

## Asymptotic model for the interplay of sedimentation and crystallization

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This paper considers a simple model for the coupled crystallization and sedimentation of a nucleated particle in a solvent. It is motivated by recent interest in understanding the effects of gravity on crystallization, arising in the context of possible future extraterrestrial manufacture of active pharmaceutical ingredients. The model is based on mass- and momentum-conservation arguments and consists of a nonlinear ordinary differential equation and an integrodifferential equation for the particle radius and its velocity, respectively, as functions of time; the second of these equations contains the well-known Basset integral history term. Nondimensionalization and subsequent asymptotic analysis indicate that there can be up to four different regimes as the growing particle sediments. The results of the analysis are compared with numerical solutions and found to give very good agreement; this is done for the crystallization of L-histidine, an essential amino acid that is used in the food and pharmaceutical industries. The availability of asymptotic solutions is particularly attractive in view of the surprisingly lengthy computational time, which is directly associated with the cumulative computational burden of the history term. An important implication is that the forced convection considered here outweighs any free convection effects arising from solute concentration gradients. Moreover, depending on the strength of the gravitational field, e.g., hypergravity or microgravity, the particle can either sediment, then grow, or grow while sedimenting. This distinction is critical for future models, as determining whether the two processes occur concurrently or sequentially influences the mathematical description of the crystallization dynamics.

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### I. INTRODUCTION

In recent years, there has been a growing interest in the crystallization of active pharmaceutical ingredients either in low-Earth-orbit microgravity or simulated hypergravity experiments on Earth [1–4]. This interest is driven by preliminary experimental evidence suggests that changing the effect of gravity may provide a route to control both physical and chemical properties of the crystallized drug. Collecting experimental data is challenging; so, there is a growing need to supplement this data with results from mechanistic models of crystallization. In contrast to large-scale industrial crystallizers in which mechanical stirring is used, gravity-influenced experiments are often carried out in small vials and in the absence of stirring [3]. In this environment, crystals nucleate in a

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supersaturated solvent, e.g., the amino acid L-histidine ( $\text{C}_6\text{H}_9\text{N}_3\text{O}_2$ ) in a mixture of water and ethanol [5–13], and sediment to the bottom of the vial. An often-used approach is therefore population balance modeling [14,15], which, at the simplest level, accounts for crystal nucleation and growth to predict the number density of crystals as a function of crystal size and time. However, the modeling of crystal growth relies on an assumption as regards mass transfer at the crystal surface; see Sec. II, and in particular Eq. (8), for more details. This motivates the study of what happens to one crystal, which will be the subject of this paper.

Working in the framework of classical nucleation theory [16], we assume that crystals form spontaneously through homogeneous nucleation, in which a collection of liquid molecules transforms into a solid nucleus. This occurs if the energetic cost of creating a solid-liquid interface is outweighed by the energetic gain in Gibbs free energy associated with removing molecules from solution. This will happen at a nucleation radius

$$r_{\text{nuc}} = \frac{0.828v_0^{1/3}}{\ln S} \ln \left( \frac{1}{N_0v_0c_e} \right), \quad (1)$$

where  $c_e$  is the equilibrium concentration in solution,  $N_0$  is the Avogadro constant,  $S$  is the supersaturation, which is given by the ratio of the solution concentration to  $c_e$ , and  $v_0$  is the nucleus molecular volume; here, Eq. (1) is obtained by combining the classical result for  $r_{\text{nuc}}$  [17], i.e.,

$$r_{\text{nuc}} = \frac{2v_0\gamma}{k_B T \ln S}, \quad (2)$$

where  $k_B$  is the Boltzmann constant and  $T$  is the absolute temperature, with the expression for  $\gamma$ , the material surface/solution composition-dependent interfacial energy, which is given, for a spherical nucleus, by Mersmann [18] as

$$\gamma = \frac{0.414k_B T}{v_0^{2/3}} \ln \left( \frac{1}{N_0v_0c_e} \right). \quad (3)$$

The particle is likely too small to begin sedimenting right away. Instead, it undergoes Brownian motion until it has grown large enough for gravitational effects to dominate, at which point the influence of Brownian motion becomes negligible. For a spherical particle of radius  $a$ , this is generally accepted to occur when  $\tilde{\text{Pe}} = 1$ , where  $\tilde{\text{Pe}}$  is the Péclet number, given by [19–23]

$$\tilde{\text{Pe}} = \frac{2\pi(\rho_p - \rho_s)g_{\text{eff}}a^4}{3k_B T}, \quad (4)$$

where  $g_{\text{eff}}$  is the acceleration due to gravity,  $\rho_p$  is the density of the crystal and  $\rho_s$  is the density of the solvent, with  $\rho_p > \rho_s$ ; note here that  $g_{\text{eff}}$  is not necessarily equal to the value of gravity at the Earth's surface, which we will denote later on as usual by  $g$ . The expectation is that  $r_{\text{nuc}} \ll a_c$ , where

$$a_c = \left( \frac{3k_B T}{2\pi(\rho_p - \rho_s)g_{\text{eff}}} \right)^{1/4} \quad (5)$$

is the critical radius at which  $\tilde{\text{Pe}} = 1$ , and hence

$$\frac{0.828v_0^{1/3}}{\ln S} \ln \left( \frac{1}{N_0v_0c_e} \right) \ll \left( \frac{3k_B T}{2\pi(\rho_p - \rho_s)g_{\text{eff}}} \right)^{1/4}, \quad (6)$$

which we will verify in due course. At the point when the particle radius  $a$  reaches the critical value  $a_c$  where  $\tilde{\text{Pe}} = 1$ , the particle begins to sediment, whilst continuing to grow in size, and eventually reaches the bottom of the vial.

The description outlined above differs in several ways from the classical one of a particle that sediments in a quiescent fluid under the influence of gravity, and eventually moves at a terminal velocity. First, the particle is continuously growing in size, meaning that there is no terminal

velocity. Also, although the particle may nucleate as a sphere, it will not necessarily retain this shape: for example, Chadam *et al.* [24] found that radially symmetric growth is obtained provided that the supersaturation is not too large, but that when the far-field supersaturation exceeds a critical value, then the radially symmetric solution ceases to exist in finite time. Finally, the motion of the surrounding fluid is complicated by the fact that crystallization results in the depletion of solute in the solvent adjacent to the crystal, giving a density gradient in the solvent which in turn will lead to a free-convective flow [25], in the same way as dissolution does [26]. However, without a detailed analysis, it is difficult to determine *a priori* which of these effects dominate and, if so, under what conditions.

An appropriate analysis could, in theory, be supplied by solving the canonical time-dependent fluid-mechanical problem of a growing axisymmetric body, initially spherical, that descends in a solvent having variable density that depends locally on the concentration of dissolved solute; this is equivalent to considering transient flow past a stationary body. Indeed, a framework for this kind of problem, albeit for a dissolving particle, was recently established in Refs. [26,27]; however, the solvent was assumed to flow past the particle with constant speed in Ref. [27], whereas in Ref. [26], the motion of the solvent was due only to free convection. Even so, even this is likely to prove computationally challenging, as this is a time-dependent axisymmetric moving-boundary problem involving cooperating mixed convection, i.e., both free and forced convection lead to solvent flow in the same direction with respect to the crystal. Furthermore, in the problems considered in Refs. [26,27], it was possible to find a frame of reference in which the center of mass of the body was stationary; in the sedimentation problem, however, even the location of the center of mass has to be determined. Thus, it is desirable to seek a simpler approach, at least to begin with; however, as an example of the opposite extreme, see Ref. [28], which considers Brownian dynamics simulations of a model of colloidal hard spheres.

For dissolution problems, which may, mathematically at least, be considered as the reverse of crystallization problems, a common simplification is to assume that the particle dissolves in a well-mixed solvent and remains spherical as it does so [29–32]. In the case of a stationary dissolving particle, this simple approach gives dissolution times that agree very well with a more detailed model for the case of forced convection [27], and that are qualitatively reasonable for free convection [26]. The case of a dissolving particle in time-dependent motion has only been considered using the simpler approach for the forced-convection case [29–32] and requires appending an additional equation for the particle’s time-dependent velocity. This is the integrodifferential equation for the conservation of momentum of a moving sphere, originally derived by Basset [33], Boussinesq [34], and Oseen [35] and now known as the BBO equation, albeit modified to take account of a changing radius and in a seemingly *ad hoc* way.

The purpose of this paper is to extend the two-equation model for dissolution under time-dependent motion to crystallization, with a view to determining the sedimentation behavior of a crystallizing particle and whether this is dominated by forced or free convection, i.e., determining the relative size of the sedimentation velocity of the particle and the buoyancy-driven flow in the solvent arising from the density gradients associated with solute concentration gradients. Also of importance will be the time necessary to sediment to the bottom of the reaction vessel, relative to the total crystallization time: if crystals are suspected to accumulate at the bottom of the vial during growth, the assumption of well-mixedness can certainly be called into question, since growing crystals will be exposed to a dissolved solute concentration that is much different to the average (well-mixed) concentration. In particular, unlike the aforementioned dissolution studies which naturally considered the Earth’s gravity, a key focus here will be on the influence of different gravitational environments (microgravity, hypergravity) in determining the dominating processes during crystallization.

The structure of the paper is as follows. In Sec. II, we formulate the problem of sedimentation of a growing crystal. Sec. III covers the nondimensionalization of the model equations. In Sec. IV, we analyze the equations by considering an asymptotic description that reveals four distinct regimes over different timescales, whilst in Sec. V we describe the method that we use to solve the system

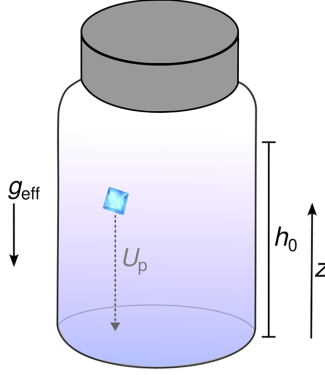


FIG. 1. A crystal, initially at  $z = h_0$ , sedimenting at speed  $U_p$  under the influence of a gravitational field of strength  $g_{\text{eff}}$  in a solvent-filled vial.

of equations numerically. In Sec. VI, we present some indicative results, and we discuss them in the context of mixed convection in Sec. VII; conclusions are drawn in Sec. VIII.

## II. MODELING SINGLE-PARTICLE GROWTH AND SEDIMENTATION

Consider a spherical particle of initial radius  $a_c$  that starts to sediment at time  $t = 0$  at a distance  $h_0$  above the base of a solvent-filled vial in a gravitational field of strength  $g_{\text{eff}}$ , as shown in Fig. 1. We will neglect any possible effect of the vial's vertical walls and its bottom on the particle motion. Moreover, although there will, in practice, be many particles that are sedimenting at the same time, each having nucleated at different locations and possibly different times, we do not take these into account. In what follows,  $r_p(t)$  will denote the radius of the particle at time  $t$  and  $U_p(t)$  its sedimentation velocity; however, we will henceforth suppress the argument on  $r_p$  and  $U_p$ , apart from in integrands, although we note that quantities which depend on  $r_p$  and/or  $U_p$  will be implicitly functions of  $t$ .

