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Tap Density Equations of Granular Powders Based on the Rate Process Theory and the Free Volume Concept

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Abstract

Tap density of a granular powder is often linked to the flowability via Carr Index that measures how tight a powder can be packed, under an assumption that more easily packed powders usually flow poorly. Understanding how particles are packed is important for revealing why a powder flows better than others. There are two types of empirical equations that were proposed to fit the experimental data of packing fractions vs. numbers of taps in literature: The inverse logarithmic and the stretched exponential. Using the rate process theory and the free volume concept under the assumption that particles will obey similar thermodynamic laws during the tapping process if the “granular temperature” is defined in a different way, we obtain the tap density equations and they can be reducible to the two empirical equations currently widely used in literature. Our equations could potentially fit experimental data better with an additional adjustable parameter. The tapping amplitude and frequency, the weight of the granular materials, and the environment temperature are grouped into this parameter that weighs the pace of packing process. The current results, in conjunction with our previous findings, may imply that both “dry” (granular) and “wet” (colloidal and polymeric) particle systems are governed by the same physical mechanisms in term of the role of the free volume and how particles behave (a rate controlled process).

Keywords: tap density; powder; rate process theory; free volume theory.

1. Introduction

Granular powders have been widely used in many practical areas spanning from pharmaceutical, nutritional, food, and engineering industries. Tap density of a granular powder is often linked to the flowability via Carr Index that measures how tight a powder can be packed, under an assumption that more easily packed powders usually flow poorly. The Carr index is proposed for estimating the relative importance of particle interactions and the flowability of powders¹, with a simple calculation of *Carr index* = $100(1 - \rho_b/\rho_t)$, where ρ_b is the freely settled bulk density and ρ_t is the tap density of a powder. Apparently, for an easily packed powder, the difference between ρ_b and ρ_t will be large and the Carr index will be large, too; This type of powders usually will have a poor flowability due to strong inter-particle interactions. In contrast, a small Carr index typically indicates that powders will likely have a good flowability. Understanding how particles are packed is thus important for revealing why a powder flows better than others and how we can handle powders properly during powder processing and manufacturing.

Packing problem is a very fundamental and intriguing issue for pure liquids, colloidal suspensions, and granular powers. In 1940, the hole theory of liquids was proposed and a liquid was considered as a continuum with a lot of holes and the number of holes was comparable with the number of particles in the liquid². This theory is still used nowadays for explaining viscosity, compressibility, and thermal conductivity of various liquids^{3,4}. In parallel, the lattice theory of liquids was also developed under an assumption that a liquid could be considered as quasi-

crystalline and the geometry of each molecules and the formed microstructure with neighboring molecules play a critical role in physical properties of liquids^{5,6}. Again, the packing structure of liquid molecules was assumed to be responsible for viscosity. The rich viscosity phenomena of both polymeric solutions and melts could be explained very well with the packing structures of polymer chains⁷, much larger molecules than that of liquids. For colloidal suspensions, the particles could form all kinds of structures similar to what we observed in crystalline and amorphous solids⁸⁻¹⁰, and the viscosities of colloidal suspensions could be well understood with the packing structures and the free volume available in the systems⁷. For granular powders, the particle packing structures become even more critical in powder flowability, as the powders could change from a free flowing state to a totally jammed state^{11, 12}. The packing structure of particles is well summarized in a monograph by Cumerland and Crawford¹³ and the configurations of jammed particle packing are excellent analyzed by Torquato and Stillinger¹⁴. How the particles pack in a system apparently has a big impact on the physical properties of liquids, colloidal suspensions, and granular powders.

Besides the packing structure that scales the occupied area in a system, the unoccupied free space available in a system would be equally important, too, especially when an external excitation is applied to the system like temperature variation or an external field like a mechanical or an electric field. The packing structure could easily change from one to another, dependent on how much unoccupied space is available when particles need to relax or re-orientate under external stimulations. The available unoccupied space in a system is typically called “free volume”, which has been widely used to determine the various equilibrium properties of both solids¹⁵ and liquids^{6, 16}. For example, the free volume theory has been successfully used to explain the location of the melting transition¹⁷, the glass transition temperature of polymers¹⁸, determination of elastic constants of small molecules like pentamers¹⁹, the viscosities of colloidal suspensions and polymeric solutions and melts without an external electric field⁷, and the yield stress of electrorheological fluids with an external electric field²⁰.

