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Derivation of Stretched Exponential Tap Density Equations of Granular Powders

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Abstract

Tap density of granular powders was found to be better fitted with the stretched exponential law. In our previous work, the stretched exponential tap density equations were derived with the rate process theory and free volume concept, under the assumption that the particle packing rate during the tapping process obeys the stretched Arrhenius equation, which, however, has an empirical origin. In this article, the assumption above is eliminated and attempts are made to obtaining the stretched exponential tap density equations from very fundamental bases. In a vertical tapping process, the probability of particles attaining certain energy states is assumed to obey Boltzmann distribution and particles traveling from one sites to another are assumed to follow a very common memoryless random exponential law. The stretched exponential tap density equation is thus derived and all parameters acquire clear physical meanings. The most important parameter, the stretched exponential, is demonstrated to correlate with the interparticle forces: a small value may indicates a strong adhesive or cohesive interaction. Therefore, the stretched exponential could be a better indicator for powder flowability correlated with particle interactions as well.

I. INTRODUCTION

Granular powder materials are easily found in daily life: the soils we see on grounds or mountain tops, the dusts we encounter everywhere, the flours we use to make breads, the cements we use in constructions, the snow we embrace in winter time, etc.. Moreover, pharmaceutical drug tablets are made from powder mixtures, wall paints originally are colloidal suspensions made from powders dispersed in a liquid medium, cosmetic lotions and sunscreen creams are also colloidal suspensions containing much finer particles, and so on. All those above indicate that granular powders are often tied together with colloidal systems and are very important in practical applications.

Although understanding the physical properties of granular powders like the density, flowability, and compressibility can be dated back to many centuries ago, there still are a lot of unknowns, as granular powders are athermal systems that may not be adequately addressed with the knowledge extracted from regular gases, liquids, and solids. Nevertheless, many studies have shown that granular powders empirically obey the laws discovered in disordered thermal systems like glassy materials and colloidal dispersions. For example, the tap density of granular powders are found to be better fitted with either the inverse logarithmic law¹⁻⁵ or the stretched exponential law.⁶⁻⁸ By utilizing Eyring's rate process theory⁹ and the free volume concept widely used in both liquids^{10,11} and solids,¹² the inverse logarithmic and stretched exponential laws were derived pretty successfully.¹³ An unsatisfactory lies in the derivation of the stretched exponential law: the tapping processing rate was assumed to obey the stretched exponential Arrhenius equation, which still has empirical origin.^{14,15} Although many physical properties were found to follow the stretched exponential laws, like Mott's variable range hopping conductivity model,¹⁶ the discharge phenomenon of a capacitor,¹⁴ dielectric spectra of polymers by Williams and Watts,¹⁵ a large range of relaxations in disordered thermal systems such as glasses,^{17,18} 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 walks of polarized molecules,¹⁹ the trapping process at long time range,²⁰ and the system size,²¹ for the purpose of directly coming up the stretched exponential law.

In this article, we will put effort on the derivation of the stretched exponential tap density equations of granular powders from more fundamental levels. The basic ideas were mainly

stimulated from Theodor Förster's theory, dealing with the energy transfer from donors to random distributed acceptors.^{22,23} A very complicated quantum mechanical treatment was employed by Förster to calculate the frequency overlap between donors and acceptors for estimating the probability that the donor and acceptor molecules will share a same frequency or energy; Only the basic mathematical backbones related to randomly distributed systems, as extracted by Blumen²⁴ and Klafter,²⁵ rather than the theoretical details is borrowed and modified to treat granular powers, where particle packing process may be considered to have randomness features. Most strikingly, largely different physical meanings must be rendered to those random distribution equations, though they share same mathematical forms. Readers shouldn't be surprised if similarities cannot be drawn from the literature cited above and from the description detailed in section II, as almost everything borrowed from literature is given a new look and the connections may be very hard to detect; Furthermore, a complete different system and problems are addressed in this article, indeed.