We begin by writing down an equation for the size of the crystal. Following the development outlined in Sec. I and already formalized for dissolution problems elsewhere [26,27,29], mass balance considerations give

$$\frac{d}{dt} \left( \frac{4}{3} \rho_p \pi r_p^3 \right) = 4\pi r_p^2 M k (c_0 - c_e), \quad (7)$$

where the term in the brackets on the left-hand side is the mass of a crystal of size  $r_p$  and density  $\rho_p$ , and the right-hand side describes the transfer of mass out of solution and onto the crystal surface. This transfer rate depends on the surface area,  $4\pi r_p^2$ , of the crystal and the mass flux of solute to the surface, which in turn depends on the molar mass,  $M$ , of the solute, its supersaturation level,  $c_0 - c_e$ , above the equilibrium concentration, and a mass transfer coefficient,  $k$ . The latter, at time  $t$ , is, in turn, related to the Sherwood number,  $\text{Sh}_p$ , via

$$\frac{k r_p}{D} = \text{Sh}_p, \quad (8)$$

where  $D$  is the diffusion coefficient for solute in the solvent; the Sherwood number can itself be thought of as the ratio of convective mass transfer to diffusive mass transfer. Moreover, although crystals are unlikely to be spherical, an often-used simplified approach is to use the Sherwood number,  $\text{Sh}^*$ , that would prevail for a sphere of corresponding radius  $r_p^*$  under steady-state conditions [9,42]; this allows the use of correlations for the Sherwood number, already available from fluid mechanics and mass transfer [36,37], as a function of the relevant dimensionless parameters.

Thence, having  $\text{Sh}^* = \text{Sh}^*(r_p^*)$ , we take  $\text{Sh}_p = \text{Sh}^*(r_p)$ , where  $r_p$  is a function of time, as stated earlier. As regards the suitability of using such steady-state correlations in time-dependent problems, we may note that this has been done by other authors in problems related to particle dissolution [29–32], and has even been tested quantitatively by ourselves for the dissolution of an initially spherical body in the presence of either free or forced convection [26,27]; in these problems, the results of two-dimensional axisymmetric computations, involving a moving-boundary problem for the remaining particle shape as a function of time, were compared against those obtained from a simplified model in which the steady-state correlations were used and the body was assumed to dissolve as a sphere. On the whole, the two approaches gave surprisingly good agreement for the dissolution time, lending credence to the use of the steady-state correlations. The specific correlation that is used depends on the nature of convection near the particle [36,37]. Focusing here on forced convection and deferring discussion of free convection to Sec. VII, the most often-used correlation is the one due to Ranz and Marshall [38], given by

$$\text{Sh}_p = 1 + 0.3\sqrt{2}\text{Re}_p^{1/2}\text{Sc}^{1/3}, \quad (9)$$

where  $\text{Re}_p$  and  $\text{Sc}$  are the particle Reynolds number and Schmidt number, respectively, representing the ratio of inertial to viscous forces and the ratio of momentum to mass diffusivity, and are given by

$$\text{Re}_p = \frac{\rho_s U_p r_p}{\mu}, \quad (10a)$$

$$\text{Sc} = \frac{\mu}{\rho_s D}, \quad (10b)$$

where  $\mu$  is the dynamic viscosity of the solvent. However, Assunção *et al.* [27] recently demonstrated that the alternative correlation

$$\text{Sh}_p = \frac{1}{2}(1 + (1 + 2\text{Pe}_p)^{1/3}), \quad (11)$$

as given in Ref. [36], works considerably better when  $\text{Re}_p \ll 1$  and  $\text{Sc} \gg 1$ , even in the highly convection-dominated regime (for which it was not originally intended). This conclusion was reached by comparing the dissolution times predicted when using the two correlations against finite-element solutions of the coupled mass, momentum, and solute concentration equations; as can be seen in Fig. 9 of Ref. [27], using Eq. (11) gave much better agreement. In Eq. (11),  $\text{Pe}_p$  denotes another Péclet number, unrelated to the one in Eq. (4), and is given by

$$\text{Pe}_p = \frac{U_p r_p}{D}; \quad (12)$$

this quantifies the relative importance of convective to diffusive transport in the bulk of the fluid. Based on this evidence, we use the correlation (11) instead of Eq. (9) in this paper. Throughout this work, nondimensional numbers with the subscript “p” are evaluated using the instantaneous particle radius  $r_p(t)$  and sedimentation velocity  $U_p(t)$ . In summary, combining Eqs. (7), (8) and (11), the evolution of the particle radius is governed by

$$\rho_p r_p \frac{dr_p}{dt} = \frac{1}{2}DM(c_0 - c_e)(1 + (1 + 2\text{Pe}_p)^{1/3}). \quad (13)$$

The particle velocity,  $U_p$ , as a function of time,  $t$ , is determined using the BBO equation for the unsteady motion of a spherical particle suspended in quiescent fluid [33–35,39], and is given by

$$m_p \frac{dU_p}{dt} = F_{\text{drag}} + F_{\text{buoy}} + F_{\text{vm}} + F_{\text{Basset}}, \quad (14)$$

where  $m_p (= 4\rho_p\pi r_p^3/3)$  denotes the mass of the particle, and  $F_{\text{drag}}$ ,  $F_{\text{buoy}}$ ,  $F_{\text{vm}}$ , and  $F_{\text{Basset}}$  denote, respectively, the drag, buoyancy, the virtual mass drag, which can be calculated from the potential flow past a sphere [40,41], and the Basset history integral, which describes the resistance due to the

unsteady flow field; these are given by

$$F_{\text{drag}} = -6\pi\mu r_p U_p, \quad (15)$$

$$F_{\text{buoy}} = \frac{4}{3}\pi r_p^3 g_{\text{eff}}(\rho_p - \rho_s), \quad (16)$$

$$F_{\text{vm}} = -\frac{2}{3}\pi r_p^3 \rho_s \frac{dU_p}{dt}, \quad (17)$$

$$F_{\text{Basset}} = -6r_p^2(\pi\mu\rho_s)^{1/2} \int_0^t \frac{dU_p}{d\xi} \frac{d\xi}{(t-\xi)^{1/2}}. \quad (18)$$

As for initial conditions, supposing that the sphere of radius  $a_c$  starts from rest, we have

$$r_p = a_c \quad \text{at } t = 0, \quad (19a)$$

$$U_p = 0 \quad \text{at } t = 0. \quad (19b)$$

A quantity of interest will be the time,  $t_{\text{sed}}$ , taken for the particle to reach the bottom of the vial. With  $z$  denoting the location of the particle above the bottom of the vial, we will have

$$z = h_0 - \int_0^t U_p(t') dt'; \quad (20)$$

consequently,  $t_{\text{sed}}$  will be given by

$$\int_0^{t_{\text{sed}}} U_p(t') dt' = h_0. \quad (21)$$

Equations (13) and (14), subject to Eqs. (19a) and (19b), constitute a closed problem where Eq. (13), governing  $r_p$ , is inherently nonlinear and Eq. (14), governing  $U_p$ , while linear in isolation, becomes nonlinear when coupled to  $r_p$  via drag and Basset terms. This problem could in principle be solved numerically, with  $z$  being determined afterwards, although this is not entirely straightforward, since Eq. (14) is an integrodifferential equation in which the integrand in the integral term appears to have a singularity. We will solve these equations numerically later on, but we focus first on understanding their behavior analytically by using nondimensionalization and determining asymptotic solutions.

### III. NONDIMENSIONALIZATION

We introduce the dimensionless variables

$$\tau = \frac{t}{a_c^2 \rho_s / DM(c_0 - c_e)}, \quad (22a)$$

$$R_p = \frac{r_p}{a_c}, \quad (22b)$$

$$W_p = \frac{U_p}{U_{\text{TS}}}, \quad (22c)$$

$$Z = \frac{z}{h_0}, \quad (22d)$$

where

$$U_{\text{TS}} = \frac{2g_{\text{eff}}a_c^2(\rho_p - \rho_s)}{9\mu}, \quad (23)$$

noting that Eq. (23) gives the terminal velocity for a spherical particle of radius  $a_c$  in the Stokes limit; observe also that the timescale in Eq. (22a) is chosen to balance the terms in the particle growth equation, and it is therefore a crystal growth timescale. Equations (13) and (14) now give

$$\rho R_p \frac{dR_p}{d\tau} = \text{Sh}_p, \quad (24)$$

$$\left(\frac{2\rho + 1}{9}\right) \varepsilon R_p^3 \frac{dW_p}{d\tau} = R_p^3 - R_p W_p - \left(\frac{\varepsilon}{\pi}\right)^{1/2} R_p^2 \int_0^\tau \frac{dW_p}{d\xi} \frac{d\xi}{(\tau - \xi)^{1/2}}, \quad (25)$$

respectively, where  $\rho = \rho_p/\rho_s (> 1)$  and

$$\varepsilon = \frac{DM(c_0 - c_e)}{\mu}; \quad (26)$$

thus,  $\varepsilon$  can be interpreted as the ratio of the momentum transfer timescale to the crystallization timescale. Furthermore,

$$\text{Sh}_p = \frac{1}{2}(1 + (1 + 2\text{Pe}W_p R_p)^{1/3}) \quad (27)$$

and

$$\text{Pe} = \frac{U_{\text{TS}} a_c}{D}. \quad (28)$$

Note that this definition of Péclet number, unlike  $\text{Pe}_p$  in Eq. (12), does not vary with time. The initial conditions (19a) and (19b) are

$$R_p(0) = 1, \quad (29a)$$

$$W_p(0) = 0, \quad (29b)$$

respectively. Furthermore, Eq. (21) becomes

$$\frac{\Gamma}{\varepsilon} \int_0^{\tau_{\text{sed}}} W_p(\tau') d\tau' = 1, \quad (30)$$

where

$$\Gamma = \frac{2g_{\text{eff}} a_c^4 (\rho_p - \rho_s) \rho_s}{9h_0 \mu^2}, \quad \tau_{\text{sed}} = \frac{t_{\text{sed}}}{a_c^2 \rho_s / DM(c_0 - c_e)}. \quad (31)$$

We observe that  $\Gamma$  can be rewritten in terms of two, more tangible, dimensionless parameters,

$$\delta = \frac{a_c}{h_0}, \quad \text{Re}_{\text{TS}} = \frac{\rho_s U_{\text{TS}} a_c}{\mu}, \quad (32)$$

so that  $\Gamma = \delta \text{Re}_{\text{TS}}$ :  $\delta$  is the ratio of the particle radius at the onset of sedimentation to the initial particle height in the vial and  $\text{Re}_{\text{TS}}$  can be interpreted as the Reynolds number at the terminal velocity for a particle of radius  $a_c$ . Note also that the quantity  $\Gamma/\varepsilon$  in Eq. (30) corresponds to the ratio of the crystal growth timescale to the sedimentation timescale,  $h_0/U_{\text{TS}}$ , and tells us if the crystal will grow substantially from its initial size before it reaches the bottom of the vial. That is, if  $\Gamma \ll \varepsilon$ , then the crystal growth timescale is comparatively short and the particle will grow before it sediments; however, if  $\Gamma \gg \varepsilon$ , then we would expect the particle to finish sedimenting before growing substantially from its initial size.

