, \mathbf{P}, t)\, d\mathbf{R}\, d\mathbf{P}\,. \tag{3.3}$$

This mean quantity characterizes globally the corpuscular system. We can describe the mean spatial distribution of $\bar{f}(t)$ if we make the averaging (3.3) by fixing one at a time the position of the particle i and integrating in terms of the positions of all the others particles. Thus we define the *mean volume density* of the quantity f at the point $\mathbf{r}$ at the moment t by

$$D_f(\mathbf{r}, t) = \sum_{i=1}^{N} \int \int f_i(\mathbf{R}, \mathbf{P}, t)\, \boldsymbol{\delta}(\mathbf{r}_i - \mathbf{r})\, P(\mathbf{R}, \mathbf{P}, t)\, d\mathbf{R}\, d\mathbf{P}\,. \tag{3.4}$$

This formula can be regarded as well as a projection on the three-dimensional Euclidean space of the functions defined on the phase space. One verifies at once that the integral in terms of $\mathbf{r}$ of $D_f(\mathbf{r}, t)$ is equal with $\bar{f}(t)$. In order to keep the formulae simple we assumed that all the N particles are different. If there were more types of identical particles, then in the statistical averages this fact have to be taken into account.

The definition relation of the mean volume density (3.4) has a linear structure. More exactly, if we have two microscopic physical quantities $f_i(\mathbf{R}, \mathbf{P}, t)$ and $g_i(\mathbf{R}, \mathbf{P}, t)$, then

$$D_{f+g}(\mathbf{r}, t) = D_f(\mathbf{r}, t) + D_g(\mathbf{r}, t)\,. \tag{3.5}$$

Consider a function $\lambda(\mathbf{r},t)$ which does not depend on i, $\mathbf{r}_i$ or $\mathbf{p}_i$. Multiplying (3.4) with $\lambda(\mathbf{r},t)$, we can introduce it under the summation and the integral from the right-hand side, we have

$$D_{\lambda f}(\mathbf{r},t) = \lambda(\mathbf{r},t)\, D_f(\mathbf{r},t)\,. \tag{3.6}$$

For physical quantities that can be expressed by functions $f_i(\mathbf{R},\mathbf{P},t)$ the average (3.4) defines the volume density ψ in the balance equation (1.1). Let us analyze the main continuous fields that can be defined this way. We obtain the simplest case if $f_i(\mathbf{R},\mathbf{P},t) = 1$, for any $i \leq N$. One can see that from the condition (3.1) it follows that the global average (3.3) is equal with the total number of particles $\bar{f}(t) = N$, hence the corresponding average density is the usual volume *concentration* $c(\mathbf{r},t)$. For this type of function f_i we use the notation

$$c(\mathbf{r},t) = D_1(\mathbf{r},t)\,. \tag{3.7}$$

The mass *density* is obtained if the physical quantity is equal with the molecules mass $f_i = m_i$

$$\rho(\mathbf{r},t) = D_m(\mathbf{r},t)\,. \tag{3.8}$$

In the balance equations (1.1), besides the volume density ψ, there are continuous fields characterizing the mean value of a physical quantity at a certain point as, for example, the average velocity $\mathbf{u}$. The average velocity can be defined either as with respect to the particles concentration, or to the mass density. If we apply (3.4) for the component α of the molecules velocity $f_i = \xi_{\alpha i}$, then D_f is the average density of the velocity. The *mean kinematic velocity* is defined by the relation

$$v_\alpha(\mathbf{r},t) = D_{\xi_\alpha}(\mathbf{r},t) \,/\, c(\mathbf{r},t)\,.$$

Using a vectorial notation, we can write this definition as

$$\mathbf{v}(\mathbf{r},t) = D_{\boldsymbol{\xi}}(\mathbf{r},t) \,/\, c(\mathbf{r},t)\,. \tag{3.9}$$

In general one uses the *mean baricentrical velocity* which is defined as the mean volume density of the momentum $f_i = p_{\alpha i} = m_i \xi_{\alpha i}$ relative to the mass density [59]

$$\mathbf{u}(\mathbf{r},t) = D_{\mathbf{p}}(\mathbf{r},t) \,/\, \rho(\mathbf{r},t)\,. \tag{3.10}$$

The advantage of this definition is that for a mixture in thermodynamic equilibrium we have $\mathbf{u} = 0$, while the kinematic velocity $\mathbf{v}$ does not in general vanish.