The bulk density of granular powders has been found to change with the number of taps applied to whole powder systems. There are many works addressing granular packing with a variety of tapping methods²¹⁻²⁶, typically employing vertical mechanical vibrations of different types of motions like simply pulsed or sinusoidal movements, sometime even under the influence of a magnetic field if particles are paramagnetic. A heuristic logarithmic law is proposed by Knight²⁵ based on the tapping experimental data of mono-dispersed 2 mm glass beads and shown below:

$$\phi = \phi_m - \frac{\phi_m - \phi_0}{1 + B \ln\left(1 + \frac{n}{\tau}\right)} \quad (1)$$

Where ϕ_0 is the initial particle volume fraction, ϕ_m is the maximum packing fraction, n is the number of taps, and B and τ are two constants dependent on the tapping amplitude, frequency, size of tube, particle sizes and shape, etc.. Eq. (1) is frequently called Chicago inverse logarithmic law. Using the free volume concept, Boutreux and de Gennes²⁷ theoretically developed a tap density equation very similar to Eq. (1). They assumed that the particle fills into the free volume available for an individual particle during tapping process. The possibility of any

free volume per particle larger than the individual particle volume $V_{ip} = \frac{4\pi r^3}{3}$ may be expressed with the Poisson's distribution and the final equation they obtained is:

$$\phi = \phi_m - \frac{\phi_m^2}{\ln n + \ln n_m} \quad (2)$$

Where n_m is a constant that roughly tells us how many taps needed to reach a steady-state tap density. Several researchers indicated that the inverse logarithmic law may fit the data at the beginning of tapping process but fail to correctly fit the data at the final tapping process up to the steady-state plateau^{26, 28}. A stretched exponential law that is often used as a phenomenological description of relaxation in disordered systems is found to better fit the experimental data²⁸ with the following form:

$$\phi = \phi_m - (\phi_m - \phi_0) \exp\left[-\left(\frac{n}{\tau}\right)^\beta\right] \quad (3)$$

Where β is a number of order 1, the stretching of the exponential. Knight²⁵ found that their data can be fitted with Eq. (3), too, though the inverse logarithmic law gives a better fit. However, Vandewalle²⁶ pointed out that both laws have limitations if they were used to fit their data. Therefore, there is a need for new equations that may work better for granular powder tapping process.

In this article, we will use the free volume concept and rate process theory with additional assumptions to derive tap density equations. We will address the inverse logarithmic law first and the stretched exponential law afterwards. The comparisons between newly derived equations and the currently widely used empirical equations are provided. The performance of newly obtained equations is evaluated in fitting experimental tap density data.

2. Theory

2.1 Inverse logarithmic law

Let's consider a simple granular system with initial particle volume fraction ϕ_0 , volume V_s , and maximum packing fraction ϕ_m . After the granular system is tapped for n times, the particle volume fraction is changed from ϕ_0 to ϕ . Since both ϕ_0 to ϕ are smaller than ϕ_m , there is free volume existing in the system and unoccupied by particles. The free volume in a system of particle volume fraction ϕ may be expressed as:

$$V_f = V_s (\phi_m - \phi) \quad (4)$$

At the beginning of a tapping process, the initial particle volume fraction is ϕ_0 , thus the free volume may be expressed as

$$V_{f0} = V_s (\phi_m - \phi_0) \quad (5)$$

We may consider the tapping process as a rate process²⁹ and treat the number of tapping n as a continuous variable, if we treat the particles during tapping processes similar to the thermodynamic laws controlled entities and the “granular temperature” is related to the external mechanical excitations and has nothing to do the regular temperature. The tapping process rate constant k may be related to how the free volume of a granular system decreases with the number of taps, therefore one may assume:

$$k = A \frac{V_f}{V_{f0}} = \frac{A(\phi_m - \phi)}{\phi_m - \phi_0} \quad (6)$$