#### IV. ASYMPTOTIC ANALYSIS OF SEDIMENTATION AND GROWTH DYNAMICS

At this stage, there are evidently four nondimensional parameters:  $\Gamma$ ,  $\varepsilon$ ,  $\text{Pe}$ ,  $\rho$ . However, only the last three of these are of significance for the main problem, although the first one,  $\Gamma$ , is of importance

TABLE I. Indicative model parameters for the crystallization of L-histidine in water. Note that the value of  $h_0$  given is of the order of magnitude of the height of a typical vial used in a Crystal16 (Technobis Crystallization Systems) reactor [3,43].

| Parameter | Value                  | Units                                       | Reference |
|-----------|------------------------|---------------------------------------------|-----------|
| $c_0$     | 100                    | $\text{mol m}^{-3}$                         | [9]       |
| $c_e$     | 50                     | $\text{mol m}^{-3}$                         | [42]      |
| $D$       | $5 \times 10^{-10}$    | $\text{m}^2 \text{s}^{-1}$                  | [25]      |
| $g$       | 9.81                   | $\text{m s}^{-2}$                           |           |
| $h_0$     | $5 \times 10^{-3}$     | m                                           |           |
| $k_B$     | $1.38 \times 10^{-23}$ | $\text{m}^2 \text{kg s}^{-2} \text{K}^{-1}$ |           |
| $M$       | 0.155                  | $\text{kg mol}^{-1}$                        |           |
| $N_0$     | $6.02 \times 10^{23}$  | $\text{mol}^{-1}$                           |           |
| $T$       | 298                    | K                                           |           |
| $v_0$     | $1.8 \times 10^{-28}$  | $\text{m}^3$                                | [42]      |
| $\beta$   | $2.23 \times 10^{-4}$  | $\text{mol}^{-1} \text{m}^3$                | [25]      |
| $\mu$     | $1 \times 10^{-3}$     | $\text{kg m}^{-1} \text{s}^{-1}$            |           |
| $\rho_p$  | 1446                   | $\text{kg m}^{-3}$                          | [6]       |
| $\rho_s$  | 1000                   | $\text{kg m}^{-3}$                          |           |

for determining the sedimentation time. Moreover, from the data in Table I, we see that  $\rho \sim O(1)$ , and that  $\varepsilon$ ,  $\text{Pe}$ ,  $\Gamma$  are small: more specifically, we have, for  $g_{\text{eff}} = 1g$ ,

$$\Gamma \approx 3 \times 10^{-11}, \quad \varepsilon \approx 6.6 \times 10^{-6}, \quad \text{Pe} \approx 6 \times 10^{-4}, \quad \rho \approx 1.4, \quad (33)$$

noting also that

$$r_{\text{nuc}} \approx 3.5 \times 10^{-9} \text{ m}, \quad a_c \approx 8.2 \times 10^{-7} \text{ m}, \quad (34)$$

giving  $r_{\text{nuc}} \ll a_c$ , as was expected, as well as

$$\delta \approx 1.6 \times 10^{-4}, \quad \text{Re}_{\text{TS}} \approx 1.7 \times 10^{-7}. \quad (35)$$

In what follows, we consider an asymptotic description based on  $\varepsilon \ll \text{Pe} \ll 1$ , as this is the order of inequalities suggested by Eq. (33). Whilst the meaning of  $\varepsilon \ll 1$  and  $\text{Pe} \ll 1$  is fairly straightforward, i.e.,  $\varepsilon \ll 1$  implies that the momentum transfer timescale (in particular, that due to momentum diffusion) is much shorter than the crystallization timescale and  $\text{Pe} \ll 1$  implies that solute diffusion dominates convection for a particle of radius  $a_c$  moving at its terminal speed, the meaning of  $\varepsilon \ll \text{Pe}$  is less clear. However, it is instructive to write this in dimensional quantities, which yields

$$g_{\text{eff}} \gg \frac{243D^8 M^4 (c_0 - c_e)^4 \pi^3}{2(\rho_p - \rho_s) k_B^3 T^3}, \quad (36)$$

on using Eqs. (5), (23), (26), and (28). Now, for a given temperature, the right-hand side of Eq. (36) is constant for a given solute-solvent combination; this constant is notably independent of the solvent's dynamic viscosity. Thus, we can interpret the original inequality as being one for  $g_{\text{eff}}$ ; in particular, using the data in Table I, we obtain  $g_{\text{eff}} \gg 10^{-9}g$ . For completeness, we note also that  $\Gamma \ll \varepsilon$ ; from Eq. (32), this is clearly a consequence of the fact that the sedimentation height is large compared to the initial radius of the particle,  $a_c$ , and that the Reynolds number corresponding to the terminal velocity of a particle with that radius is very small also.

It will turn out that Eqs. (24) and (25) admit four different asymptotic regimes (I–IV) over four different timescales, which we will describe sequentially below. In fact, from the discussion hitherto as regards the nondimensionalization, it is already evident that the problem will have multiple timescales, although it is not perhaps clear *a priori* how many there will actually be. For the case

of a particle of fixed size, there would only be one timescale. However, the fact that the particle grows introduces more. In particular, as it grows, the effect of convection due to sedimentation will increase, which will then make it grow faster. However, such a qualitative discussion can still not enumerate how many timescales or, equivalently, asymptotic regimes there will be; for this, a systematic analysis is necessary. In summary:

- (1) on the shortest timescale, the particle sediments but without growing (regime I);
- (2) thereafter, it continues to sediment and begins to grow in size, but without convection affecting its rate of growth (regime II);
- (3) after that, we have growth-affected sedimentation and sedimentation-affected growth, with the sedimentation velocity increasing quadratically with particle size, as a consequence of drag balancing buoyancy (regime III);
- (4) finally, we have altogether more complicated coupling between particle size and sedimentation velocity (regime IV).

#### A. Four asymptotic regimes

##### 1. Regime I: Rapid acceleration without growth ( $\tau \sim \varepsilon$ )

At first sight, because  $\tau \sim \varepsilon \ll 1$ , Eq. (25) reduces, at leading order, to

$$R_p(R_p^2 - W_p) = 0, \quad (37)$$

whence either  $R_p = 0$  or  $W_p = R_p^2$ . However, neither of these will satisfy the initial conditions and we will need to have a boundary layer in time in which the time derivative in Eq. (25) is brought back into the leading-order balance. Setting  $\tau = \varepsilon \tilde{\tau}$ , where  $\tilde{\tau} \sim O(1)$ , we have

$$\rho R_p \frac{dR_p}{d\tilde{\tau}} = \varepsilon \text{Sh}_p, \quad (38)$$

$$\left(\frac{2\rho+1}{9}\right) R_p^3 \frac{dW_p}{d\tilde{\tau}} = R_p^3 - R_p W_p - \frac{R_p^2}{\pi^{1/2}} \int_0^{\tilde{\tau}} \frac{dW_p}{d\xi} \frac{d\xi}{(\tilde{\tau} - \xi)^{1/2}}, \quad (39)$$

subject to

$$R_p = 1, \quad (40a)$$

$$W_p = 0 \quad \text{at } \tilde{\tau} = 0. \quad (40b)$$

Assuming for the moment that  $\text{Sh}_p \sim O(1)$ , Eq. (38) gives, at leading order,

$$\frac{dR_p^2}{d\tilde{\tau}} \approx 0, \quad (41)$$

whence, on using Eq. (40a), we have  $R_p = 1$ , so that Eq. (39) gives

$$\left(\frac{2\rho+1}{9}\right) \frac{dW_p}{d\tilde{\tau}} = 1 - W_p - \frac{1}{\pi^{1/2}} \int_0^{\tilde{\tau}} \frac{dW_p}{d\xi} \frac{d\xi}{(\tilde{\tau} - \xi)^{1/2}}. \quad (42)$$

Then, since it is clear that  $R_p, W_p \sim O(1)$  for this regime, we will have  $\text{Pe} R_p W_p \ll 1$ , and thence  $\text{Sh}_p \sim O(1)$ , as was assumed prior to Eq. (41). Equation (42) is the usual equation of motion for a spherical particle released from rest in a stagnant medium [36,40,44], and would have been obtained if we had nondimensionalized  $t$  with the momentum transfer timescale,  $a_c^2 \rho_s / \mu$ , as was done in Ref. [36], rather than the crystallization timescale,  $a_c^2 \rho_s / DM(c_0 - c_e)$ .

It is well-established [36,45] that the first-order integrodifferential equation (42) can be turned into a linear second-order ordinary differential equation,

$$\frac{d^2 W_p}{d\tilde{\tau}^2} + B(2-B) \frac{dW_p}{d\tilde{\tau}} + B^2 W_p = B^2 \left(1 - \frac{1}{\pi^{1/2} \tilde{\tau}^{1/2}}\right), \quad (43)$$

where  $B = 9/(2\rho + 1)$ , subject to the initial conditions

$$W_p = 0, \quad (44a)$$

$$\frac{dW_p}{d\tilde{\tau}} = B \quad \text{at } \tilde{\tau} = 0. \quad (44b)$$

As documented in Ref. [36], the problem has an analytical solution which takes a different form, depending on whether  $\rho < 5/8$ ,  $\rho = 5/8$ , or  $\rho > 5/8$ . However, the solution for  $\rho > 5/8$ , which is the case that we need here, is given in a rather inconvenient form in Ref. [36], as it requires the evaluation of complex-valued integrals; furthermore, even to solve it numerically, and to obtain the expected  $\tilde{\tau}^{-1/2}$ -decay to  $W_p = 1$  as  $\tilde{\tau} \rightarrow \infty$ , turns out to be far from straightforward. Thus, for completeness, we discuss the analytical and numerical solution of Eq. (43) in Appendix A. The analytical solution,  $W_{p,1}$ , as a function of dimensionless time  $\tau$  is given by the composition of Eqs. (A5) and (A9), derived and explained in detail in the Appendix and presented here for convenience:

$$W_{p,1} = 1 - \left(\frac{1}{\pi}\right)^{1/2} \sum_{n=0}^{\infty} \frac{A_n}{B^n \tilde{\tau}^{n+1/2}}, \quad (45)$$

where  $(A_n)_{n \geq 0}$  are constants that are determined from Eqs. (A10) and (A11).

Finally, noting that, since

$$\int_0^{\tilde{\tau}} W_p(\tau') d\tau' \sim \tilde{\tau}, \quad (46)$$

as can be deduced from Eq. (45), then, if sedimentation is completed during this regime, we must have, from Eq. (30),

$$\tau_{\text{sed}} \sim \frac{\varepsilon}{\Gamma}. \quad (47)$$

If sedimentation is not completed on the  $\tau = O(\varepsilon)$  timescale, then the particle will continue to grow and descend until  $\tau = O(1)$  and a new regime begins.

## 2. Regime II: Terminal velocity with square-root growth ( $\tau \sim O(1)$ )

For this regime, at leading order in  $\varepsilon$ , the equation for the particle acceleration, Eq. (25), gives

$$W_p \approx R_p^2, \quad (48)$$

whence Eq. (24) gives

$$\rho R_p \frac{dR_p}{d\tau} = \frac{1}{2} (1 + (1 + 2\text{Pe} R_p^3)^{1/3}), \quad (49)$$

subject to

$$R_p = 1 \quad \text{at } \tau = 0. \quad (50)$$

Now, assuming for the moment that  $\text{Pe} R_p^3 \ll 1$ , the right-hand side of Eq. (49) can be simplified to give

$$\rho R_p \frac{dR_p}{d\tau} \approx 1. \quad (51)$$

Integrating Eq. (51) and applying the initial condition (50) yields

$$R_p \approx \left(1 + \frac{2\tau}{\rho}\right)^{1/2}, \quad (52)$$

with Eq. (48) then giving

$$W_p \approx \left(1 + \frac{2\tau}{\rho}\right). \quad (53)$$

Hence, since  $\tau \sim O(1)$  in this regime, we will have that  $R_p, W_p \sim O(1)$  also, and thus  $\text{Pe}R_p^3 \ll 1$ , as was assumed prior to Eq. (51). If sedimentation is completed during the  $\tau = O(1)$  regime, the sedimentation time can be calculated by substituting the velocity result (30) into the sedimentation formula (53) to give

$$\Gamma \tau_{\text{sed}}^2 + \rho \Gamma \tau_{\text{sed}} - \rho \varepsilon \approx 0, \quad (54)$$

which can be solved to give

$$\tau_{\text{sed}} \approx \frac{-\rho \pm \sqrt{\rho^2 + 4\rho\varepsilon/\Gamma}}{2}, \quad (55)$$

whence, since  $\rho \sim O(1)$  and  $\varepsilon \gg \Gamma$ , we will have

$$\tau_{\text{sed}} \approx \left(\frac{\rho\varepsilon}{\Gamma}\right)^{1/2}. \quad (56)$$

Substituting the sedimentation time (56) into Eqs. (52) and (53) yields

$$R_p \approx \left(1 + 2\left(\frac{\varepsilon}{\rho\Gamma}\right)^{1/2}\right)^{1/2}, \quad W_p \approx \left(1 + 2\left(\frac{\varepsilon}{\rho\Gamma}\right)^{1/2}\right), \quad (57)$$

respectively, and again exploiting  $\varepsilon \gg \Gamma$  leads to

$$R_p \sim \left(\frac{\varepsilon}{\Gamma}\right)^{1/4}, \quad W_p \sim \left(\frac{\varepsilon}{\Gamma}\right)^{1/2}. \quad (58)$$

Note that, in an asymptotic sense, Eqs. (56) and (58) may be calculated independently of what has happened in regime I, since what happens in the first regime occurs over a much shorter timescale; in addition, the evolution of  $R_p$  is asymptotically zero, as seen from the point of view of regime II.