For the purpose of applying fundamental principles extracted from the thermal systems to granular powders, we have to assume that the energy will be transferred from the external mechanical movements to the internal powder bed during tapping process; Such an energy injected from an external mechanical source is responsible for particle movements, which is quite random due to the randomness of particle distribution spatially in the powder column at the beginning. It is the particle movements that induce particle packing process, driving the system reach a steady state where particles cannot be packed more densely at current conditions. Such a movement induced by external mechanical vibration could be analogously compared to the thermal motion observed in thermal systems, and therefore fundamental principles extracted from thermal systems could be utilized to describe granular powders.

II. THEORY

Let's consider a granular powder residing in a column like a graduated cylinder as showed in Fig.1. This cylinder can move up and down repeatedly in a controllable manner, $L = L_0 \exp(i\omega t)$, where L_0 is the tapping amplitude and ω is the radian tapping frequency, and t is time. The energy flow rate into the powder system due to the vertical tapping process may be expressed as²⁶:

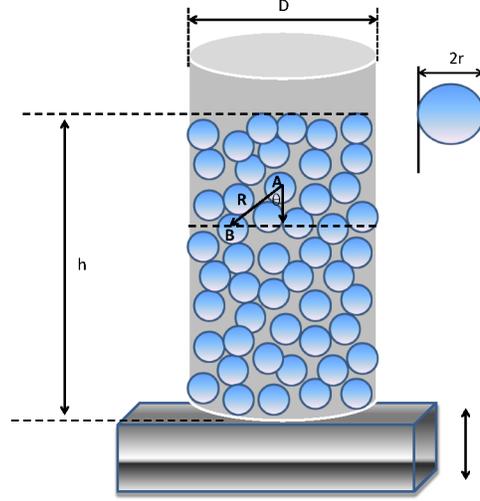


FIG. 1: Tapping process is illustrated as powder residing in a cylinder that can move up and down

$$E(t) = \frac{Mg\omega L_0}{2\pi} \quad (1)$$

where Mg is the weight of the powder, and g is the gravity constant. The time elapses after one tap should be the periodical cycling time of the vibration, $2\pi/\omega$, and thus after a series of tapping processes with the tapping number, n , the time spent should be $2n\pi/\omega$. Therefore, the total energy flowing into the powder after a series of tapping processes, may be equal to the energy flow rate expressed in Eq.1 times the time spent during the tapping processes:

$$E = \frac{2n\pi E(t)}{\omega} = nMgL_0 \quad (2)$$

It is interesting to note that the energy input into granular powders under a vibration is only related to the amplitude of the vibration, and surprisingly has nothing to do with the vibration frequency. As stated earlier, granular powders are athermal systems and the regular environment temperature is unable to drive particles move around in the systems, as it usually does in thermal systems where the molecules or the dispersed particles are always moving, due to the thermal energy or Brownian motion. However, during tapping process, the particles do move around inside the cylinder, not because of the temperature but due to the external mechanical excitation. The particle movements may be analogously compared with the thermal driven phenomena if we define the granular temperature in a

similar way: causing particle motions in a confined space. In such a scenario, we may expect granular powders behave similarly and obey the laws extracted from thermal systems. In condensed matter physics and statistic mechanics, there basically are three types of distribution statistics called Boltzmann distribution, Bose-Einstein distribution, and Fermi-Dirac distribution, when N identical particles present in a confined system.^{27,28} Boltzmann distribution²⁹ works for identical but distinguishable particle systems like classic gases, while both Bose-Einstein and Fermi-Dirac distributions work for identical and indistinguishable particle systems like electrons or Bosons. We thus use Boltzmann distribution to describe granular powders, which can be expressed as:

$$P(E) = A \exp\left(\frac{-E}{k_B T}\right) \quad (3)$$

where P is the probability of particles that can achieve the energy state E , A is constant, k_B is Boltzmann constant and T is the temperature, and $k_B T$ scales molecular kinetic energy. However, as we stated earlier, in granular powder systems the thermal energy is unable to drive particles move around and thus $k_B T$ must be replaced with a different term, $w(R)$, which is analogously assumed to be the energy required to drive particles move in powder systems. Therefore, for granular powders, Eq. 3 may be re-written as:

$$P(E) = A \exp\left[\frac{-E}{w(R)}\right] \quad (4)$$

For a particle A traveling to the position of the particle B, there are many possible routes available in the powder bed, as shown in Fig. 2. The particle may take the route R , the straight line between the sites A and B. However, we know it is unlikely, as during tapping process the particles may stick with other neighboring particles due to the interparticle interactions, or may collide frequently with neighbored particles, and the actual route to reach the site B may be the route R_2 or R_3 , depending on micro-environment. Especially, the particles at the different depth of the column may experience different pressure from the particles sitting above, as shown in Janssen's Equation³⁰ expressed below:

$$P_v = \frac{\rho g D}{4\mu K} \left[1 - \exp\left(-\frac{4\mu K z}{D}\right)\right] \quad (5)$$

where ρ is the density of particle material, g is again the gravity constant, D is the diameter of the cylinder, μ is the frictional coefficient between the particles and the cylinder wall when particles move vertically down, K is the ratio of the lateral stress to the vertical pressure, and z is the depth where the particle A resides, counted from the top of the powder bed. If

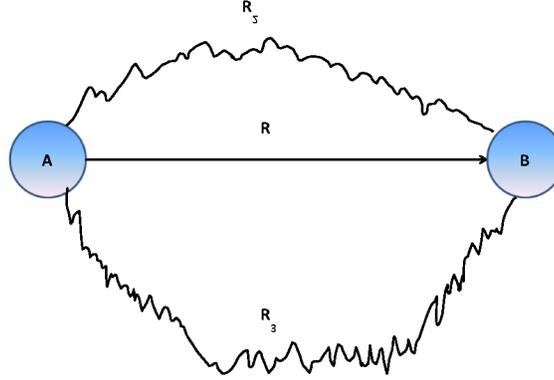


FIG. 2: Schematic diagram of a particle traveling from the sites A to B

the particle takes the route R , and the work needed to drive a particle from the sites A to B may be expressed as:

$$w(R)_1 = (mg + P_v A_p)R \sin \theta \quad (6)$$

as both the gravitational force and the force resulted from the particles sitting above is straight downward. Note that θ is the angle between the route R and the vertical direction, m is the mass of a particle, A_p is the projected area of the particle, $A_p = \pi r^2$, r is the radius of a particle. Eq. 6 tells us that for a particle to have a freedom to move laterally for filling the interstitial space during tapping process, the minimum work $w(R)_1$ is required for overcoming the vertical forces resulted from the mass of the particle itself and the pressure from other particles sitting on the top. Since P_v is dependent on the depth, we may use the pressure at the half height of the powder column as the average pressure for all particles for simplicity reason. Apparently, no pressure is on the very top layer of the powder column and the largest pressure is at the bottom. Using the pressure at the half height of the powder column could be a good approximation for averaging all pressures that the particles may experience. Thus one may re-write Eq. 6 as:

$$\begin{aligned}
w(R)_1 &= \left[\frac{4\pi r^3 \rho g}{3} + \frac{\rho \pi r^2 g D}{4\mu K} \left[1 - \exp\left(-\frac{2\mu K h}{D}\right) \right] \right] R \sin \theta \\
&= (\pi r^2 \rho g) \left[\frac{4r}{3} + \frac{D}{4\mu K} \left[1 - \exp\left(-\frac{2\mu K h}{D}\right) \right] \right] R \sin \theta \\
&= BR \sin \theta
\end{aligned} \tag{7}$$

where h is the height of the powder column, as shown in Fig. 1, B is a material and cylinder shape related constant, $B = (\pi r^2 \rho g) \left[\frac{4r}{3} + \frac{D}{4\mu K} \left[1 - \exp\left(-\frac{2\mu K h}{D}\right) \right] \right]$.