The time variation of the dynamic variable $f_i(\mathbf{R},\mathbf{P},t)$ is due to the displacement of the state of the corpuscular system on the trajectories of the phase space, hence we have

$$\dot{f}_i = \partial_t f_i + \sum_{j=1}^{N} (\boldsymbol{\xi}_j \cdot \nabla_{\mathbf{r}_j} f_i + \dot{\mathbf{p}}_j \cdot \nabla_{\mathbf{p}_j} f_i) \,.$$

If we multiply this equation by the probability density $P(\mathbf{R},\mathbf{P},t)$ and the result is added to the Liouville equation (3.2) multiplied by $f_i(\mathbf{R},\mathbf{P},t)$, we obtain

$$\dot{f}_i\, P = \partial_t (f_i\, P) + \sum_{j=1}^{N} \left[\nabla_{\mathbf{r}_j} \cdot (\boldsymbol{\xi}_j\, f_i\, P) + \nabla_{\mathbf{p}_j} \cdot (\dot{\mathbf{p}}_j\, f_i\, P) \right] \,, \tag{3.11}$$

where we take account of the hypothesis that the force $\dot{\mathbf{p}}_i$ on the particle i does not depend on its velocity. We multiply this equation by $\boldsymbol{\delta}(\mathbf{r}_i - \mathbf{r})$, then a summation over all the particles is made and we integrate on the phase space, so that the terms of the equation take the form of the mean density (3.4). We notice that the term on the left-hand side becomes $D_{\dot{f}}$. Because the partial derivative with respect to time commutes with the integral on the phase space, it results that the first term on the right-hand of the equation (3.11) becomes $\partial_t D_f$. All the terms of the summation, excepting that containing $\nabla_{\mathbf{r}_i}$ can be integrated in terms of $\mathbf{r}_j$ or $\boldsymbol{\xi}_j$. These integrals vanish because we assume that P converges to zero sufficiently fast for $|\mathbf{r}_j| \to \infty$ and $|\boldsymbol{\xi}_j| \to \infty$. For the term with $j = i$ we have

$$\begin{aligned} \int [\nabla_{\mathbf{r}_i} \cdot (\boldsymbol{\xi}_i\, f_i\, P)]\, \boldsymbol{\delta}(\mathbf{r}_i - \mathbf{r})\, d\mathbf{r}_i &= -\int (\boldsymbol{\xi}_i\, f_i\, P) \cdot \nabla_{\mathbf{r}_i} \boldsymbol{\delta}(\mathbf{r}_i - \mathbf{r})\, d\mathbf{r}_i \\ &= \nabla_{\mathbf{r}} \cdot \int (\boldsymbol{\xi}_i\, f_i\, P)\, \boldsymbol{\delta}(\mathbf{r}_i - \mathbf{r})\, d\mathbf{r}_i \,. \end{aligned}$$

Thus we obtain the macroscopic evolution equation of the mean volume density D_f

$$\partial_t D_f + \nabla_{\mathbf{r}} \cdot D_{f\,\boldsymbol{\xi}} = D_{\dot{f}} \,. \tag{3.12}$$

In order to give to this equation a form as similar as possible with the balance equation (1.1) we introduce the mean velocity (3.10). Using (3.5) and (3.6) we have

$$D_{f\,\xi_\alpha} = D_{f\,u_\alpha} + D_{f\,(\xi_\alpha - u_\alpha)} = u_\alpha D_f + D_{f\,(\xi_\alpha - u_\alpha)} \,.$$

Then (3.12) becomes

$$\partial_t D_f + \nabla \cdot (D_f\, \mathbf{u}) + \nabla \cdot D_{f(\boldsymbol{\xi} - \mathbf{u})} = D_{\dot{f}}\,, \tag{3.13}$$

where we separated the term related with the transport due to the mean movement of the particles. The quantity $D_{f(\boldsymbol{\xi}-\mathbf{u})}$ is the flux of f due to the "thermic movement" of the particles, that is of the relative velocity of the particles in comparison with their mean movement. However, the equations (1.1) and (3.13) cannot be identified term by term using only the hypotheses introduced by now. The terms $\boldsymbol{\Phi}$, p, and s from (1.1) correspond to the terms $D_{f(\boldsymbol{\xi}-\mathbf{u})}$ and $D_{\dot{f}}$ from (3.13). For each physical quantity this correspondence depends on the available information on the microscopic structure of the physical system. In the following we particularize (3.13) for the main physical quantities and we show how the usual balance equations in continuum mechanics can be obtained.