If sedimentation is not completed on the  $\tau = O(1)$  timescale, particle growth will continue until the assumption  $\text{Pe}R_p^3 \ll 1$  breaks down, and a new description is required.

### 3. Regime III: Terminal velocity and dynamics-dependent growth ( $\tau \sim \text{Pe}^{-2/3}$ )

Since  $R_p$  is increasing, it is evident that a regime switch should occur when  $\text{Pe}W_pR_p \sim 1$ , meaning that mass transport is no longer diffusion-dominated, and the particle velocity and radius can no longer be neglected when evaluating the Sherwood number in Eq. (27); on using Eqs. (52) and (53), this implies that

$$\text{Pe} \left(1 + \frac{2\tau}{\rho}\right)^{3/2} \sim 1, \quad (59)$$

i.e.,  $\tau \sim \text{Pe}^{-2/3}$ . For this regime, we rescale according to

$$\tau = \text{Pe}^{-2/3} \bar{\tau}, \quad R_p = \text{Pe}^{-1/3} \bar{R}_p, \quad W_p = \text{Pe}^{-2/3} \bar{W}_p,$$

so that Eqs. (24) and (25) give, at leading order,

$$2\rho\bar{R}_p \frac{d\bar{R}_p}{d\bar{\tau}} \approx 1 + (1 + 2\bar{W}_p\bar{R}_p)^{1/3}, \quad (60)$$

$$\bar{W}_p \approx \bar{R}_p^2, \quad (61)$$

subject to

$$\bar{R}_p = 0, \quad (62a)$$

$$\bar{W}_p = 0 \quad \text{at } \bar{\tau} = 0. \quad (62b)$$

Thus, we obtain  $\bar{R}_p$  and  $\bar{W}_p$  implicitly via

$$2\rho \int_0^{\bar{R}_p} \frac{r dr}{1 + (1 + 2r^3)^{1/3}} = \bar{\tau}, \quad (63a)$$

$$\rho \int_0^{\bar{W}_p} \frac{dr}{1 + (1 + 2r^{3/2})^{1/3}} = \bar{\tau}, \quad (63b)$$

respectively.

Now, since  $\bar{W}_p$  cannot be determined explicitly, it is not possible to give a general closed-form expression for  $\tau_{\text{sed}}$ , in contrast to Eqs. (47) and (56).

#### 4. Regime IV: Late-stage coupled dynamics ( $\tau \sim \varepsilon^{-1} \text{Pe}^{-2/3}$ )

Regime III will prevail as long as  $\varepsilon(\text{Pe}R_pW_p)^{1/3} \sim 1$ . However, there turns out to be a final, long timescale when the time derivative and the integral term in Eq. (25) both participate in the leading-order momentum balance. For this regime, we set

$$\tau = \text{Pe}^{-2/3} \varepsilon^{-1} \hat{\tau}, \quad (64a)$$

$$R_p = \text{Pe}^{-1/3} \varepsilon^{-1} \hat{R}_p, \quad (64b)$$

$$W_p = \text{Pe}^{-2/3} \varepsilon^{-2} \hat{W}_p. \quad (64c)$$

Now, Eqs. (24) and (25) become, respectively,

$$2^{2/3} \rho \frac{d\hat{R}_p}{d\hat{\tau}} = \hat{W}_p^{1/3} \hat{R}_p^{-2/3}, \quad (65)$$

$$\hat{R}_p^2 \frac{d\hat{W}_p}{d\hat{\tau}} = B \left( \hat{R}_p^2 - \hat{W}_p - \frac{\hat{R}_p}{\pi^{1/2}} \int_0^{\hat{\tau}} \frac{d\hat{W}_p}{d\zeta} \frac{d\zeta}{(\hat{\tau} - \zeta)^{1/2}} \right), \quad (66)$$

subject to

$$\hat{R}_p = 0, \quad (67a)$$

$$\hat{W}_p = 0 \quad \text{at } \hat{\tau} = 0. \quad (67b)$$

Although there is a trivial solution to Eqs. (65)–(67), considering small- $\hat{\tau}$  behavior helps to establish that there is also a nontrivial solution and indicates a strategy for finding it numerically if necessary.

For small  $\hat{\tau}$ , suppose that

$$\hat{R}_p \sim a_1 \hat{\tau}^{b_1}, \quad (68a)$$

$$\hat{W}_p \sim a_2 \hat{\tau}^{b_2}, \quad (68b)$$

where  $a_1, a_2, b_1, b_2 > 0$  and are all to be determined. From Eq. (65), we will need

$$\rho a_1 b_1 \hat{\tau}^{b_1-1} \sim \frac{(a_2 \hat{\tau}^{b_2})^{1/3} (a_1 \hat{\tau}^{b_1})^{-2/3}}{2^{2/3}}, \quad (69)$$

whence equating the exponents and premultiplicative factors gives

$$a_2 = 4\rho^3 a_1^5 b_1^3, \quad (70a)$$

$$b_2 = 5b_1 - 3. \quad (70b)$$

Similarly, from Eq. (66), we will need

$$a_1^2 a_2 \hat{\tau}^{2b_1+b_2-1} \sim B \left( \hat{\tau}^{2b_1} - \hat{\tau}^{b_2} - \frac{\hat{\tau}^{b_1}}{\pi^{1/2}} \int_0^{\hat{\tau}} \frac{\zeta^{b_2-1} d\zeta}{(\hat{\tau} - \zeta)^{1/2}} \right). \quad (71)$$

Now, on noting that, for  $\hat{\tau} \ll 1$ ,

$$\int_0^{\hat{\tau}} \frac{\zeta^{b_2-1} d\zeta}{(\hat{\tau} - \zeta)^{1/2}} \sim 2 \hat{\tau}^{b_2-1/2}, \quad (72)$$

Eq. (71) gives

$$a_1^2 a_2 \hat{\tau}^{2b_1+b_2-1} \sim B \left( a_1^2 \hat{\tau}^{2b_1} - a_2 \hat{\tau}^{b_2} - \frac{2a_1 a_2 \hat{\tau}^{b_1+b_2-1/2}}{\pi^{1/2}} \right), \quad (73)$$

and then, on using Eq. (70b), we have

$$a_1^2 a_2 \hat{\tau}^{5b_1-1} \sim B \left( a_1^2 \hat{\tau}^3 - a_2 \hat{\tau}^{3b_1} - \frac{2a_1 a_2 \hat{\tau}^{4b_1-1/2}}{\pi^{1/2}} \right). \quad (74)$$

Thus, a self-consistent leading-order balance is obtained with  $b_1 = 1$ , and hence  $b_2 = 2$  from Eq. (70b). Also, from Eq. (74), we must have  $a_2 = a_1^2$ , and hence Eq. (70a) gives

$$a_1 = \frac{1}{4^{1/3} \rho}, \quad a_2 = \frac{1}{4^{2/3} \rho^2}. \quad (75)$$

Details of how this analysis helps in the numerical solution of Eqs. (65)–(67) are given in Appendix B.

Similar analysis can be used to determine the large- $\hat{\tau}$  behavior for  $W_p$  and  $R_p$ . In this case, Eq. (69) holds as before, but instead of Eq. (74) we have

$$a_1^2 a_2 \hat{\tau}^{2b_1+b_2-1} \sim B \left( a_1^2 \hat{\tau}^{2b_1} - a_2 \hat{\tau}^{b_2} - \frac{a_1 a_2 C \hat{\tau}^{b_1+b_2-1/2}}{\pi^{1/2}} \right), \quad (76)$$

where

$$C = \int_0^1 \frac{\zeta^{b_2-1} d\zeta}{(1 - \zeta)^{1/2}}. \quad (77)$$

This time, a self-consistent leading-order balance is obtained with

$$b_1 = 4/5, \quad (78a)$$

$$b_2 = 1, \quad (78b)$$

which constitutes a balance between the time-derivative term and the first term on the right-hand side of Eq. (66); consequently, we also obtain

$$a_1 = \left( \frac{125B}{256\rho^3} \right)^{1/5}, \quad (79a)$$

$$a_2 = B. \quad (79b)$$

Finally, we note that, as there are no explicit expressions for  $\hat{W}_p$  and  $\hat{R}_p$  as functions of time for this regime, it is not possible to write down an explicit expression for  $\tau_{\text{sed}}$  either, as in regime III.

## B. Composite solutions

We are also now able to approximate  $R_p$ ,  $W_p$ , and  $Z$  analytically as functions of  $\tau$ ; to do this, we can simply use the theory of matched asymptotic expansions [46] and the results from Secs. IV A 1–IV A 4 to construct composite solutions, which we can later compare with the full numerical results.

For  $\phi = (R_p, W_p, Z)$ , we have

$$\phi^{\text{comp}} = \sum_{i=\text{I,II,III,IV}} (\phi_i(\tau_i) + \phi_{i+1}(\tau_{i+1}) - \phi_{i,i+1}^{\text{common}}), \quad (80)$$

where  $\tau_i$  is the independent variable for regime  $i$ ,  $\phi_i$  is the dependent variable for regime  $i$  and  $\phi_{i,i+1}^{\text{common}}$  is the common parts of  $\phi_i(\tau_i)$  and  $\phi_{i+1}(\tau_{i+1})$  in the limits as  $\tau_i \rightarrow \infty$  and  $\tau_{i+1} \rightarrow 0$ . However, since there are no closed-form expressions for the solutions in regimes III and IV, and since the parameters that we will use for the results in Sec. VI are for a case where sedimentation is complete just before regime III is reached, we will just present here the composite solution for regimes I and II, valid until sedimentation is completed. So, with

$$\tau_{\text{I}} = \varepsilon \tau, \quad \tau_{\text{II}} = \tau,$$

we have

$$R_p^{\text{comp}} = \left(1 + \frac{2\tau}{\rho}\right)^{1/2}, \quad (81)$$

$$W_p^{\text{comp}} = W_p, \text{I}\left(\frac{\tau}{\varepsilon}\right) + \frac{2\tau}{\rho}, \quad (82)$$

$$Z^{\text{comp}} = 1 - \int_0^\tau W_p, \text{I}\left(\frac{\tau'}{\varepsilon}\right) d\tau' - \frac{\tau^2}{\rho}, \quad (83)$$

respectively, where  $W_p, \text{I}$  is as described in Eq. (45) and further explained in Appendix A.

### C. Constraints and timescale-dependent dynamics of regime transitions

As already stated, whether all four regimes occur during sedimentation will depend on whether the value of  $\Gamma$  is small enough, i.e., the descent height is great enough. However, a further requirement is that the particle Reynolds number,  $\text{Re}_p$ , is much smaller than one. Tracking back through the algebra, this means that  $\text{Re}_{\text{TS}} R_p W_p \ll 1$ . For regimes I and II, this gives

$$\text{Re}_{\text{TS}} \ll 1, \quad \text{Re}_{\text{TS}} \left(\frac{\varepsilon}{\Gamma}\right)^{3/4} \ll 1, \quad (84)$$

respectively. The analogous conditions cannot be obtained for regimes III and IV, as neither  $W_p$  nor  $R_p$  can be determined explicitly in these regimes.