Where A is a constant, dependent on the tapping amplitude and frequency, the weight of powders, particle size distribution and so on. We may further assume that the change of particle volume fraction with the tap number n is directly proportional to the available free volume per unit volume in the system, as the more free volume the system has, the faster the particle volume fraction will increase. In contrast, we know that the particle volume fraction increase will be much slower at the end of the tapping process when the tap density approaches to a plateau region. Therefore, the change of particle volume fraction with the number of taps should be inversely proportional to the number of taps, with a fast pace at low tap numbers but a slow pace at high tap numbers. Suppose that for reaching a steady-state tap density, the maximum number of taps, n_m , is required to make the particle volume fraction very close to ϕ_m . Thus (n/n_m) may be used to scale how close the number of taps is, in comparison with the final tap numbers, n_m . So the change of particle volume fraction with the number of taps should inversely proportional to (n/n_m) instead of the number of taps, n . With those assumptions, one may easily write:

$$\frac{d\phi}{dn} = k \frac{(\phi_m - \phi)}{n/n_m} \quad (7)$$

Note that the free volume per unit volume is used in above equation. Since n is treated as a continuous number, for avoiding $n=0$ and Eq. (7) becoming invalid, one may use $(n/n_m + 1)$ to replace n/n_m and re-write Eq. (7) as:

$$\frac{d\phi}{dn} = k \frac{(\phi_m - \phi)}{n/n_m + 1} \quad (8)$$

Substituting Eq. (6) into Eq. (8) and re-arranging yields

$$\frac{(\phi_m - \phi_0)}{A(\phi_m - \phi)^2} d\phi = \frac{dn}{n/n_m + 1} \quad (9)$$

Integrating both sides within the volume fraction range (ϕ_0, ϕ) and using the boundary condition ($n=0$, the particle volume fraction is ϕ_0 , and $n=n$, the particle volume fraction is ϕ) yields:

$$\frac{(\phi_m - \phi_0)}{(\phi_m - \phi)} - 1 = \frac{A}{n_m} \ln \left(\frac{n}{n_w} + 1 \right) \quad (10)$$

Re-arranging Eq. (10) yields

$$\phi = \phi_m - \frac{\phi_m - \phi_0}{1 + \frac{A}{n_m} \ln \left(1 + \frac{n}{n_m} \right)} \quad (11)$$

Eq. (11) has an exact form as Eq. (1), clearly telling what are the physical meanings of the constants, B and τ , in the empirical logarithm law expressed in Eq. (1).

Hao has developed a precise way for calculating the free volume of particulate systems using the inter-particle spacing (IPS) concept^{7, 30, 31}. The inter-particle spacing (IPS) that scales the distance between two particle surfaces, which was discussed extensively in literature⁶, was used for estimating the free volume of whole systems to derive the viscosity of colloidal suspension systems^{7, 31}. For calculating IPS, Hao³⁰ used Kuwabara's cell model³² that was extended by many other researchers³³⁻³⁵ for calculating the electrophoretic and electroacoustic mobility of particles. The cell model assumes that each particle is surrounded by a virtual cell (see Figure 1) and the particle/liquid volume ratio in a unit cell is equal to the particle volume fraction throughout the entire system. Given that the particle is spherical and mono-dispersed, the IPS should be zero when particles reach the maximum particle packing fraction, ϕ_m , as particles intimately contact each another at the maximum packing fraction. When the particle volume fraction, ϕ , is less than ϕ_m , there is a free volume unoccupied by particles. If the volume of a system is V_s , then the free volume of the particles should have in this system may be expressed as Eq. (4). The free volume per particle should be:

$$V_s (\phi_m - \phi) / (V_s \phi / V_{ip}) = (\phi_m - \phi) V_{ip} / \phi \quad (12)$$

Where V_{ip} is the volume of individual particle, and is equal to $(4\pi r^3)/3$. r is the particle radius. The total volume that each particle occupies in the system is the volume of each individual particle plus the free volume per particle:

$$V_{ip} + (\phi_m - \phi) V_{ip} / \phi = \phi_m V_{ip} / \phi \quad (13)$$

If the radius of particle plus the virtue cell is d , then the IPS defined in Figure 1 may be expressed as:

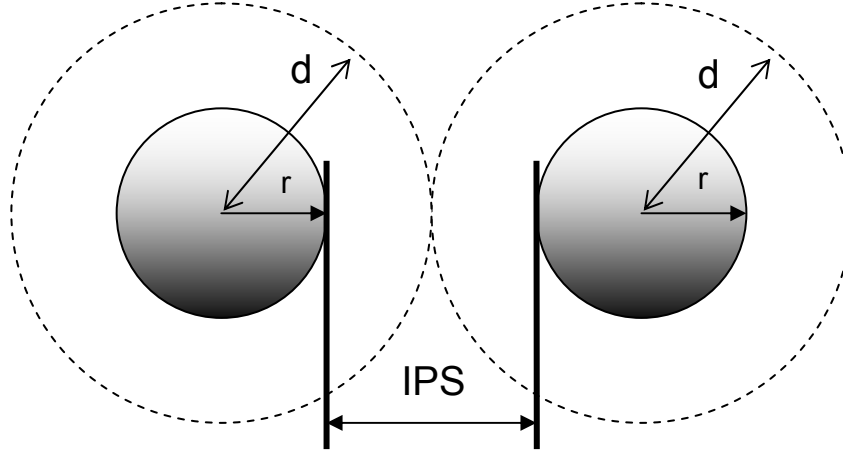


Figure 1. Illustration of Kuwabara's cell model used for calculating IPS in a particulate system. From Hao, 2005, *Electrorheological fluids: the non-aqueous suspensions*, Amsterdam: Elsevier. With permission.

$$\text{IPS} = 2(d - r) \quad (14)$$

Since d can be calculated from Eq. (13) using the following equation:

$$\frac{4\pi}{3} d^3 = \frac{\phi_m V_{ip}}{\phi} \quad (15)$$

Eq. (14) is thus rewritten as:

$$\text{IPS} = 2 \left(\sqrt[3]{\phi_m / \phi} - 1 \right) r \quad (\phi \leq \phi_m) \quad (16)$$

Eq. (16) indicates that IPS is zero when the particle volume fraction reaches the maximum packing fraction, which is consistent with our assumption at the beginning. The parameter, ϕ , should be always less than ϕ_m . Once the maximum packing fraction and particle size of a powder system is known, the IPS can be easily estimated using Eq. (16). Suppose that the particle can freely move either to left side or right side, as shown in Figure 2, with a distance of IPS until it touches the nearest neighbors, then the free volume of this particle should be

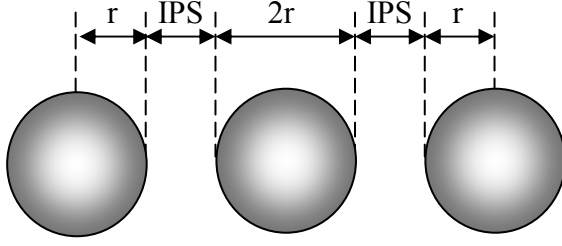


Figure 2. Determination of the free volume of particles. From Hao, 2005, *Electrorheological fluids: the non-aqueous suspensions*, Amsterdam: Elsevier. With permission

$$V_{fp} = (2IPS)^3 = 64(\sqrt[3]{\phi_m/\phi} - 1)^3 r^3 \quad (17)$$

as the particle moves three dimensionally, where V_{fp} is the free volume of an individual particle. The total free volume may be expressed as the free volume of an individual particle times the number of particles in the system,

$$\begin{aligned} V_f &= 64(\sqrt[3]{\phi_m/\phi} - 1)^3 r^3 \times \frac{\phi V_s}{\frac{4\pi}{3} r^3} \\ &= \frac{48\phi}{\pi} (\sqrt[3]{\phi_m/\phi} - 1)^3 V_s \end{aligned} \quad (18)$$

Eq. (18) gives the total free volume when the particle volume fraction is ϕ . Similarly when the particle volume fraction is ϕ_0 , the total free volume should be

$$V_{f0} = \frac{48\phi_0}{\pi} (\sqrt[3]{\phi_m/\phi_0} - 1)^3 V_s \quad (19)$$

Again, using the similar way to define the rate constant k yields

$$k = A \frac{\phi(\sqrt[3]{\phi_m/\phi} - 1)^3}{\phi_0(\sqrt[3]{\phi_m/\phi_0} - 1)^3} \quad (20)$$

Eq. (9) may be analogically written as:

$$\frac{\phi_0(\sqrt[3]{\phi_m/\phi_0} - 1)^3}{15.29A\phi^2(\sqrt[3]{\phi_m/\phi} - 1)^6} d\phi = \frac{dn}{n/n_m + 1} \quad (21)$$