3.1 Mass

We choose $f_i = m_i$, so $\dot{f}_i = 0$ and taking into account the definition (3.10) we have

$$D_{m(\boldsymbol{\xi}-\mathbf{u})} = D_{\mathbf{p}} - \mathbf{u}\, D_m = 0$$

and the relation (3.13) becomes

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{u}) = 0, \tag{3.14}$$

that is, the continuity equation or the balance equation for mass (1.2).

The mass balance equation of the component of a mixture can be derived similarly [65]. We consider that there is Γ types of molecules and the number of particles of γtype, $1 \leqslant \gamma \leqslant \Gamma$, is equal with N_γ. To simplify the mathematical relations we make the notations

$$n'_1 = 1,\; n'_\gamma = 1 + \sum_{\alpha=1}^{\gamma-1} N_\alpha \text{ for } \gamma > 1,\; n''_\gamma = \sum_{\alpha=1}^{\gamma} N_\alpha\ .$$

In this way we identify the molecules of γ type by the condition $n'_\gamma \leqslant i \leqslant n''_\gamma$. The concentration of the component γ, denoted c_γ, is given by the volume density D_f for the function

$$f_i(\mathbf{R}, \boldsymbol{\xi}, t) = \left\{ \begin{array}{lll} 1 & \text{if} & n'_\gamma \leqslant i \leqslant n''_\gamma \\ 0 & \text{if} & i < n'_\gamma \text{ or } i > n''_\gamma \end{array} \right. ,$$

that is f_i is nonvanishing only for the particles of γ type. Then $\dot{f}_i = 0$. We notice that

$$f_i \boldsymbol{\xi}_i = \begin{cases} \boldsymbol{\xi}_i & \text{if} \quad n'_\gamma \leqslant i \leqslant n''_\gamma \\ 0 & \text{if} \quad i < n'_\gamma \text{ or } i > n''_\gamma \end{cases}$$

and then $D_{f\boldsymbol{\xi}}$ is the sum of the particles velocities of γ type and we denote it by $D_{\boldsymbol{\xi}\gamma}$. Analogously to (3.9), we define the velocity of the γ component by

$$\mathbf{v}_\gamma(\mathbf{r},t) = D_{\boldsymbol{\xi}\gamma}(\mathbf{r},t) \,/\, c_\gamma(\mathbf{r},t) \,. \tag{3.15}$$

Substituting these results in (3.12) we obtain the balance equation of the concentration of the component γ

$$\partial_t c_\gamma + \nabla_{\mathbf{r}} \cdot (c_\gamma \mathbf{v}_\gamma) = 0 \ . \tag{3.16}$$

In order to establish the relation between the equation (3.16) and the continuity equation (3.14), we notice that from the definitions (3.9) and (3.15) it follows that

$$c\mathbf{v} = \sum_{\gamma=1}^{\Gamma} c_\gamma \mathbf{v}_\gamma \ .$$

Then summing up the equations (3.16) with respect to all γ, we obtain the balance equation for the total concentration

$$\partial_t c + \nabla_{\mathbf{r}} \cdot (c\mathbf{v}) = 0 \ . \tag{3.17}$$

Although its form is similar to the equation (3.14), in this equation it is the kinematic velocity $\mathbf{v}$ that occurs instead of baricentric velocity $\mathbf{u}$. This change is important since the mechanical equilibrium is described by a vanishing baricentric velocity. Within a macroscopic body in which $\mathbf{u} = 0$ it is possible that $\mathbf{v} \neq 0$, i.e., the diffusion also takes place in an environment in mechanical equilibrium.

3.2 Momentum

In this case $f_i = p_{\alpha i} = m_i \xi_{\alpha i}$ and then $\dot{f}_i = F_{\alpha i}$ where $\mathbf{F}_i$ is the force acting on the particle i. According to (3.10) in this case $D_f = \rho\, u_\alpha$. For the third term in (3.13) we use (3.5) and (3.6), so that

$$D_{p_\alpha(\xi_\beta - u_\beta)} = D_{m(\xi_\alpha - u_\alpha)(\xi_\beta - u_\beta)} - u_\alpha D_{m(\xi_\beta - u_\beta)} \,.$$

According to the relation (3.10) the second term vanishes and (3.13) can be written as

$$\partial_t(\rho u_\alpha) + \sum_{\beta=1}^{3} \partial_\beta(\rho u_\alpha u_\beta) - \sum_{\beta=1}^{3} \sigma'_{\alpha\beta} = D_{F_\alpha}, \tag{3.18}$$

where we have introduced the kinetic part of the stress tensor

$$\sigma'_{\alpha\beta} = -D_{m\,(\xi_\alpha - u_\alpha)\,(\xi_\beta - u_\beta)}\,. \tag{3.19}$$

We have obtained the momentum balance equation (3.18) under the most general conditions.