Qualitative schematics of the evolution of  $R_p$  and  $W_p$  as functions of  $\tau$  are given in Figs. 2 and 3, respectively. The profiles evolve through four distinct regimes, as expected from the timescale analysis above. Initially, the particle accelerates rapidly on a  $\tau = O(\varepsilon)$  timescale which is too fast for substantial growth; all four forces outlined in Eqs. (15)–(18) contribute to this acceleration. The particle then begins to grow and sediment simultaneously on a  $\tau = O(1)$  timescale. It initially sediments at its terminal velocity, which increases as the particle grows, which in turn begins to affect the growth rate on a  $\tau = O(\text{Pe}^{-2/3})$  timescale; over these timescales, the leading-order force balance is between drag and buoyancy. Finally, all four forces once again begin to affect the particle when  $\tau = O(\varepsilon^{-1} \text{Pe}^{-2/3})$ . Also, as regards Figs. 2 and 3, we note that, although analytical expressions are not available for regimes III and IV, the qualitative forms of the curves that have been drawn for these regimes bear some connection to the analysis: for Fig. 2, we use the fact that Eq. (63a) gives that  $\hat{R}_p \sim \bar{\tau}$  for  $\hat{R}_p \gg 1$  in regime III, whereas Eqs. (68a) and (78a) give that  $\hat{R}_p \sim \hat{\tau}^{4/5}$  for  $\hat{R}_p \gg 1$  in regime IV; for Fig. 3, Eq. (63b) gives that  $\hat{W}_p \sim \bar{\tau}^2$  for  $\hat{W}_p \gg 1$  in regime III, whereas Eqs. (68b) and (78b) give that  $\hat{W}_p \sim \hat{\tau}$  for  $\hat{W}_p \gg 1$  in regime IV.

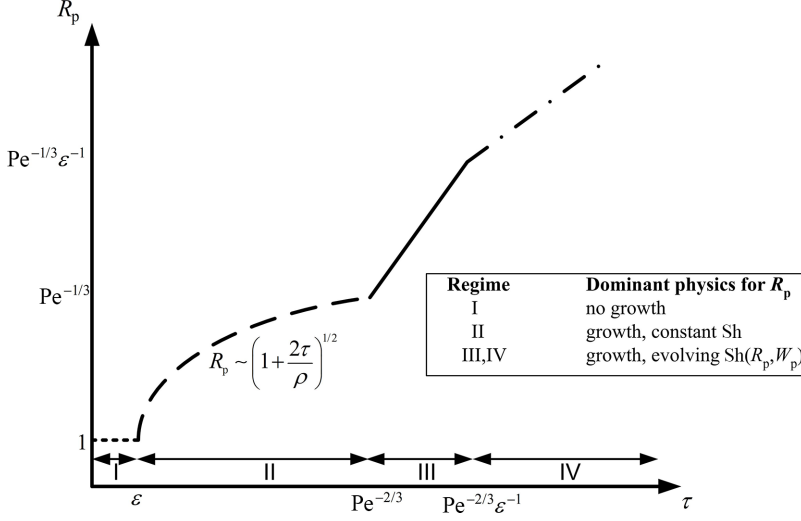


FIG. 2. Schematic for the evolution of  $R_p$  as a function of  $\tau$ . Simple, closed-form expressions for  $R_p$  are only available for regimes I and II. For regime I,  $R_p = 1$ .

## V. NUMERICAL IMPLEMENTATION

The remaining numerical task is to solve Eqs. (24) and (25), subject to Eqs. (29a) and (29b). We should note that Eq. (25) with  $R_p$  constant is identical to the Maxey-Riley equation [47] under the assumption that the background fluid is quiescent, which reduces to the BBO equation [33–35] under the assumption of Stokes flow ( $Re_p \ll 1$ ). There is, by now, an extensive literature on the numerical solution to the problem when the background fluid is not quiescent [48,49]. Regardless of whether the fluid is quiescent or not, one approach adopted by some is to simply neglect the Basset-integral term [50], in view of the well-known difficulties associated with computing it; however, the analysis in Sec. IV clearly indicates that this is not justified in the current context. Here, we

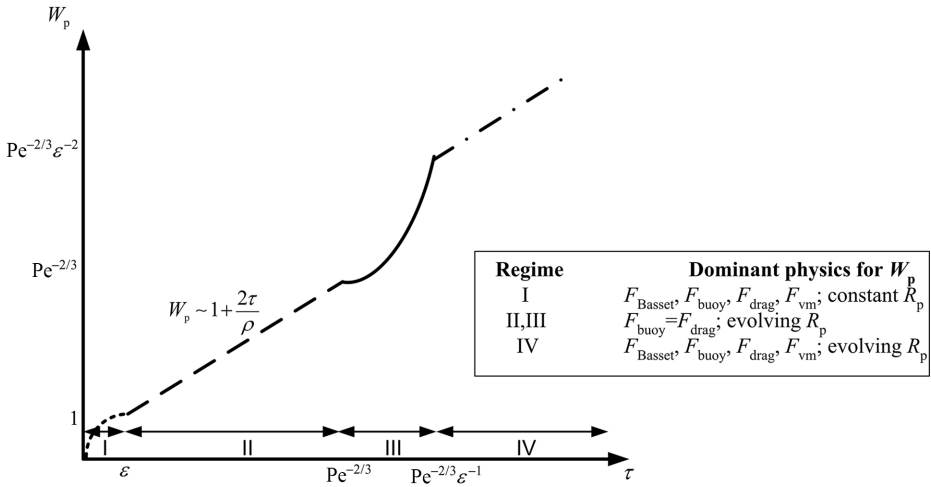


FIG. 3. Schematic for the evolution of  $W_p$  as a function of  $\tau$ . Simple, closed-form expressions for  $W_p$  are only available for regimes I and II. For regime I,  $W_p$  is given nominally by Eq. (A5).

needed to solve Eqs. (24) and (25) in tandem, which necessitated a different approach. We note that a similar system of ordinary differential equations was solved in Refs. [29–32], albeit in the context of dissolution rather than crystallization.

The details of our numerical method are as follows. The solution was obtained using a fourth-order Runge-Kutta method to solve the system of equations, along with an adaptive time-stepping algorithm to control the step size. In this approach, the solution obtained after one step of size  $2\Delta\tau$  is compared to the solution obtained after two steps of size  $\Delta\tau$ . If the relative error does not exceed  $10^{-6}$ , the larger time step ( $2\Delta\tau$ ) is used for future steps. If the relative error falls between  $10^{-6}$  and  $10^{-5}$ , the simulation proceeds with step size  $\Delta\tau$ . If the relative error exceeds  $10^{-5}$ , the time step is halved ( $\Delta\tau/2$ ). Alternatively, different approaches could be implemented to refine the step size, depending on the size of the observed error [51]. The methodology adopted here to compute the integral in Eq. (25) is based on the computationally stable implementation of the popular L1 method of time-fractional problems described in Refs. [52–54], which is especially appropriate for initially small particle radii. Following that methodology, and denoting the time at the  $j$ th step as  $\tau_j$ , with a step size of  $\Delta\tau_j$ , where the initial step corresponds to  $j = 1$  and the current step to  $j = m$ , the integral term at time  $\tau_m$  is rewritten as

$$\int_0^{\tau_m} \frac{dW_p}{d\xi} \frac{d\xi}{(\tau_m - \xi)^{1/2}} \approx -2 \sum_{j=1}^m \frac{(W_{p,j} - W_{p,j-1})}{\Delta\tau_j} (\tau_m - \xi)^{1/2} \Big|_{\xi=\tau_{j-1}}^{\xi=\tau_j}. \quad (85)$$

The computation of the history term entails continuous integration over an expanding array of past velocity data, making the task both memory- and computation-intensive. As the number of time steps increases, so does the storage requirement and the associated computational effort, leading to prolonged simulation times.

The numerical results were obtained on a high-performance computing node configured with dual Intel Xeon Gold processors (2 GHz, 28 cores) and equipped with 384 GB of RAM. The code, written in C, was parallelized using the message passing interface (MPI) to exploit the node's multi-core architecture. Under these specifications, the computational run time for the particle to reach the bottom of the vial under the different gravitational conditions ( $g_{\text{eff}} = 10^{-2}g, 1g, 5g$ ) was roughly of the order of one hour, with the run time increasing as  $g_{\text{eff}}$  is decreased. At first sight, this may seem surprising: if one were solving the equations in dimensional variables, one might think that, because the particle travels more slowly for lower gravity, the computation would take longer. However, in dimensionless variables, it takes more or less the same time because  $\Gamma$  is independent of  $g_{\text{eff}}$  and  $\text{Pe}$  is only weakly dependent on it: on using Eqs. (5) and (28), we find that  $\text{Pe}$  is proportional to  $g_{\text{eff}}^{1/4}$ . In fact, the number of computational time steps (and corresponding nondimensional sedimentation times,  $\tau_{\text{sed}}$ ) were approximately 8.9 million (297.43), 8.6 million (279.61), and 8.4 million (272.20), ordered from weakest to strongest gravity. We will return to this point in Sec. VI.

## VI. RESULTS

In presenting the results, we consider first a comparison of the solutions obtained via the analytical and numerical methods; this is done in Sec. VIA. Then, in Sec. VIB, we consider the effect of gravity.

### A. Comparison of the analytical and numerical solutions

It is of interest to apply the above analytical and numerical approaches to the data given in Table I, which are of relevance to the crystallization of L-histidine, an essential amino acid that is used in the food and pharmaceutical industries; although a solvent consisting of water and ethanol is typically used, we will just consider results for water. First, we have that, for  $\tau \sim \varepsilon$ ,

$$\int_0^\tau W_p(\tau') d\tau' \sim \varepsilon. \quad (86)$$

Then, referring to Eq. (30), since  $\Gamma \ll 1$ , the crystal will not reach the bottom during regime I. Next, by the end of regime II,  $\tau \sim \text{Pe}^{-2/3}$ , giving

$$\int_0^\tau W_p(\tau') d\tau' \sim \text{Pe}^{-4/3}; \quad (87)$$

now, since  $\Gamma \text{Pe}^{-4/3} \varepsilon^{-1} \approx 0.02$ , this suggests that the crystal will be approaching the bottom by the end of regime II. By the end of regime III,  $\tau \sim \text{Pe}^{-2/3} \varepsilon^{-1}$ , with

$$\int_0^\tau W_p(\tau') d\tau' \sim \text{Pe}^{-4/3} \varepsilon^{-2}; \quad (88)$$

since  $\Gamma \text{Pe}^{-4/3} \varepsilon^{-3} \gg 1$ , we should thus expect

$$\text{Pe}^{-2/3} \leq \tau_{\text{sed}} \ll \text{Pe}^{-4/3} \varepsilon^{-1}. \quad (89)$$

Although nondimensional variables were useful for the analysis above to easily identify the orders of magnitudes of various terms, as well as formulating the leading-order problem, it turns out to be more useful to return to dimensional variables to consider actual model predictions. To this end, Figs. 4(a)–4(c) show comparisons of the profiles obtained numerically and asymptotically for  $r_p$ ,  $U_p$ , and  $z$ , respectively, as functions of time,  $t$ ; for these results, the value of gravity at the Earth's surface was used. In Fig. 4(a), the negligible changes in the radius observed up to  $t \sim 10^{-2}$  s, along with the velocity increase in Fig. 4(b) toward the terminal velocity for a particle with the initial radius, correspond to regime I depicted in Figs. 2 and 3, respectively. Overall, it is observed that the agreement between the numerical and asymptotic solutions is very good. We can note that the values of the dimensionless parameters are such that the particle is just about on the brink of entering regime III by the time sedimentation is complete, since the curves in Figs. 4(a)–4(c) do not exhibit the kind of kink or sudden rapid change in behavior that one would associate with a change in regime. Moreover, in the context of an actual experiment, the sedimentation time computed here, which is around 50 s, is short as compared to the overall crystallization time, which can be in the order of hours [3]. Note also that setting  $\tau_{\text{sed}} = \text{Pe}^{-2/3}$  from Eqs. (89) and (22a) gives around 17 s, which is in good qualitative agreement with the computed time. It is also worth commenting on the slopes of the curves in Figs. 4(a) and 4(b). As these are both log-log plots, we can simply extract the slopes from the exponents to which  $\tau$  is raised in the relevant asymptotic regime. Thus, in Fig. 4(a), the curve in regime II has slope 1/2, whilst the curve in regime II in Fig. 4(b) has slope 1. However, it is not possible to extract a clean value for the slope of the curve in regime I in Fig. 4(b), since the analysis gave that  $1 - W_p \sim \tilde{\tau}^{-1/2}$ ; consequently, we should not expect to see a constant slope on log-log plot for  $U_p$  against  $t$ .