Again, integrating both sides within the particle volume fraction range (ϕ_0, ϕ) and using the boundary condition ($n=0$, the particle volume fraction is ϕ_0 , and $n=n$, the particle volume fraction is ϕ) yields:

$$\frac{(\sqrt[3]{\phi_m} - \sqrt[3]{\phi_0})^3}{10} \left[\frac{(\phi_m^{2/3} - 5\phi^{1/3}\phi_m^{1/3} + 10\phi^{2/3})}{(\sqrt[3]{\phi_m} - \sqrt[3]{\phi})^5} - \frac{(\phi_m^{2/3} - 5\phi_0^{1/3}\phi_m^{1/3} + 10\phi_0^{2/3})}{(\sqrt[3]{\phi_m} - \sqrt[3]{\phi_0})^5} \right] = \frac{15.29A}{n_m} \ln\left(\frac{n}{n_m} + 1\right) \quad (22)$$

For comparison, the particle volume fraction increase $(\phi - \phi_0)$ predicted with Eq. (11) and Eq. (22) is plotted against $(n+1)$ in Figure 3. It looks like the generalized Chicago logarithmic law expressed in Eq. (11) predicts a relatively small increase of particle volume fraction at small number of taps and a dramatic increase in the middle area; For reaching equilibrium steady state, a lot of taps is predicted to be required. In contrast, Eq. (22) gives a relative slow and gentle tapping process that reaches the equilibrium steady state much earlier, though both two equations use same parameters ($A=2000$, $n_m=1000$, $\phi_m=0.63$) for calculation. The random dense packing structure with the maximum packing fraction 0.63 is assumed.

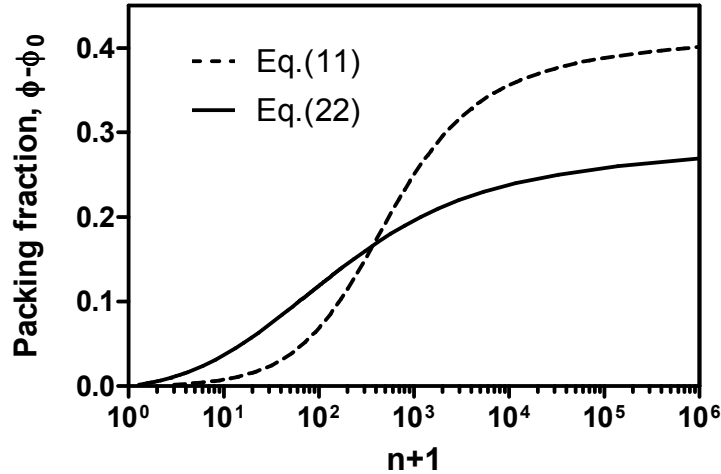


Figure 3 Particle volume fraction increase $(\phi - \phi_0)$ predicted with Eq. (11) and Eq. (22) is plotted against $(n+1)$ under assumptions $A=2000$, $n_m=1000$, $\phi_m=0.63$, the maximum particle packing fraction of random dense packing structure. The initial particle volume fraction is 0.2.

2.2 Stretched exponential law

Let's turn attention to the stretched exponential law. Suppose the powder is under a vertical tapping process, $L = L_0 \exp(i\omega t)$, where L_0 is the tapping amplitude and ω is the tapping frequency. The energy flowing from the shaker to the powder³⁶ is:

$$E(t) = \frac{MgL_0\omega}{\pi} \quad (23)$$

Where Mg is the weight of powder. The total energy flowing to the powder after a series of tapping processes with the tapping number, n , may be expressed as:

$$E = n \cdot E(t) = \frac{nMgL_0\omega}{\pi} \quad (24)$$

We may consider the tapping process as a rate process again and this rate process obeys the stretched Arrhenius equation as powder systems may be considered as disordered systems, in which many physical properties have the stretched exponential form, such as the conductivity of disordered systems that obeys Mott's variable range hopping model³⁷. The stretched exponential function was first introduced by Kohlrausch³⁸ in 1854 to describe the discharge phenomenon of a capacitor, later extended to describe dielectric spectra of polymers by Williams and Watts³⁹, and now frequently applied to a large range of relaxations in disordered thermal systems such as glasses⁴⁰. The origin of the stretched exponential is physically not clear, and the attempts have been made to assume that relaxations are dependent on the random walk of polarized molecules⁴¹, the trapping process at long time range⁴², and the system size⁴³. The stretched Arrhenius equation may be expressed as:

$$k = A \exp \left[- \left(\frac{E}{RT} \right)^\beta \right] \quad (25)$$

Where k is the rate constant of a tapping process, A is temperature related pre-factor, and β is the stretching of the exponential of values between 0 and 1. The microscopic theory proposed by Phillips^{40,44} suggested that β has the following physical meanings: $\beta=3/5$ for intrinsic molecular level short range interactions, $\beta=3/7$ for intrinsic long range Coulomb interactions, and $\beta=2/3$ for extrinsic interactions. Substituting Eq. (24) into Eq. (25) yields

$$\begin{aligned}
k &= A \exp \left[- \left(\frac{nMgL_0\omega}{\pi RT} \right)^\beta \right] \\
&= A \exp \left[- \left(\frac{n}{\tau} \right)^\beta \right]
\end{aligned} \tag{26}$$

Where τ is a constant of $\tau = \pi RT / (MgL_0\omega)$. We may use two approaches to represent the tapping rate constant. First, suppose that the tapping process rate constant is related to how the free volume of a granular system decreases with the number of taps, as shown in Eq. (6). Combining Eq. (6) and (26) together yields:

$$\frac{\phi_m - \phi}{\phi_m - \phi_0} = A \exp \left[- \left(\frac{n}{\tau} \right)^\beta \right] \tag{27}$$

Re-arranging Eq. (27) yields:

$$\phi = \phi_m - A(\phi_m - \phi_0) \exp \left[- \left(\frac{n}{\tau} \right)^\beta \right] \tag{28}$$

Eq. (28) is identical to Eq. (3) if A is assumed to be 1. Again, τ is a constant, $\tau = \pi RT / (MgL_0\omega)$, dependent on the tapping amplitude and frequency, the weight of the granular materials, and the temperature. Second, one may use Eq. (20) to express the tapping rate constant. Substituting k in Eq. (25) with Eq. (20) yields

$$\frac{\phi(\sqrt[3]{\phi_m/\phi} - 1)^3}{\phi_0(\sqrt[3]{\phi_m/\phi_0} - 1)^3} = A \exp \left[- \left(\frac{n}{\tau} \right)^\beta \right] \tag{29}$$

Re-arrange Eq. (29) yields

$$\phi^{1/3} = \phi_m^{1/3} - A^{1/3}(\phi_m^{1/3} - \phi_0^{1/3}) \exp \left[- \frac{1}{3} \left(\frac{n}{\tau} \right)^\beta \right] \tag{30}$$

For comparing the difference between Eq. (28) and (30), the predicted packing fraction difference vs. the number of taps is plotted in Figure 4. At same relaxation time and

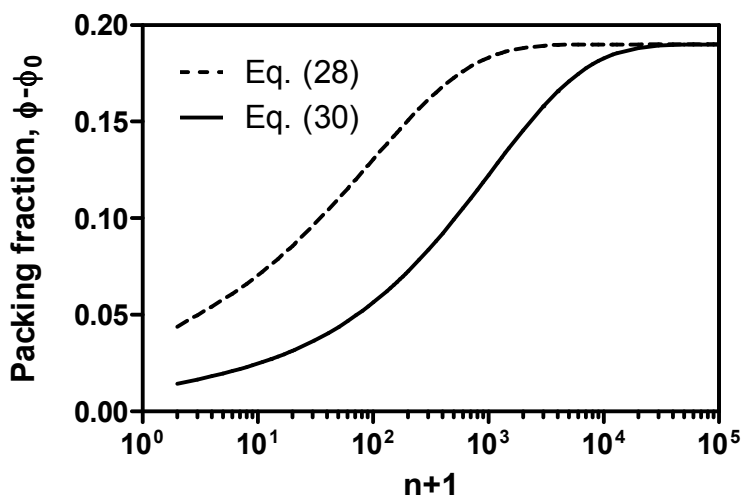


Figure 4. The predicted packing fraction less the initial particle volume fraction with Eq. (28) and (30) is plotted against $(n+1)$, n is the number of taps, under assumptions that the particles will have Rhombohedral pack structure with the maximum packing fraction 0.74, the initial particle packing fraction is 0.55, $\beta=0.5$, $\tau=100$, and $A=0.85$.

