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FUNDAMENTAL EQUATIONS FOR FLOW PROCESSES IN THE ULTRACENTRIFUGE

A. INTRODUCTION

The starting point for the phenomenological theory of sedimentation processes in the ultracentrifuge is the derivation of flow (or flux) equations which describe the isothermal mass transport of thermodynamic components in a centrifugal field. For a binary solution, that is, a system which consists of a homogeneous solute and a solvent, a useful flow equation for the solute may be derived by resorting to a kinetic theory approach, in which transport of solute molecules through the solvent is considered to be the result of a centrifugal force, a buoyant force, and a diffusion force. This approach prevailed in the early days of the development of sedimentation theory; even now some textbooks of physical chemistry or biophysical chemistry adopt it in an account of sedimentation phenomena, probably because of its simplicity.

It has become clear in recent years that the kinetic theory must be replaced by nonequilibrium thermodynamics (or thermodynamics of irreversible processes) in order to achieve the general and rigorous derivation of flow equations for the ultracentrifuge. Although many others have contributed, the chief credit for this important recognition must be given to Hooyman.¹ In this chapter, we show how the flow equations basic to the whole subject of this monograph are deduced from fundamental principles of nonequilibrium thermodynamics. In doing this, we shall often cite basic assumptions (or postulates) and equations of this new thermodynamics without going into their details. The reader will find necessary information on them in any of the recently published textbooks²⁻⁶ or review articles.^{7,8}

B. THE COORDINATE SYSTEM

The ordinary ultracentrifuge cell is a truncated sector of a cylinder as shown in Fig. 1.1. It is necessary to use a cell of this type because the force causing the motion of components in it acts radially from the axis of the rotor; use of a rectangular cell would produce convection arising from accumulation of matter at the side walls of the cell. Strictly speaking, even a sector-shaped cell is unable to prevent the components from convective

flows. The Coriolis force, which is necessarily involved in a rotating system as considered here, produces a transverse effect. Hooyman et al.⁹ showed that the Coriolis effect is almost completely negligible under the ordinary working conditions with the current ultracentrifuges. Therefore, we neglect it in the theoretical treatments given in the present monograph.

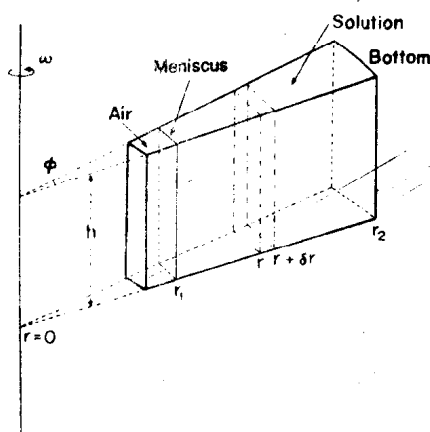


Fig. 1.1. The sector-shaped ultracentrifuge cell. A thin slice of volume indicated by chain lines is for the convenience of discussions given later. $r_2 - r_1$ is the length of solution column, h is the depth of solution column, and ϕ is the sector angle.

The flow equations assume simple forms if use is made of the system of cylindrical coordinates as shown in Fig. 1.1. Here r is the radial distance measured from the rotor axis, h is the distance parallel to the rotor axis, and ϕ is the sector angle. For cells designed for the Beckman-Spinco Model E ultracentrifuge, ϕ is 2, 2.5, or 4° and h ranges from 1.5 to 30 mm. The cell is filled with a solution which extends from $r = r_1$ to $r = r_2$. At the cylindrical boundary at $r = r_1$, the solution is in contact with an air bubble so that we have at this position a liquid-air interface, which is called the *meniscus*. Because the air bubble is admitted into the cell at atmospheric pressure while filling and before sealing the cell, the pressure of the solution at the meniscus is maintained at that of the atmosphere even though the rotor may spin under vacuum. The rigid cylindrical boundary at $r = r_2$ is called the *cell bottom*. Sometimes a thin layer of immiscible liquid which is denser than a given solution is inserted between the cell bottom and the solution in order to facilitate the measurement of the distribution of refractive indices or refractive index gradients in the region near the cell bottom. Such a liquid is usually called *bottom liquid*. When this is used, the liquid-liquid interface between it and the solution must be taken as the position for r_2 . The distance between r_1 and r_2 is referred to as

the length of the solution column, or simply the solution depth or height. This length may be adjusted by changing the volume of a solution admitted into the cell. In conventional sedimentation velocity experiments it is about 1 cm. whereas in current sedimentation equilibrium experiments it may be adjusted to less than about 3 mm in order to speed up the attainment of the equilibrium (for the reason see Chapter 7).