The next question is how likely the particle A may take the exact straight route R . In a random process environment, it is very likely that the particle A may take other routes like R_2 and R_3 as shown in Fig. 2. Eq. 7 may never work for real situations. Any other routes will be longer than R , and a modification of Eq. 7 is definitely needed. We may assume there is a simple power law relationship between $w(R)_1$ and R :

$$w(R)_1 = BR^f \tag{8}$$

where f is a positive number that can change with the routes that the particle A is going to take. For example, f would be less than 1 if the particle A takes the straight route, or larger than 1 if the particle A takes other routes longer than the route R . This simplistic relationship may well cover all possible routes, as no matter which route that the particle A may take, one may always find a suitable value of f to scale the traveling distance. We may also assume a more complicated exponential relationship, $w(R)_1 = B \exp(-\gamma R)$, where both γ and B are some numerical constants. As indicated in literature²⁴²⁵, this exponential relationship would lead to an "enhanced" stretched exponential law in the end with just more complicated mathematical derivations. The readers are referred to those two articles cited above for more detailed information if interested in. In other words, no matter which assumption is used, a similar stretched exponential form will be derived in the end. For simplification reason, we will only consider the simple power law relationship as shown in Eq. 8. If there are N particles in the system, the total minimum work should be $w(R) = Nw(R)_1 = BNR^f$. Finally, Eq. 4 may be rewritten as:

$$P(E) = A \exp\left(\frac{-ER^{-f}}{NB}\right) \tag{9}$$

In the meanwhile, even the particle A is assumed to only take straight routes, there are many other sites that locate at the same level as the site B and can allow the particle A straightly reach there, as shown in Fig. 3. The probability of the particle A moving to

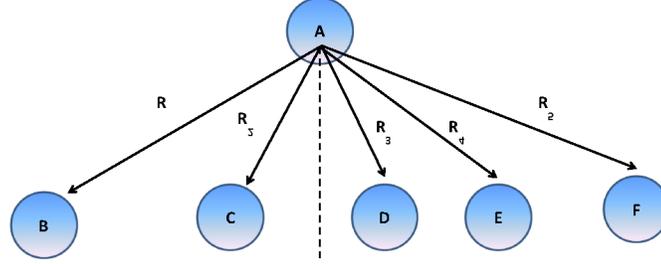


FIG. 3: Schematic diagram of a particle moving straightly from the sites A to many other possible neighboring sites

the site B with the distance R , $P(R)$, may be expressed as:

$$P(R) = p \exp(-pR) \quad (10)$$

where p is a constant parameter and $1/p$ represents the mean probability. Eq. 10 is a very common memoryless exponential distribution equation in random process.³¹ It is called memoryless because the past has no impact on the future random behaviors and every instant looks like a new random event, which would be the exact case for particle packing during the tapping process. The rate that the particles move to the next equilibrium state during the tapping process, k , may be directly proportional to the probability of particles attaining energy E capable of moving laterally times the probability of particles taking the route R at the distance R :

$$\begin{aligned} k &= \int_0^{\infty} P(E)P(R)dR = \int_0^{\infty} Ap \exp(-pR) \exp\left(\frac{-ER^{-f}}{NB}\right)dR \\ &= Ap \int_0^{\infty} \exp\left(-pR - \frac{ER^{-f}}{NB}\right)dR \end{aligned} \quad (11)$$

The solution to Eq. 11 with the help of the saddle point integration method leads to:

$$k = Ap \exp[-(CE)^{\frac{1}{1+f}}] \quad (12)$$

under the assumption that E is larger enough, $E \gg 1/C$. A same solution was shown to similar integrals in literature.^{20,25} C is a constant can be expressed as:

$$C = (NB)^{-1}(p/f)^f(1+f)^{1+f} \quad (13)$$

Clearly, Eq. 12 shows that the particle packing rate k has a stretched exponential relationship with the energy input into the powder system. By assuming $\beta = \frac{1}{1+f}$, substituting Eq. 2 into Eq. 12 leads to:

$$k = Ap \exp[-(nMgL_0C)^\beta] = Ap \exp[-(\frac{n}{\tau})^\beta] \quad (14)$$

with τ as:

$$\begin{aligned} \tau &= \frac{NB}{MgL_0(p/f)^f(1+f)^{1+f}} \\ &= \frac{1}{L_0(p/f)^f(1+f)^{1+f}} \left[1 + \frac{3D}{16r\mu K} \left[1 - \exp\left(-\frac{2\mu Kh}{D}\right) \right] \right] \end{aligned} \quad (15)$$

as $Mg = \frac{4\pi r^3 N \rho g}{3}$ by the definition. τ may be called as a characteristic rate constant and seems to have nothing to do with the weight of powder particles in the column and the tapping frequency. It is inversely proportional to the tapping amplitude, probably because this parameter will make the tapping process reach the steady state in a much quick pace; It is also related to the diameter of the cylinder and the particle radius: smaller particles tend to take longer time to reach the steady state; It correlates with the frictional coefficient, the height of the column, and the ratio between the lateral and the vertical stresses. Most interestingly, the characteristic rate constant is related to the particle interaction parameter f or β : strong particle interaction results in longer time to reach steady state, which seems to be reasonable. As one may tell from Eq. 8, if the cohesive or adhesive interaction forces between particles are larger, there should be a strong drag force preventing particles from traveling from one site to another during tapping process, thus f should be large and one may have a small β . Now the stretched exponential acquires a physical meaning: it actually scales the interaction force between particles with large values for weak interactions between particles and small ones for strong interactions. One may expect that there may be no or little interparticle forces when $\beta = 1$. β may thus be a better parameter for indicating particle interactions and then powder flowability than the popular Carr index.^{13,32}

Once we have the relationship between the particle packing rate k and the tapping number n , as described in Eq. 14, the remaining derivations will be the same as detailed in ref.,¹³

with the utilization of both Eyring's rate process theory and free volume concept. For avoiding redundancy, please go to the reference¹³ for details, and we just provide the final equations below:

$$\phi = \phi_m - Ap(\phi_m - \phi_0) \exp[-(\frac{n}{\tau})^\beta] \quad (16)$$

when a simple free volume calculation formula is used; or

$$\phi^{1/3} = \phi_m^{1/3} - (Ap)^{1/3}(\phi_m^{1/3} - \phi_0^{1/3}) \exp[-\frac{1}{3}(\frac{n}{\tau})^\beta] \quad (17)$$

when a precise free volume calculation formula is used. ϕ is packing volume fraction at tapping number n , ϕ_m is the maximum packing volume fraction where the steady packing state is achieved, ϕ_0 is the initial particle volume fraction. Other parameters remain the same meanings as indicated earlier. Again, when $Ap = 1$, Eq. 16 will be reducible to the empirical stretched exponential equation widely used in literature.

III. DISCUSSION

The derivation ideas used in this article are stimulated from several excellent publications that deal with energy transfer between donors and randomly distributed acceptors or relaxation phenomena observed in disordered systems. However, as emphasized previously, only the backbone mathematical formulas rather than the detailed treatment methods are borrowed and more importantly, they are rendered with new and intuitive physical meanings. Although granular powder systems are athermal systems, substantially different from all the systems presented in the literature where the backbone mathematical formulas are used, similarities can be definitely drawn if the tapping process is analogously considered as a driving force to move particles around as the thermal energy does in regular thermal systems. The success of utilization of both Eyring's rate process theory and free volume concept that are extracted from thermal systems to derive both the Chicago logarithmic and stretched exponential laws of tap density of granular powders demonstrates that "dry" granular powders may share similar physical mechanisms as are discovered in liquids and colloidal suspensions. Attempts made in this article may further strengthen the similarities mentioned above: even the randomness distribution is same for both granular powders and regular thermal systems, which may lay the foundation for utilizing other fundamental principles observed in many thermal systems to model granular powders in the future.

One thing we want to emphasize is that the laws we borrowed from thermal systems can only be applied to the granular powders where particles can randomly move around like in tapping processes we focus on now. Those laws may not be applicable to a granular powder system without particle movements. The particle movements don't need to be excited from an external source, and a free flowing powder may obey those laws, too.