initial packing fraction, Eq. (30) gives a relatively slower pace of compaction process with lower initial tapping impact on the packing fraction. For reaching a steady-state packing structure, Eq. (30) requires a large number of taps above 10^5 ; while Eq. (28) predicts that the steady-state packing may be reached at relatively small number of taps about 10^3 . In both Eq. (28) and (30), there is one more parameter that may be used for fitting the data in comparison with the original stretched exponential law, Eq. (3), thus a better fit may be obtained with both Eq.(28) and (30) than Eq. (3).

3. Experimental

3.1 Materials and instrument

Fumed silica from Cabot Corp., Cab-O-Sil M5P, is mixed at the concentration of 1.5 wt% with microcrystalline cellulose from FMC BioPolymer, Avicel PH 200. Cab-O-Sil is a very fluffy powder of a high surface area $200 \text{ m}^2/\text{g}$ and a small particle size between 100 and 200 nm. The particle surfaces of Cab-O-Sil M5P are coated with hydroxyl groups and the particles are thus hydrophilic. Those small particles can stick on the large particle surfaces of Avicel PH 200 of particle size about $180 \mu\text{m}$ through hydrogen bonds, substantially improving the flow and tap characteristics. This mixture is selected for the reason that Cab-O-Sil is a very common flow improving and anti-caking agent and microcrystalline cellulose is a very common binder agent frequently used in pharmaceutical and nutritional tablet formulations.

The tap density was measured with a tap density tester, model TD-12, from Pharma Alliance Group Inc, USA. About 23 g sample was transferred into a 100 ml graduated cylinder and the USP I test method recommended by The United States Pharmacopeia (USP) Convention was used. The sample was raised up to a height about $14 \pm 2 \text{ mm}$ and then dropped nominally 300 ± 15

taps per minute. The number of taps was counted automatically and the volume of the powder in the cylinder was recorded for calculating the tap density or the packing volume fraction.

3.2 Results

The obtained tap density data of 1.5 wt% Cab-O-Sil mixed with Avicel PH 2000 are shown in Figure 5, plotted as the packing fraction difference against $n+1$, where n is the number of taps. To fit the experimental data with Eq. (22), both n_m and ϕ_0 are taken on the basis of experimental results, $n_m=600$, $\phi_0=0.2$. Other two parameters with the following values, $A=3000$, and $\phi_m=0.52$, are found to generate the best fit. To fit the experimental data with Eq. (30), the following parameters, $\beta=0.66$, $\tau=10$, $\phi_0=0.2$, $\phi_m=0.36$, and $A=0.70$, are found to give the best fit. As one may see, Eq. (22) gives a good fit when the number of taps is below 200, and deviates from the experimental data at high tap numbers; while Eq. (30) gives a relative good fit at high tap numbers, but deviates at low tap numbers. Note that the maximum packing fraction values used in Eq. (22) and Eq. (30) are different, and the value used by Eq. (30) is more close to the reality, as it reaches a steady plateau at the end. The parameter A used in both equations is quite different too, which is not surprising as the parameter A in those two equations are defined differently. One thing worth mentioning is the value of stretched exponential, $\beta=0.66$, and only at this value Eq. (30) gives the best fit to the experimental data. As mentioned earlier and suggested by Macdonald and Phillips⁴⁴, $\beta=0.66$ may indicates that the extrinsic interactions between particles during tap process play a critical role, which is intuitively true for granular powder systems.