Physically, it is obvious that under the geometrical conditions described above (with the neglect of the Coriolis effect), each component in the solution column moves only in the radial direction (either centrifugal or centripetal) when it is subjected to a centrifugal force, and that the physical situation at any given time during the centrifugation is identical along a circular arc of fixed radius. This suggests that for a given speed of rotation only r and time t appear as independent variables in the final forms of equations which describe flow processes in the ultracentrifuge cell.

C. DEFINITIONS OF FLOWS (OR FLUXES)

Consider a system which consists of $q + 1$ nonreacting components. For convenience in presentation, the component 0 is specified as the solvent, and all others (labeled $1, 2, \dots, q$) are called solutes. For the moment, all solutes are assumed to be nonelectrolytes. Introduction of electrolyte components is deferred to Section K.

Suppose for simplicity that this system is contained in a straight tube of uniform cross section and is subject to some "forces" which may produce a unidirectional motion of each component along the tube. Such forces may be gradients of the total potential [the chemical potential plus the potentials due to external forces (mechanical, electric, magnetic, etc.)] and of temperature along the tube. Because any uniform motion of the tube as a whole does not give rise to irreversible processes in the system, we omit it from the subsequent considerations.

We set a coordinate origin 0 at some point on the tube and express the distance in the direction of the tube in terms of a variable x . Suppose there is at a certain point x a plane frame which is perpendicular and fixed to the tube. Each component passes through this frame either in the positive or the negative direction of the x -axis. We define the flow or flux of component k as the number of grams of component k per second which crosses 1 cm^2 of this frame, and we designate it by the symbol $(J_k)_c$. The unit of $(J_k)_c$ is $\text{g/cm}^2\text{-sec}$. Here the subscript c implies that the frame considered is fixed to the tube. At a given time $(J_k)_c$ may vary with x , and at a given x it may change with time t . Let the c -scale concentration

(grams of a component per cubic centimeter of solution) be denoted by c_k and let the average velocity of molecules (or particles) of component k at the position x and a given time t be denoted by $(u_k)_c$. Then we have

$$(J_k)_c = c_k(u_k)_c \quad (1.1)$$

It should be noted that $(u_k)_c$ does not mean the local velocity of a particular molecule of component k but the average of velocities of all molecules of component k in a volume element at the position considered, where the volume element is taken very small macroscopically but large enough microscopically to accommodate a great number of molecules. Also we should notice that $(u_k)_c$ is the velocity *relative to the tube* fixed in space. Both c_k and $(u_k)_c$ are generally functions of x and t .

Next we allow the frame to move at each point on the x -axis with the velocity of solvent, $(u_0)_c$, at that point, and we denote the flow of component k relative to this solvent-fixed frame by $(J_k)_0$. Then we have obviously

$$(J_0)_0 = 0 \quad (1.2)$$

The value of $(J_k)_0$ for component k ($k \neq 0$) is the product of c_k and the velocity of component k relative to the solvent-fixed frame. Hence

$$(J_k)_0 = c_k[(u_k)_c - (u_0)_c] \quad (1.3)$$

We refer to $(J_k)_0$ as the *solvent-fixed flow* of component k , whereas $(J_k)_c$ defined by equation 1.1 is called the *cell-fixed flow* of that component. The combination of equations 1.1 and 1.3 yields

$$(J_k)_0 = (J_k)_c - c_k(u_0)_c \quad (1.4)$$

Use of equation 1.2 gives

$$(u_0)_c = \frac{(J_0)_c}{c_0} \quad (1.5)$$

Hence we have the relation

$$(J_k)_0 = (J_k)_c - \left(\frac{c_k}{c_0} \right) (J_0)_c \quad (1.6)$$

We define a velocity $(u)_M$ by

$$(u)_M = \frac{\sum_{k=0}^q c_k (u_k)_c}{\sum_{k=0}^q c_k} \quad (1.7)$$

and call it the velocity of the local center of mass (relative to the tube) or the local barycentric velocity. The value of this velocity depends on the position x and the time t considered. Equation 1.7 may be put in the form

$$(u)_M = \frac{1}{\rho} \sum_{k=0}^q (J_k)_c \quad (1.8)$$

where ρ , the local density of the solution, is expressed by the sum of c_k over all components, that is,

$$\rho = \sum_{k=0}^q c_k \quad (1.9)$$

Obviously, ρ is a function of x and t . We define still another flow of component k relative to the frame moving with the velocity $(u)_M$, denote it by $(J_k)_M$, and term it the *mass-fixed flow* of component k . The frame to which this quantity is referred is called the *mass-fixed frame*. By definition we have