The equation (3.18) cannot be more explicit unless further hypotheses on the interaction between particles are made. As discussed in the chapter 2 such hypotheses particularize the physical system and the form taken by the terms in (3.18) expressed by means of some constitutive relations valid only for the considered type of physical system. However, there are certain general hypotheses which do not imply the formulation of constitutive relations. For example, in statistical mechanics it is assumed that the potential energy of a particle can be separated into a component of interaction with the environment and a component describing the particles interaction. Then the force acting on a particle can be written as

$$\mathbf{F}_i = m_i\,\mathbf{g}(\mathbf{r}_i) - \sum_{\substack{j=1\\ j\neq i}}^{N} \nabla_{\mathbf{r}_i} V_{ij}(\mathbf{r}_i, \mathbf{r}_j), \tag{3.20}$$

where $\mathbf{g}$ is the intensity of the exterior forces field (for example the gravitational field) and V_{ij} is the potential energy of interaction between the particles i and j. Then D_{F_α} from (3.18) is also separated into two terms. The first term is equal with

$$\sum_{i=1}^{N} \int\!\!\int m_i\, g_\alpha(\mathbf{r}_i)\; \boldsymbol{\delta}(\mathbf{r}_i - \mathbf{r})\, P(\mathbf{R}, \mathbf{P}, t)\, d\mathbf{R}\, d\mathbf{P} \;= g_\alpha(\mathbf{r})\, \rho(\mathbf{r}, t)\,.$$

Thus (3.18) becomes

$$\partial_t(\rho u_\alpha) + \sum_{\beta=1}^{3} \partial_\beta(\rho u_\alpha u_\beta) - \sum_{\beta=1}^{3} \sigma'_{\alpha\beta} = \rho\, g_\alpha + (D_{F_\alpha})_V, \tag{3.21}$$

where

$$(D_{F_\alpha})_V(\mathbf{r}, t) = -\sum_{i=1}^{N} \sum_{\substack{j=1\\ j\neq i}}^{N} \int\!\!\int \frac{\partial V_{ij}(\mathbf{r}_i, \mathbf{r}_j)}{\partial\, x_{\alpha i}}\, \boldsymbol{\delta}(\mathbf{r}_i - \mathbf{r})\, P(\mathbf{R}, \mathbf{P}, t)\, d\mathbf{R}\, d\mathbf{P}\;. \tag{3.22}$$

In order to obtain the usual equation of the momentum from the continuum mechanics (1.3), the quantity (3.22) must be expressed by a constitutive relation. This is possible only if other hypotheses on the molecules interaction are assumed. We shall discuss this problem at the end of the next section.

3.3 Energy

First consider the case of the kinetic energy $f_i = \mathbf{p}_i^2/(2m_i) = m_i\boldsymbol{\xi}_i^2/2$ and denote by $e_c = D_f$ the mean volume density of the kinetic energy

$$e_c = \frac{1}{2}\sum_{\alpha=1}^{3} D_{m\xi_\alpha^2} \,.$$

In the same as we have obtained the equation (3.18), we can separate e_c into two parts

$$e_c = \frac{1}{2}\rho\,\mathbf{u}^2 + \frac{1}{2}\sum_{\alpha=1}^{3} \sigma'_{\alpha\alpha} \,. \tag{3.23}$$

The first term is the kinetic energy density of the mean motion of the particles and the second one is the mean density of the kinetic energy due to the relative motion of the particles in comparison with their mean motion.

In this case $\dot{f}_i = \dot{\mathbf{p}}_i \cdot \mathbf{p}_i/m_i = \boldsymbol{\xi}_i \cdot \mathbf{F}_i$ and using for the force the formula (3.20) the term $D_{\dot{f}}$ in (3.13) is separated into two components. The part due to the exterior potential has the form

$$\sum_{i=1}^{N} \int\!\!\int \boldsymbol{\xi}_i \cdot m_i\,\mathbf{g}(\mathbf{r}_i)\;\boldsymbol{\delta}(\mathbf{r}_i - \mathbf{r})\,P(\mathbf{R},\mathbf{P},t)\,d\mathbf{R}\,d\mathbf{P} \;= \mathbf{g}(\mathbf{r}) \cdot D_{\mathbf{p}}(\mathbf{r},t)\,.$$