### B. Effect of gravity

The effect of gravity on crystallization and sedimentation as a function of time is assessed by introducing a dimensionless effective gravity,  $G_{\text{eff}}$ , defined as

$$G_{\text{eff}} = g_{\text{eff}}/g. \quad (90)$$

In the results presented next in Figs. 5(a)–5(c), for  $r_p$ ,  $U_p$ , and  $z$ , respectively, the curves correspond to different values of effective gravity, ranging from microgravity ( $g_{\text{eff}} = 10^{-2}g$ ) to hypergravity ( $g_{\text{eff}} = 5g$ ), noting that similar values to denote microgravity were adopted elsewhere [25]. Using the base case parameters given in Table I, and focusing on Fig. 5(c) with the aid of results in Fig. 5(a), we identify two distinct scenarios: (a) sediment first, then crystallize, as clearly observed in hypergravity ( $G_{\text{eff}} = 5$ ), where the particle grows to only 13  $\mu\text{m}$  by the time it reaches the bottom of the vial; (b) crystallize while sedimenting, which corresponds more closely to the behavior observed in microgravity ( $G_{\text{eff}} = 10^{-2}$ ), where the particle grows to 58  $\mu\text{m}$  while

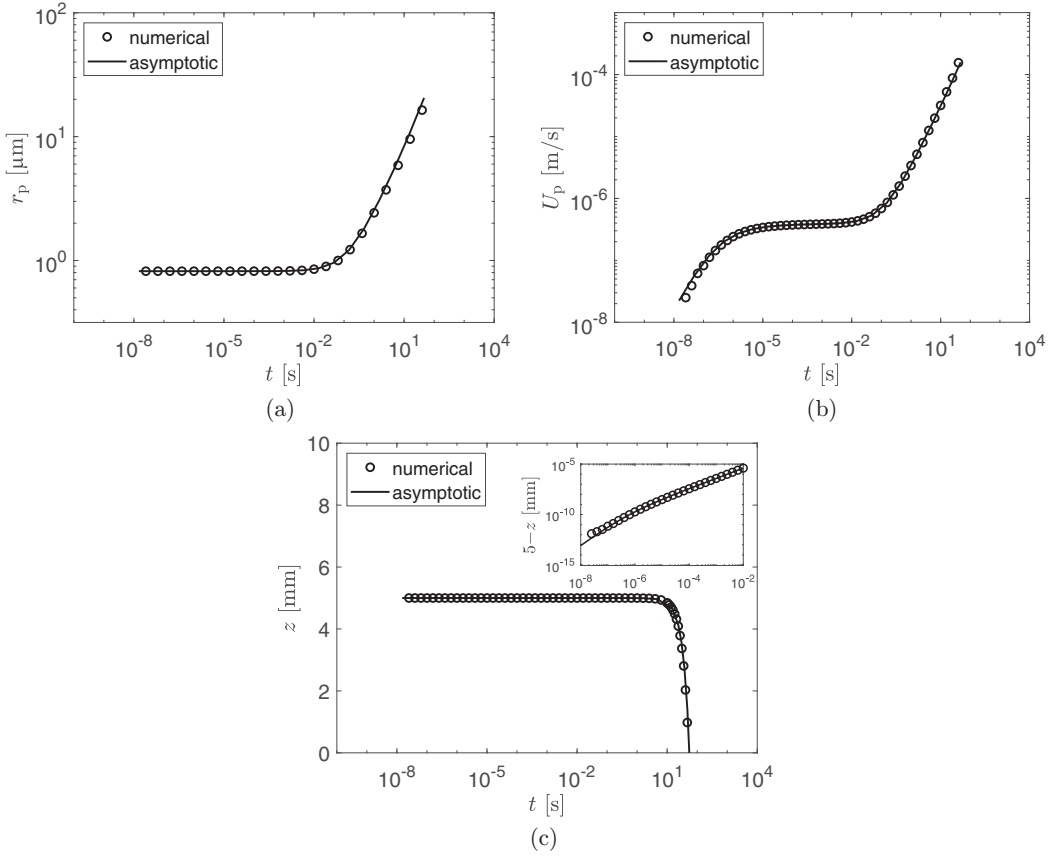


FIG. 4. Comparison of the numerical solutions of Eqs. (24)–(29) and the composite asymptotic solutions for: (a) particle radius,  $r_p$ , in microns; (b) particle velocity,  $U_p$ , in meters per second; and (c) distance traveled by the particle,  $z$ , in millimeters, with an inset showing a detailed view of vertical displacement,  $(5 - z)$ , over the interval  $10^{-8} \text{ s} < t < 10^{-2} \text{ s}$ . The composite solutions for these quantities are given by Eqs. (81)–(83), respectively.  $g_{\text{eff}} = 1g$ .

covering the same sedimentation distance. For context, L-histidine crystals obtained by one common crystallization method under Earth’s gravity can reach dimensions on the order of a hundred microns [9]. Moreover, Fig. 5(b) reveals that the final velocity attained by the particle as it reaches the bottom of the vial in hypergravity is around 30 times greater than its velocity in microgravity.

In the scenario where the crystals sediment first, then crystallize, as crystals continue to grow after sedimenting, an accumulation layer may build at the bottom. This buildup can cause localized solute depletion near the bottom while leaving the upper regions solute-rich, creating a concentration gradient. In hypergravity, this effect is intensified due to rapid sedimentation, leading to potentially uneven crystal sizes; however, in microgravity, where sedimentation is significantly slower, particles remain suspended longer, promoting more uniform crystal growth throughout the medium. However, as crystallization proceeds, even minor settling could eventually create localized solute depletion zones.

Finally, we point out that, although we have not compared the results obtained numerically with those obtained asymptotically for  $10^{-2}g$  and  $5g$  in Fig. 5, we should nevertheless expect the agreement to be as good as it was for the  $1g$  case in Fig. 4. This is because, as mentioned in Sec. V,

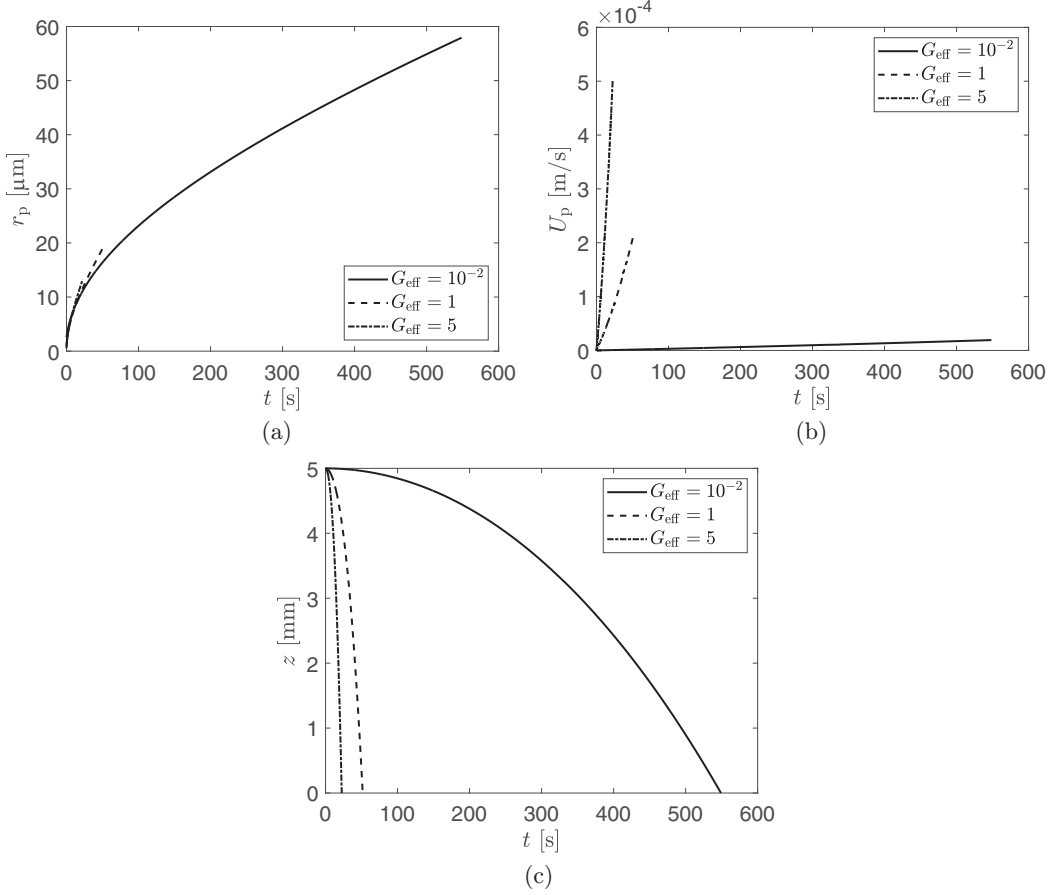


FIG. 5. Numerical solutions as a function of time for three different gravitational environments: (a) particle radius,  $r_p$ , in microns; (b) particle velocity,  $U_p$ , in meters per second; and (c) distance traveled by the particle,  $z$ , in millimeters.  $B = 45/19 (\approx 2.36)$ .

$Pe$  is proportional to  $g_{\text{eff}}^{1/4}$ , meaning that the order of the inequalities given after Eq. (35) will still hold for the gravitational environments considered in this paper.