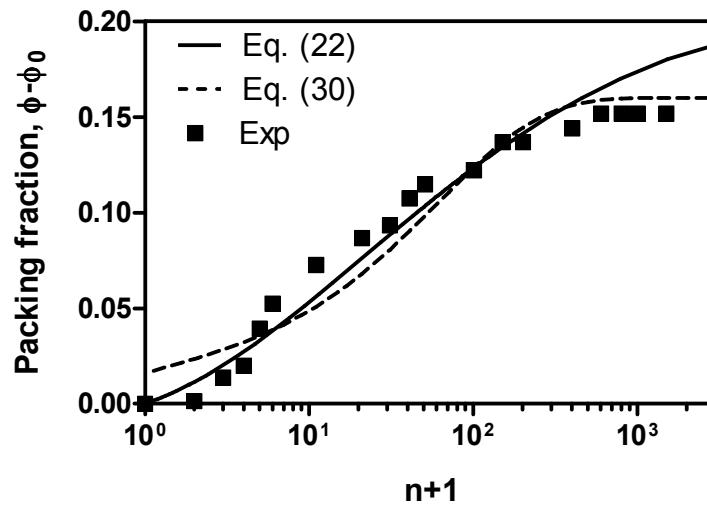


Figure 5 The packing fraction less the initial particle volume fraction is plotted against $(n+1)$, n is the number of taps, obtained experimentally and predicted with both Eq. (22) and (30). To fit the experimental data with Eq. (22), the following parameters, $n_m=600$, $A=3000$, $\phi_m=0.52$, and $\phi_0=0.2$, are assumed, but both n_m and ϕ_0 are taken on the basis of experimental results; To fit the

experimental data with Eq.(30), the following parameters, $\beta=0.66$, $\tau=10$, $\phi_0=0.2$, $\phi_m=0.36$, and $A=0.70$, are assumed.

4. Discussion

The current work is actually motivated by the success of my previous attempts in deriving viscosity equations of pure liquids, colloidal suspensions, and polymeric systems^{7, 31}. As we know, each system has its own viscosity dependences, but I personally believe that they should share same physical origins, as the viscosity comes from the frictional interactions between entities under shear. When I read Eyring's rate process theory²⁹ and the hole theory of liquids², I immediately realize that colloidal suspensions indeed share the same physical origins as liquids, and I may be able to combine both the rate process theory and the free volume theory together for deriving the viscosities of both liquids and colloidal suspensions with same principles. Under the assumption that the viscosity should be inversely proportional to the free volume and the viscosity increase rate against the particle volume fraction obeys the Einstein's simple viscosity relationship⁴⁵, the obtained viscosity equations are found to be very successful^{7, 31}, covering wide particle volume fraction ranges and reducible to well-known Kreiger-Dougherty equation⁴⁶ and Frankel-Acrivos equation⁴⁷. In addition, the introduced particle shape parameter can extend the obtained viscosity equations to predict the viscosity of colloidal suspensions containing not only the spherical shape particles but also the fiber shape particles, the latter makes me believe that the viscosity of polymeric solutions and melts could be derived with the same principles, too, as the polymer chains can be analogously considered as fiber shaped particles. Under appropriate assumptions, the derived viscosity equations can correctly predict the viscosities of both polymer solutions and polymer melts. For example, the viscosity of polymer melts increases with the 3.5 power of molecular weight when polymer chains are long enough and the chain entanglements happen and the 0.83 power of molecular weight when polymer chains are small enough and no chain entanglement happens^{7, 31}. For non-aqueous colloidal suspensions like electrorheological fluids, the yield stress under an electric field can be derived with the free volume theory²⁰, too. All the successes mentioned above drive me believe that the same rate process and free volume theories can be employed to treat granular powders, which can be analogously considered to obey the same physical principles but have a different definition of "granular temperature" arisen from any excitations rather than thermal energy that can drive particles move around. This article is my first attempt and more follow-ups will be presented in the near future.

5. Conclusions

In summary, we assume that the particles during tapping processes will behave similarly to the thermodynamic laws controlled entities and the "granular temperature" is related to the external mechanical excitations and has nothing to do the regular temperature. Under those assumptions, the rate process theory is utilized to treat the powder packing process and the free volume in a powder system is believed to control how quick particles can be packed. The derived equations can be reducible to the two widely used empirical equations under special circumstances, and could potentially fit the experimental data better with an additional adjustable parameter. The

tapping amplitude and frequency, the weight of the granular materials, and the environment temperature are grouped into this parameter that weighs the pace of packing process. An exact same treatment method employing the theory of rate process and the free volume concept was successfully used to derive the viscosity equations of liquids, colloidal suspensions, and polymeric systems^{7,31}, implying that both “dry” and “wet” particle systems are governed by the same physical mechanisms in term of the role of the free volume and how particles behave (a rate controlled process).

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