The part due to the interactions between the particles is denoted by

$$(D_{\boldsymbol{\xi}\cdot\mathbf{F}})_V(\mathbf{r},t) = -\sum_{i=1}^{N}\sum_{\substack{j=1\\ j\neq i}}^{N} \int\!\!\int \boldsymbol{\xi}_i \cdot [\nabla_{\mathbf{r}_i} V_{ij}(\mathbf{r}_i,\mathbf{r}_j)]\;\boldsymbol{\delta}(\mathbf{r}_i - \mathbf{r})\,P(\mathbf{R},\mathbf{P},t)\,d\mathbf{R}\,d\mathbf{P} \;. \tag{3.24}$$

For the term $D_{f(\xi_\alpha - u_\alpha)}$ in (3.13) we use (3.5) and (3.6) and we obtain

$$\begin{aligned}\tfrac{1}{2}D_{m\boldsymbol{\xi}^2(\xi_\alpha-u_\alpha)} = \; & \tfrac{1}{2}\textstyle\sum_{\beta=1}^{3} D_{m(\boldsymbol{\xi}_\beta-u_\beta)^2(\xi_\alpha-u_\alpha)} + \tfrac{1}{2}\textstyle\sum_{\beta=1}^{3} u_\beta D_{m(\boldsymbol{\xi}_\beta-u_\beta)(\xi_\alpha-u_\alpha)} + \\ & \tfrac{1}{2}\mathbf{u}^2 D_{m(\xi_\alpha-u_\alpha)}\,.\end{aligned}$$

According to (3.10), the last term is vanishing. Thus (3.13) can be written as

$$\partial_t e_c + \nabla\cdot(e_c\mathbf{u}) + \nabla\cdot\mathbf{q}' - \sum_{\alpha,\beta=1}^{3} u_\beta\sigma'_{\alpha\beta} = \rho\,\mathbf{u}\cdot\mathbf{g} + (D_{\boldsymbol{\xi}\cdot\mathbf{F}})_V, \tag{3.25}$$

where we have introduced the kinematic part of the heat flux density

$$\mathbf{q}' = \frac{1}{2}D_{m(\boldsymbol{\xi}-\mathbf{u})^2(\boldsymbol{\xi}-\mathbf{u})}\,. \tag{3.26}$$

Again the quantity (3.24) can not be made more explicit but by means of some additional hypotheses on the molecules interaction and it will be discussed at the end of this section.

The potential energy V_{ij} characterizes the interaction between the particles i and j, so that each of these particles benefits of half of this potential energy. Then the interaction potential energy of the particle i is

$$f_i = \frac{1}{2} \sum_{\substack{j=1 \\ j \neq i}}^{N} V_{ij}(\mathbf{r}_i, \mathbf{r}_j) \,,$$

and we introduce the notation $e_V = D_f$ for the volume density of the interaction potential energy. Then

$$\dot{f}_i = \frac{1}{2} \sum_{\substack{j=1 \\ j \neq i}}^{N} [(\nabla_{\mathbf{r}_i} V_{ij}) \cdot \boldsymbol{\xi}_i + (\nabla_{\mathbf{r}_j} V_{ij}) \cdot \boldsymbol{\xi}_j]$$

and taking into account that $V_{ij} = V_{ji}$, it follows from (3.24) that $D_{\dot{f}} = -(D_{\boldsymbol{\xi}\cdot\mathbf{F}})_V$. Thus (3.13) can be written in this case as

$$\partial_t e_V + \nabla \cdot (e_V \, \mathbf{u}) + \nabla \cdot \mathbf{q}'' = -(D_{\boldsymbol{\xi}\cdot\mathbf{F}})_V \,, \tag{3.27}$$

where we have introduced the potential component of the heat flux density

$$\mathbf{q}''(\mathbf{r}, t) = \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} \int \int (\boldsymbol{\xi}_i - \mathbf{u}) V_{ij}(\mathbf{r}_i, \mathbf{r}_j) \, \boldsymbol{\delta}(\mathbf{r}_i - \mathbf{r}) \, P(\mathbf{R}, \mathbf{P}, t) \, d\mathbf{R} \, d\mathbf{P} \;. \tag{3.28}$$

The total energy is $e = e_c + e_V$ and its balance equation is obtained by summing up the equations (3.25) and (3.27)

$$\partial_t e + \nabla \cdot (e\mathbf{u}) + \nabla \cdot (\mathbf{q}' + \mathbf{q}'') - \sum_{\alpha,\beta=1}^{3} u_\beta \sigma'_{\alpha\beta} = \rho \, \mathbf{u} \cdot \mathbf{g} \tag{3.29}$$

This equation is identical to (1.4).