## VII. DISCUSSION

Thus far, the analysis has neglected the effect of concentration gradients on crystal sedimentation. In reality, crystal growth depletes solute near the crystal surface, creating density gradients in the surrounding solvent, which in turn generate free convective flow. In this section, we investigate whether this free convection could produce solvent velocities comparable to or greater than the sedimentation velocity calculated in Secs. IV–VI. If they are, it will mean that the above analysis would need significant modification, since it neglected the possibility of free convection completely. The question as posed is whether free convection dominates forced convection. As explained in Ref. [55, page 130], it is necessary to consider the Richardson number,  $Ri$ , which quantifies the ratio of buoyancy forces, driven by solute concentration gradients, to inertial forces from particle sedimentation, and is given by

$$Ri = \frac{Gr}{Re^2}, \quad (91)$$

where Gr is the Grashof number, and Re is the Reynolds number, given by

$$\text{Re} = \frac{\rho_s U l}{\mu},$$

where  $l$  is a characteristic length scale for the problem and  $U$  is an imposed velocity scale. Although the description in Ref. [55] is in the context of heat transfer, it will equally apply for solutal transfer. Thus, Gr can be written in terms of the Rayleigh and Schmidt numbers, Ra and Sc, respectively, as

$$\text{Gr} = \frac{\text{Ra}}{\text{Sc}}, \quad (92)$$

where

$$\text{Ra} = \frac{\rho_s g_{\text{eff}} l^3 \beta \Delta c}{D \mu}, \quad (93)$$

Sc is as already given in Eq. (10b),  $\Delta c$  in Eq. (93) denotes a characteristic concentration difference, and  $\beta$  is the solutal expansion coefficient; more simply, Eq. (91) can be written as

$$\text{Ri} = \frac{l g_{\text{eff}} \beta \Delta c}{U^2}. \quad (94)$$

Now, natural convection will dominate forced convection if  $\text{Ri} \gg 1$ , i.e.,

$$U \ll (l g_{\text{eff}} \beta \Delta c)^{1/2}. \quad (95)$$

However, this result comes with a caveat, which was considered only recently [27]. The above assumes that Re is  $O(1)$  or greater; the corresponding analysis for  $\text{Re} \ll 1$  gives that natural convection will dominate if  $\text{RiRe} \gg 1$ . Physically, the differences in criteria arise because, when  $\text{Re} \gg 1$ , the dominant terms that are being compared are buoyancy and inertia, whereas when  $\text{Re} \ll 1$ , the comparison is between buoyancy and viscous forces. Thus, the new criterion gives that natural convection will dominate if

$$U \ll \frac{\rho_s \beta \Delta c g_{\text{eff}} l^2}{\mu}. \quad (96)$$

Of course, these results were obtained for the case when  $U$  and  $l$  are constants. However, in the present context, with  $U$  and  $l$  being identified with  $U_p$  and  $r_p$ , respectively, we have

$$U_p \ll \frac{\rho_s \beta \Delta c g_{\text{eff}} r_p^2}{\mu}.$$

Thence, in dimensionless quantities, we have

$$W_p \ll \left( \frac{\rho_s \beta \Delta c g_{\text{eff}} a^2}{\mu U_{\text{TS}}} \right) R_p^2,$$

i.e.,

$$W_p \ll \left( \frac{9 \beta \Delta c}{2(\rho - 1)} \right) R_p^2.$$

In the current context, we will have  $\Delta c = c_0 - c_e$ , i.e., the difference between the concentration of solute in the solvent and the solubility concentration. On using the data in Table I, we have  $\beta \Delta c \sim O(10^{-2})$ , i.e.,  $\beta \Delta c \ll 1$ . Moreover, with  $(\rho - 1) \sim O(1)$ , we will have that  $W_p \ll R_p^2$ , and we can conclude that natural convection will only be of significance toward the very start of regime

I, i.e., when

$$W_p \ll \frac{9\beta\Delta c}{2(\rho - 1)},$$

since  $W_p \approx R_p^2$  in regime II, as obtained in Sec. IV A 2.

### VIII. CONCLUSIONS

In this paper, we have considered a simple model for the crystallization of a sedimenting nucleated particle in a solvent. The model is based on mass- and momentum-conservation arguments and consists of an ordinary differential equation and an integrodifferential equation for the particle radius and its velocity, respectively, as functions of time; the second of these equations contains the well-known Basset integral history term. Nondimensionalization and subsequent asymptotic analysis indicate that there can be up to four different regimes as the growing particle sediments. The results of the analysis are compared with numerical solutions and found to give very good agreement; the availability of asymptotic solutions is particularly attractive in view of the surprisingly lengthy computational time, which is directly associated to the history term. A corollary to the main results is that even though crystallization can give rise to free convection, as solute depletion in the solvent adjacent to the crystallizing particle's surface gives rise to density gradients, the effective forced convection will nevertheless dominate for the parameters considered in this work. Moreover, depending on the strength of the gravitational field, e.g., hypergravity or microgravity, the particle can either sediment, then grow whilst stationary on the bottom of the reaction vessel, or grow while still sedimenting.

The dynamics of sedimentation time and the associated potential for an accumulation layer at the bottom of the vial underscore the critical need for tailored process designs based on the gravitational environment. In hypergravity conditions, flow-driven mixing or staged crystallization strategies might be required to reduce crystal crowding at the bottom. Conversely, in microgravity, gentle agitation systems could help prevent concentration gradients. Understanding whether sedimentation and crystallization occur sequentially or simultaneously is essential for accurate process modeling, ultimately guiding the design of efficient crystallization systems for both terrestrial and extraterrestrial manufacturing.

We can envisage a variety of uses for this model, with the most obvious, in view of our recent work [4], being a more detailed account for polymorphism in gravity-driven, antisolvent crystallization. In antisolvent crystallization, a solution of a specific molecule, such as L-histidine, in a solvent, e.g., water, is mixed with an antisolvent, e.g., ethanol. This process reduces the molecule's solubility in the mixture, creating a supersaturated state. As a result, different crystalline forms, known as polymorphs, which may be stable or unstable, are produced. The goal is to explore the use of either microgravity or hypergravity to obtain polymorphs that are difficult to produce under normal gravitational conditions [3].

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### DATA AVAILABILITY

The data that support the findings of this article are openly available [56].

**APPENDIX A: ANALYTICAL AND NUMERICAL SOLUTIONS TO EQ. (43) FOR  $\rho > 5/8$** 

For  $\rho > 5/8$ , which corresponds to  $B < 4$ , the solution to Eq. (43), subject to Eq. (44), is given in Refs. [36,57,58] as

$$W_p = 1 - R_W - \frac{X}{Y} I_W, \quad (\text{A1})$$

where

$$X = \frac{1}{2}B, \quad Y = \frac{1}{2}(B(4-B))^{1/2},$$

and  $R_W$  and  $I_W$  denote the real and imaginary part, respectively, of

$$\mathcal{W}(\mathcal{Z}) = e^{-\mathcal{Z}^2} \left( 1 + \frac{2i}{\pi^{1/2}} \int_0^{\mathcal{Z}} e^{\xi^2} d\xi \right), \quad (\text{A2})$$

with  $i$  as the imaginary unit and  $\mathcal{Z} = (Y + iX)\tilde{\tau}^{1/2}$ ; note also that, more recently, the case of  $\rho > 5/8$  was analyzed in depth by Langlois *et al.* [59], and that a spectral expression for  $W_p$  that is valid for all values of  $\rho$  was derived by Prasath *et al.* [49]. As Eq. (A2) is in a rather cumbersome complex form, we seek a simpler representation for  $W_p$  in terms of real quantities.

To cut down on the algebra, set  $\tilde{\tau}_B = B\tilde{\tau}$  and  $W_p = 1 - \tilde{W}_p$ , so that Eqs. (43) and (44) give

$$\frac{d^2 \tilde{W}_p}{d\tilde{\tau}_B^2} + (2-B) \frac{d\tilde{W}_p}{d\tilde{\tau}_B} + \tilde{W}_p = \frac{B^{1/2}}{\pi^{1/2} \tilde{\tau}_B^{1/2}}, \quad (\text{A3})$$

subject to

$$\tilde{W}_p = 1, \quad \frac{d\tilde{W}_p}{d\tilde{\tau}_B} = -1 \quad \text{at } \tilde{\tau}_B = 0. \quad (\text{A4})$$

In principle, the problem should be amenable to the method of variation of parameters [46], whereby the solution is represented as the sum of a complementary function and a particular integral. Skipping the details of the subsequent algebra, we obtain

$$W_p = 1 - \exp(\lambda \tilde{\tau}_B) \left\{ (1 + A_3(\tilde{\tau}_B)) \cos(\nu \tilde{\tau}_B) + \left( A_4(\tilde{\tau}_B) - \left( \frac{1+\lambda}{\nu} \right) \right) \sin(\nu \tilde{\tau}_B) \right\}, \quad (\text{A5})$$

where

$$\lambda = \frac{B}{2} - 1, \quad (\text{A6a})$$

$$\nu = \frac{\sqrt{B(4-B)}}{2}, \quad (\text{A6b})$$

and

$$A_3(\tilde{\tau}_B) = -\frac{2B^{1/2}\tilde{\tau}_B^{1/2}}{\nu\pi^{1/2}} \int_0^1 \sin(\nu \tilde{\tau}_B Y^2) \exp(-\lambda \tilde{\tau}_B Y^2) dY, \quad (\text{A7})$$

$$A_4(\tilde{\tau}_B) = \frac{2B^{1/2}\tilde{\tau}_B^{1/2}}{\nu\pi^{1/2}} \int_0^1 \cos(\nu \tilde{\tau}_B Y^2) \exp(-\lambda \tilde{\tau}_B Y^2) dY. \quad (\text{A8})$$

Figure 6(a) compares the solution for  $W_p$  obtained using Eqs. (A1) and (A5); both equations require the computation of numerical quadratures, and these were carried out in Matlab. However, in both cases, we find that oscillations begin to creep in at around  $\tilde{\tau} = 70$ ; a likely explanation is round-off error that appears in the numerical quadratures. To further underline that the solution of Eq. (43), subject to Eq. (44), is not straightforward, it was solved numerically as an initial-value problem using three different methods: two Matlab subroutines, `ode15s` and `ode45`, and the "Global ODEs

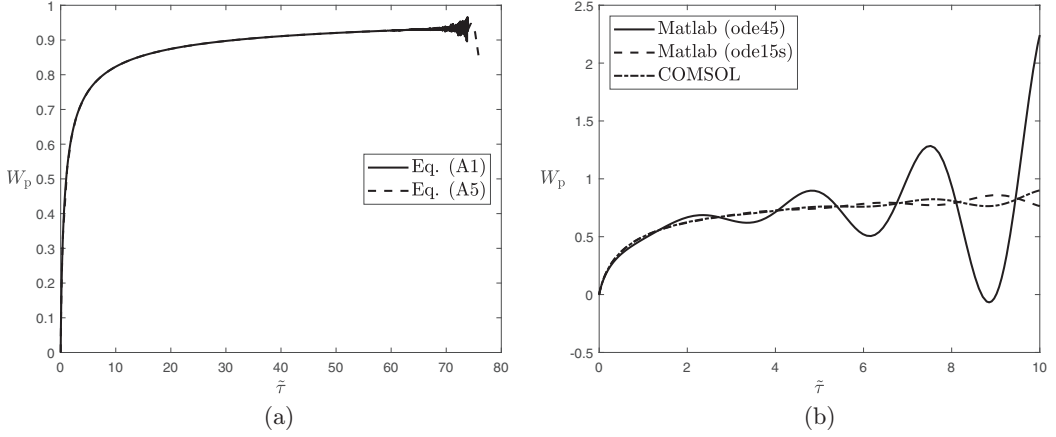


FIG. 6. Comparison of solutions to Eq. (43), subject to Eq. (44): (a) analytical; (b) numerical.

and DAEs" interface from the finite element software Comsol Multiphysics; however, as seen in Fig. 6(b), oscillations appear even earlier than in Fig. 6(a).

As an alternative, we consider the possibility of representing  $\tilde{W}_p$  as a power series in  $\tilde{\tau}_B$  for large  $\tilde{\tau}_B$ , which we will try to patch to Eq. (A5) for some intermediate value of  $\tilde{\tau}_B$ . The form of Eq. (A3) suggests that we should set

$$\tilde{W}_p = \left(\frac{B}{\pi}\right)^{1/2} \sum_{n=0}^{\infty} \frac{A_n}{\tilde{\tau}_B^{n+1/2}}, \quad (\text{A9})$$

where  $(A_n)_{n \geq 0}$  are constants that are to be determined. Considering Eq. (A3) for  $\tilde{\tau}_B \gg 1$  at  $\tilde{\tau}_B^{-1/2}$  and  $\tilde{\tau}_B^{-3/2}$ , we obtain

$$A_0 = 1, \quad A_1 = \frac{1}{2}(2 - B), \quad (\text{A10})$$

respectively. In general, at  $\tilde{\tau}_B^{-(n+1/2)}$ , where  $n \geq 2$ , we have

$$A_n = \left(n - \frac{1}{2}\right) \left[(2 - B)A_{n-1} - \left(n - \frac{3}{2}\right)A_{n-2}\right], \quad (\text{A11})$$

which, in tandem with Eq. (A10), can be considered as a recurrence relation for  $(A_n)_{n \geq 2}$ . Note also that this is not quite patching in the sense discussed in the textbook by Bender and Orszag [46] and elsewhere [60], since  $(A_n)_{n \geq 0}$  can all be determined without considering the solution to Eq. (A5).