IV. CONCLUSION

The stretched exponential tap density equations of granular powders are derived on the basis of two general assumptions: 1) Since particles are vigorously moving around during tapping process, the energy that particles can acquire may follow the fundamental Boltzmann distribution; 2) The probability of a particle moving from one site to another neighboring site may follow the simple exponential relationship with the distance. Both these two principles are commonly used in describing particle random walks in disordered thermal systems. The particle packing rate is assumed to be directly proportional to the product of the probability of particles acquiring the necessary energy to move freely both laterally and vertically and the probability of particles moving to the next equilibrium site. The obtained stretched exponential tap density equations clearly tell that the tapping rate has nothing to do with how much amount of powders are placed into the column and the tapping frequency. The tapping rate is inversely proportional to tapping amplitude; Smaller particles tend to take a longer time to reach the steady state; It also correlates with the frictional coefficient, the height of the column, and the ratio between the lateral and the vertical stresses. Most importantly, the obtained equations demonstrate that the characteristic rate constant is dependent on particle interaction parameter f or β : a large f or small β may indicate strong particle interactions. The parameter β may thus be a better indicator for scaling particle interactions and then powder flowability than the popular Carr index. All parameters in original empirical stretched exponential equation now render clear physical meanings. The characteristic tapping rate constant τ now have an exact relationship with the parameters that are supposed to make a contributions to tapping processes.

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The author sincerely appreciate the reviewers' comments and suggestion on my previous article published on Soft Matter.¹³ It is the reviewers' comments that stimulate me to work out a method that eventually leads to the stretched exponential tap density equations from more fundamental levels.

APPENDIX A:

SADDLE POINT INTEGRATION OF EQ. 11

Here briefly is showing how we come up Eq. 12 from Eq. 11 using the saddle point integration method. Please refer to the classical literature³³ and³⁴ for detailed information on this method. For a integration equation with a generic form:

$$I(S) = \int_0^{\infty} f(x)e^{Sg(x)} dx \quad (\text{A1})$$

where f and g are some real functions of x , and S is a constant. The function $f(x)e^{Sg(x)}$ will very likely go through either a maximum or minimum points (called saddle points), the integration is thus dominated by those peaks, especially the biggest peak. Assume at $x = x_0$, the function reaches the peak point, the integration thus can be approximated as:

$$I(S) = f(x_0)e^{Sg(x_0)} \sqrt{\frac{2\pi}{-Sg''(x_0)}} \quad (\text{A2})$$

under an assumption that S is a large number. Back to Eq. 11, one may find:

$$f(x) = \exp(-pR) \quad (\text{A3})$$

$$g(x) = R^{-f} \quad (\text{A4})$$

$$S = -\frac{E}{NB} \quad (\text{A5})$$

It would be very easy to find out R_0 at which the integrated function reaches the minimum or maximum by simple differentiating it and assigning the obtained differential function is equal to zero:

$$R_0 = \left(-\frac{Sf}{p}\right)^{\frac{1}{1+f}} = \left(\frac{Ef}{pNB}\right)^{\frac{1}{1+f}} \quad (\text{A6})$$

Thus one may find

$$f(R_0) = \exp\left[-p\left(\frac{Ef}{pNB}\right)^{\frac{1}{1+f}}\right] \quad (\text{A7})$$

$$g(R_0) = \left(\frac{Ef}{pNB}\right)^{-\frac{f}{1+f}} \quad (\text{A8})$$

$$g''(R_0) = f(1+f)\left(\frac{Ef}{pNB}\right)^{-\frac{f+2}{1+f}} \quad (\text{A9})$$

Substituting the equations showing above into Eq. A2, one may obtain:

$$k = Ap \exp\left[-\frac{E}{NB}\left(\frac{p}{f}\right)^f(1+f)^{1+f}\right]^{\frac{1}{1+f}} = Ap \exp(-CE)^{\frac{1}{1+f}} \quad (\text{A10})$$

which exactly is Eq.12. Again, A is a constant.

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