Resuming the results in this chapter we can say that for a Hamiltonian system we have derived the balance equations (3.14), (3.21), and (3.29), with no specification on the interaction forces between the component particles. In comparison with the general balance equations (1.2)-(1.4) we notice that the difference occurs only in (3.21) due to the term (3.22). Taking additional assumptions on the interaction potential V_{ij} it can be shown that the term (3.22) is expressed as the divergence of a dynamic stress tensor $\sigma''_{\alpha\beta}$ [27].

Subsequently we should obtain the constitutive relations corresponding to the quantities (3.19), (3.22), (3.24), and (3.28) and express the internal energy density (3.23) in terms of the temperature. The simplest situation is that of the ideal gas when the molecules interact only through perfectly elastic collisions. Then all the terms depending on V_{ij} vanish and the usual balance equations in hydrodynamics are obtained [11] and [12]. If the interaction between molecules is not negligible, then the terms depending on V_{ij} in the equations (3.22), (3.24), and (3.28) have to be explicitly calculated. In the case of the identical particles interacting through central forces, this computation has been performed in [27]. Since we are interested in the derivation of balance equations we will not discuss the derivation of the constitutive relations.

3.4 Other mechanic quantities

The equations (3.12) and (3.13) are valid for any physical quantity f which can be assigned to the individual particles, not only for the so-called collisional invariants (mass, momentum, and energy). For example, in [65] we have shown how a balance equation can be written for the velocity of one of the components of a mixture. Here we present two simpler cases.

The balance equation for the angular momentum is obtained by choosing $f_i = L_{\alpha i} = (\mathbf{r}_i \times \mathbf{p}_i)_\alpha = \sum_{\beta,\gamma=1}^{3} e_{\alpha,\beta,\gamma} x_{\beta,i} p_{\gamma,i}$ where $e_{\alpha,\beta,\gamma}$ is the antisymmetric Levi-Civita tensor. It is easy to show that (3.10) takes the form

$$\sum_{\beta,\gamma=1}^{3} e_{\alpha,\beta,\gamma} x_\beta \left[\partial_t(\rho u_\gamma) + \sum_{\delta=1}^{3} D_{p_\gamma \xi_\delta} - D_{F_\gamma}\right] + \sum_{\beta,\gamma=1}^{3} e_{\alpha,\beta,\gamma} D_{p_\gamma \xi_\beta} = 0.$$

The second sum vanishes because $D_{p_\gamma \xi_\beta} = \frac{1}{m} D_{p_\gamma p_\beta}$ is a symmetrical tensor, therefore this equation reduces to the momentum equation (3.18).

The balance equation for the kinetic component of the stress tensor is obtained if we choose $f_i = -m_i(\xi_{\alpha i} - u_\alpha)(\xi_{\beta i} - u_\beta)$ and then from (3.19) we have $D_f = \sigma'_{\alpha\beta}$. Also

$$\dot{f}_i = m_i[(\xi_{\alpha i} - u_\alpha)\partial_t u_\beta + (\xi_{\beta i} - u_\beta)\partial_t u_\alpha] - \dot{p}_{\alpha i}(\xi_{\beta i} - u_\beta) - \dot{p}_{\beta i}(\xi_{\alpha i} - u_\alpha)$$

and then (3.13) becomes

$$\partial_t \sigma'_{\alpha\beta} + \nabla \cdot (\sigma'_{\alpha\beta} \mathbf{u}) + \sum_{\gamma=1}^{3} \partial_\gamma \Sigma_{\alpha\beta\gamma} = \pi_{\alpha\beta} \tag{3.30}$$

where we have introduced the symmetric tensors

$$\Sigma_{\alpha\beta\gamma} = -D_{m(\xi_\alpha - u_\alpha)(\xi_\beta - u_\beta)(\xi_\gamma - u_\gamma)}$$

$$\pi_{\alpha\beta} = -D_{F_\alpha(\xi_\beta - u_\beta) + F_\beta(\xi_\alpha - u_\alpha)}.$$

Even if the equation (3.30) does not have an effective utilization, the possibility to write it proves the generality of the equations (3.12) and (3.13).