Figure 7 compares the solution for  $W_p$  obtained by solving the original integrodifferential equation, Eq. (42), numerically and that obtained by patching Eqs. (A5) and (A9), with the patching having been carried out at  $\tilde{\tau} = 10^2/B (\approx 42.4)$  and with Eq. (A9) truncated at ten terms; as is evident, the patching is seamless and the agreement between the analytical and numerical solutions is very good, even for  $\tilde{\tau}$  as great as  $10^5$ .

Although our main interest was the particular value of  $\rho$  emanating from the parameter values given in Table I, it is worth considering the range in the values of  $\rho$  for which the issues that we have encountered will occur. Additional numerical experimentation indicated that there are no difficulties if  $0 < B < 2$ , which is as may be expected in view of Eq. (A6a); the complementary-function solutions will be of the form  $e^{m\tilde{\tau}_B}$ , where  $m$  satisfies

$$m^2 + (2 - B)m + 1 = 0, \quad (\text{A12})$$

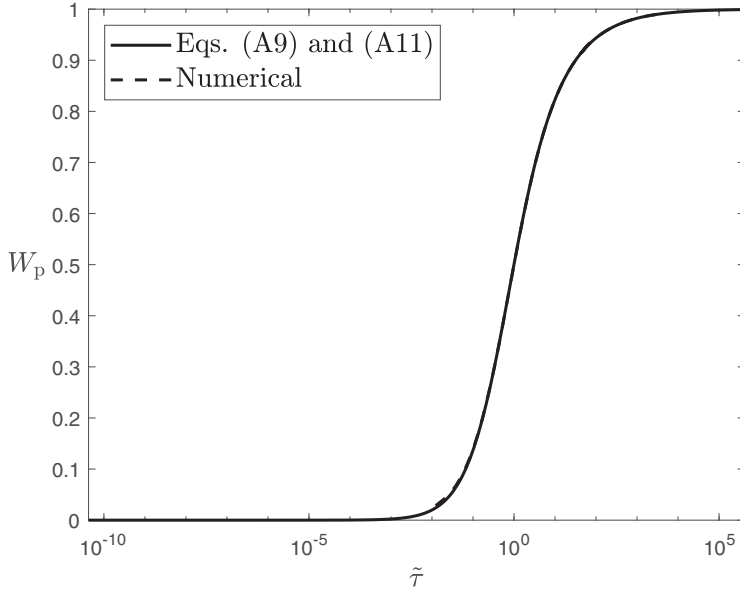


FIG. 7. Comparison of the solution for  $W_p$  obtained by solving Eq. (42) numerically and that obtained by using Eqs. (A5) and (A9).  $B = 45/19 (\approx 2.36)$ .

giving

$$m = \frac{B - 2 \pm \sqrt{B(B - 4)}}{2}, \quad (\text{A13})$$

whence the real part of  $m$  is negative for  $0 < B < 2$ , indicating exponentially decaying solutions. In summary, it is only the range  $2 < B < 4$ , corresponding to  $5/8 < \rho < 7/4$ , that will be problematic. A further point is whether the method to generate  $(A_n)_{n \geq 0}$  will succeed for all values of  $\rho$  in this interval, since the behavior of  $A_n$  as  $n$  increases is not self-evident from Eq. (A11). To address this, Fig. 8 shows  $(|A_n|)_{n \geq 0}$  as a function of  $n$  for  $\rho = 0.8, 1.2$  and  $1.6$ ; we have chosen to plot  $(|A_n|)_{n \geq 0}$ , rather than just  $(A_n)_{n \geq 0}$ , because  $A_n$  takes positive and negative values and its absolute

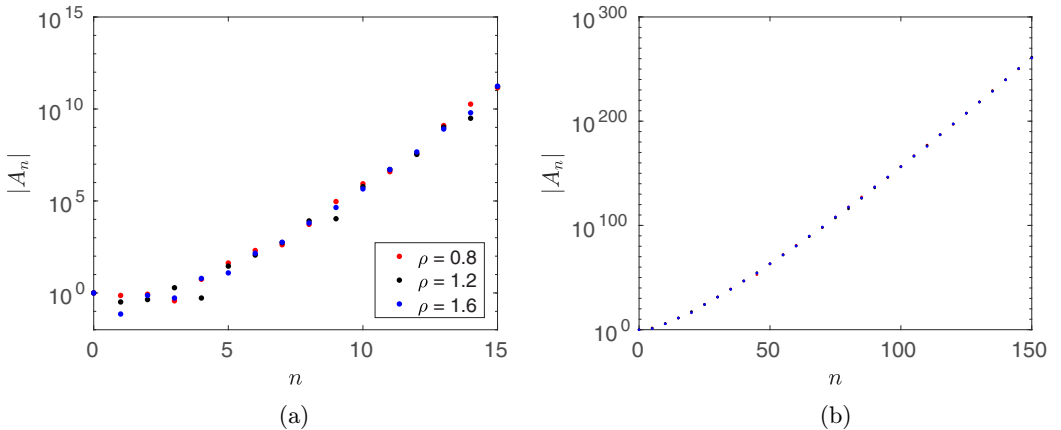


FIG. 8.  $|A_n|$  as a function of  $n$ , as generated by Eq. (A11): (a)  $0 \leq n \leq 15$ ; (b)  $0 \leq n \leq 150$ .

value increases very quickly with  $n$ , as seen in Fig. 8(a). Moreover, for large  $n$ , Fig. 8(b) suggests that  $\ln(|A_n|)$  is proportional to  $n$ . If we take the constant of proportionality as  $\lambda(>0)$ , although this appears to be very weakly dependent on  $\rho$ , then we have that  $|A_n| \sim e^{n\lambda}$ . Returning to Eq. (A9), we should expect the infinite series to be convergent provided that  $e^\lambda/\tilde{\tau}_B < 1$ . Also, Fig. 8(b) suggests that  $1 < \lambda < 2$ ; thus, even if we take  $\lambda = 2$ , then taking  $\tilde{\tau}_B$  as small as 10 should still provide a convergent series. However, taking  $\tilde{\tau}_B$  greater than this will mean that fewer terms in the series are required.

Finally, we may also surmise why such difficulties in calculating  $W_p$  have arisen, even though the relevant figure in Ref. [36, Figure 11.1] does not suggest any difficulties at all. In our notation, the figure in question shows  $W_p$  as a function of  $\tilde{\tau}$  for different values of  $\rho$ ; however, only one of the curves lies in the interval  $5/8 < \rho < 7/4$ , and even this one is actually for the case ( $\rho = 1$ ) when the particle would not move at all, since  $\rho_p = \rho_s$ . This observation notwithstanding, it is likely that this curve would have been constructed using tabulated values from a standard handbook of mathematical functions of the time [61], rather than relying on nowadays standard subroutines that exhibit roundoff error precisely as  $W_p \rightarrow 1$ .

## APPENDIX B: REFORMULATION OF EQS. (65)–(67)

Solving these equations as they stand seems problematic as there is initially a zero-over-zero indeterminacy on the right-hand side of Eq. (65) and all of the terms are zero in Eq. (67). However, since the analysis in Sec. IV A 4 gives that

$$\hat{R}_p \sim \frac{\hat{\tau}}{4^{1/3}\rho}, \quad \hat{W}_p \sim \frac{\hat{\tau}^2}{4^{2/3}\rho^2},$$

we set

$$\hat{R}_p = \hat{\tau}\mathcal{R}, \quad \hat{W}_p = \hat{\tau}^2\mathcal{W},$$

which will give

$$\rho \left( \hat{\tau} \frac{d\mathcal{R}}{d\hat{\tau}} + \mathcal{R} \right) = \frac{\mathcal{W}^{1/3}\mathcal{R}^{-2/3}}{2^{2/3}}, \quad (\text{B1})$$

$$\hat{\tau}\mathcal{R}^2 \left( \hat{\tau} \frac{d\mathcal{W}}{d\hat{\tau}} + 2\mathcal{W} \right) = B \left( \mathcal{R}^2 - \mathcal{W} - \frac{\mathcal{R}}{\pi^{1/2}\hat{\tau}} \int_0^{\hat{\tau}} \left( \zeta^2 \frac{d\mathcal{W}}{d\zeta} + 2\zeta\mathcal{W} \right) \frac{d\zeta}{(\hat{\tau} - \zeta)^{1/2}} \right), \quad (\text{B2})$$

subject to

$$\mathcal{R} = \frac{1}{4^{1/3}\rho}, \quad (\text{B3a})$$

$$\mathcal{W} = \frac{1}{4^{2/3}\rho^2} \quad \text{at } \hat{\tau} = 0. \quad (\text{B3b})$$

In the limit as  $\hat{\tau} \rightarrow 0$ , Eq. (B1) is consistent with Eq. (B3b), but there still appears to be a zero-over-zero indeterminacy in Eq. (B2); note, however, that the indeterminacy does not involve the term involving the Basset integral in Eq. (B2), since Eq. (72) implies that

$$\int_0^{\hat{\tau}} \left( \zeta^2 \frac{d\mathcal{W}}{d\zeta} + 2\zeta\mathcal{W} \right) \frac{d\zeta}{(\hat{\tau} - \zeta)^{1/2}} \sim \hat{\tau}^{5/2}. \quad (\text{B4})$$

So, we set

$$\mathcal{W} = \mathcal{R}^2 + \hat{\tau}\hat{\mathcal{W}},$$

with Eqs. (B1) and (B2) now becoming

$$\rho \left( \hat{\tau} \frac{d\mathcal{R}}{d\hat{\tau}} + \mathcal{R} \right) = \frac{1}{2^{2/3}} \left( 1 + \frac{\hat{\tau}}{\mathcal{R}^2} \right)^{1/3}, \quad (\text{B5})$$

$$\begin{aligned} \hat{\tau}^2 \frac{d\hat{\mathcal{W}}}{d\hat{\tau}} = & -\frac{2\mathcal{R}^{1/3}}{\rho} \left( 1 + \frac{\hat{\tau}}{\mathcal{R}^2} \right)^{1/3} - \left( 3\hat{\tau} + \frac{B}{\mathcal{R}^2} \right) \hat{\mathcal{W}} \\ & - \frac{B}{\pi^{1/2} \mathcal{R} \hat{\tau}^2} \int_0^{\hat{\tau}} \left( \frac{2\mathcal{R}^{1/3}}{\rho} \left( 1 + \frac{\zeta}{\mathcal{R}^2} \right)^{1/3} + \zeta^2 \frac{d\hat{\mathcal{W}}}{d\zeta} + 3\zeta \hat{\mathcal{W}} \right) \frac{\zeta d\zeta}{(\hat{\tau} - \zeta)^{1/2}}, \end{aligned} \quad (\text{B6})$$

respectively, subject to

$$\mathcal{R} = \frac{1}{2^{2/3} \rho}, \quad (\text{B7a})$$

$$\hat{\mathcal{W}} = -\frac{1}{2^{5/3} B \rho^4} \quad \text{at } \hat{\tau} = 0. \quad (\text{B7b})$$

In summary, the remaining numerical task would be to solve Eqs. (B5) and (B6), subject to Eq. (B7), and this can be done using the method detailed in Sec. V.

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