$$(J_k)_M = c_k [(u_k)_c - (u)_M] \quad (1.10)$$

After summation of equation 1.10 over all components and use of equation 1.7, we obtain

$$\sum_{k=0}^q (J_k)_M = 0 \quad (1.11)$$

This relation is basic for the mass-fixed flows, and it may be compared to equation 1.2, which applies for solvent-fixed flows. It is seen that the mass-fixed flows of $q+1$ components are not independent of each other, but are related linearly. Thus if q of them are known, the remaining one is automatically determined. By combining equations 1.1, 1.8, and 1.10 we obtain

$$(J_k)_M = (J_k)_c - \frac{c_k}{\rho} \sum_{k=0}^q (J_k)_c \quad (1.12)$$

which is to be compared to equation 1.6 for $(J_k)_0$. Obviously, $(J_k)_M$ is a function of x and t .

Finally, we define a velocity $(u)_V$ by

$$(u)_V = \frac{\sum_{k=0}^q \bar{v}_k c_k (u_k)_c}{\sum_{k=0}^q \bar{v}_k c_k} \quad (1.13)$$

where \bar{v}_k is the partial specific volume of component k in the solution at the position x and the time t considered. By using the well-known relation¹⁰

$$\sum_{k=0}^q \bar{v}_k c_k = 1 \quad (1.14)$$

equation 1.13 is reduced to

$$(u)_v = \sum_{k=0}^q \bar{v}_k c_k (u_k)_c \quad (1.15)$$

We call $(u)_v$ the velocity of the local center of volume; it generally varies with x and t . The *volume-fixed flow* of component k is then defined as the flow relative to that frame which moves with the velocity $(u)_v$, and is denoted here by $(J_k)_v$. It is a function of x and t and can be represented by

$$(J_k)_v = c_k [(u_k)_c - (u)_v] \quad (1.16)$$

or

$$(J_k)_v = (J_k)_c - c_k (u)_v \quad (1.17)$$

Introduction of equation 1.1 into equation 1.15 gives

$$(u)_v = \sum_{k=0}^q \bar{v}_k (J_k)_c \quad (1.18)$$

Therefore, equation 1.17 may be written

$$(J_k)_v = (J_k)_c - c_k \sum_{i=0}^q \bar{v}_i (J_i)_c \quad (1.19)$$

If both sides are multiplied by \bar{v}_k and summed over all components, there results

$$\sum_{k=0}^q \bar{v}_k (J_k)_v = 0 \quad (1.20)$$

where equation 1.14 has been used. Equation 1.20 indicates that the volume-fixed flows of $q+1$ components are not independent of each other, but are related linearly. It may be compared to equation 1.11 for mass-fixed flows.

The solvent-fixed, mass-fixed, and volume-fixed flows defined above all may be regarded as special cases of the flows $(J_k)_R$ defined by a general relation:

$$\sum_{k=0}^q (a_k)_R (J_k)_R = 0 \quad (1.21)$$

where the $(a_k)_R (k=0, 1, \dots, q)$ are the set of coefficients characterizing the frame to which the $(J_k)_R$ refer.

For

$$(a_0)_R = 1, \quad (a_k)_R = 0 \quad (k=1, 2, \dots, q) \quad (1.22)$$

equation 1.21 reduces to equation 1.2 for solvent-fixed flows; for

$$(a_k)_R = 1 \quad (k=0, 1, \dots, q) \quad (1.23)$$

equation 1.21 agrees with equation 1.11 for mass-fixed flows; and for

$$(a_k)_R = \bar{v}_k \quad (k=0, 1, \dots, q) \quad (1.24)$$

equation 1.21 is identical to equation 1.20.

By assigning other values to $(a_k)_R$ we may define various frames of reference. The group of such frames is hereafter called the *R-group of reference frames* for flows. It should be noted that the cell-fixed frame is in general not contained in this group: No set of $(a_k)_R$ exists that satisfies equation 1.21 when the $(J_k)_R$ are taken to be $(J_k)_c$, except for a special case which is discussed in Section G.3. In other words, except for such a case, the cell-fixed flows of all components in the solution are linearly independent of each other.

It can be shown that flows referred to any frame of the R-group are linearly related to those corresponding to any other frame of this group. Let two frames of reference belonging to the R-group be denoted by R' and R'' . By definition

$$\sum_{k=0}^q (a_k)_{R'} (J_k)_{R'} = 0, \quad \sum_{k=0}^q (a_k)_{R''} (J_k)_{R''} = 0 \quad (1.25)$$

If the local velocity of frame R'' relative to frame R' is represented by $(u)_{R'R'}$, we have the relation

$$(J_k)_{R''} = (J_k)_{R'} - c_k (u)_{R'R'} \quad (1.26)$$