Cluster kinetics of density relaxation in granular materials

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Of the many complex processes of granular materials, vibrational settling and compaction are common phenomena that have attracted much attention. In this work, we investigate vibrational, or tapping, compaction, and propose that the underlying kinetics involves clusters fragmenting and aggregating, and individual grains attaching and dissociating at cluster surfaces. The periodic vibrations cause cluster breakage and interchange between individual free grains and the clusters. The population balance equations for the concurrent kinetics are solved by a moment method, yielding easily solved differential equations. The compaction ratio defined in terms of the mass moments agrees well with experimental data [Knight *et al.*, Phys. Rev. E. **51**, 3957 (1995); Nowak *et al.*, *ibid.* **57**, 1972 (1998)] and other models. A change in tapping acceleration can produce reversible or irreversible transitions between densities, depending on the number of clusters that have evolved.

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INTRODUCTION

Settling and compaction of powders and grains occur in a myriad of natural and industrial processes. When lightly packed granular materials are tapped, vibrated, or shaken in a gravity field, the packing density can increase by relaxation mechanisms that are not well understood. In a seminal study, Knight *et al.* [1] reported that monodisperse spherical glass particles shaken in a vertical cylindrical tube evolved from a low initial density to a final density that depended on the tapping intensity. As proposed earlier by Barker and Mehta [3], the complex time dependence of the density relaxation required two time constants, suggesting that two types of packing are involved. The slow (logarithmic) transition between packing states was explained by individual particle movements similar to automobile parking [4]. We hypothesize that two types of packing are involved: free grains amorphously packed at low density and coherent clusters of larger density. The transition between them can be explained by individual grains attaching and detaching from the densely packed clusters. The experiments of Nowak *et al.* [2] showed that reversible or irreversible changes between density states occurred for different changes in tapping intensity. This dependence on the process history is an additional intriguing and challenging issue that, according to our proposal, is related to the cluster evolution. A realistic theory of granular compaction should describe both kinds of experimental observations.

We explore the possibility that cluster kinetics based on population balance (distribution kinetics) modeling can describe the observations. Goldhirsch and Zanetti [5] and Jaeger *et al.* [4], through two-dimensional simulations, reported the tendency for free grains to aggregate into clusters, which are sometimes chainlike. Since interactions among particles in a granular medium are inherently inelastic, energy is lost in each collision, allowing particles to aggregate. When the grains are in a gravitational field, they will tend to fall into aggregates or ordered domains. The process is similar to a liquid-solid phase transition with free grains analogous to a liquid phase and clusters to the crystalline phase. The proposed distribution kinetics method has been used to describe a range of crystallization processes, including crystal growth [6(a)], coupled with nucleation [6(b)] and Ostwald ripening [6(c)]. The dynamics of polymorphic crystalline forms has also yielded to this approach [6(d)]. The clusters considered here are close-packed crystalline forms that perhaps grow near the container walls [2]. Free single grains are those not associated with a cluster during the vibrational agitation of the granular medium. When the tapping vibrations in the experiments cause more consolidation, the number of free grains decreases as the compact clusters grow. The amount of compaction will depend on the strength of the agitation process; stronger accelerations typically allow more grains to seek the closer-packed configuration. Extremely vigorous and continuous vibration, however, would cause greater cluster breakup and detachment of free grains, a process similar to soil liquefaction during earthquakes. One might anticipate, therefore, that compaction versus tapping intensity will show a maximum [2].

Vibrational compaction is one of many processes important to handling particulate solids [7]; flow, mixing, arching, compression compaction, shearing, and fluidization are other processes that may be influenced by cluster kinetics. Our approach to the kinetics and dynamics of clusters is similar in philosophy to chemical kinetics. There, rate coefficients enter the models via constitutive relations, just as rate coefficients proposed for Eqs. (1) and (2) below appear in the rate equations. Such parameters obviously depend on underlying molecular or microscopic processes, but much can be learned by considering how they vary with experimental conditions.

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For example, our approach has been applied to granular mixing by tumbling operations [6(e)], whereby loose particles slide down the inclined surface and/or particle clusters fragment and fall down the incline. The method allowed straightforward derivation of experimentally observed asymptotic power law or exponential behavior of segregation metrics for various rate coefficient expressions. In another instance, application of cluster kinetics to phase transition dynamics correctly predicted the asymptotic scaled coarsening of the cluster size distribution [6(f)].

The initial condition for density relaxation experiments [1] was prepared by blowing dry nitrogen gas up through the granular medium. Before the vibration began, the packing fraction was 0.58 [1] or 0.59 [2]. An experiment consisted of well-separated accelerations, or taps, of the vertical cylindrical tube holding the granular material. Given that the system relaxes following each tap, grain transfer to or from clusters occurs only during the acceleration. The tapping intensity was measured by the ratio of the peak acceleration of a tap to the gravitational acceleration $\Gamma = a/g$. According to the present model, the initial condition for computations is the state of the granular medium caused by the tapping, i.e., during the agitated state. Thus, in the initial low-density condition, many grains are detached and free to aggregate in different clusters.

Starting at an initial packing fraction $\rho(t=0)=0.59$, Nowak *et al.* [2] investigated the reversibility of the granular compaction process by observing steady state values of density after 10 000 taps when the tapping intensity Γ was increased in steps of approximately 0.5 between steady states. As a result the packing fraction ρ increased *irreversibly* to 0.635 at the critical value $\Gamma^* \approx 3.3$. A further increase of Γ led to slightly reduced density ($\rho \approx 0.63$), whereas decreasing Γ caused ρ to asymptotically approach 0.658 as Γ neared zero. These transitions were *reversible*, in contrast to the initial transition from small Γ up to Γ^*. In terms of the cluster hypothesis, this history effect, manifested as reversible/irreversible behavior, suggests that clusters grown irreversibly to a critical size can then be reversibly grown or reduced.

Several theoretical and phenomenological models have been advanced to interpret the granular relaxation experiments [1], but there has been less comment on the reversibility results [2]. Hong *et al.* [8] considered relaxation under tapping a problem of diffusing voids. They numerically solved a one-dimensional diffusion equation for voids moving upward through the granular medium. When the void diffusion was related to the traffic problem, it was found that voids arrived periodically at the top of the packed bed. Barker and Mehta [3] suggested that independent particles and clusters interact through diffusion in vibrated powders. Applying Monte Carlo computations to a collection of frictionless hard spheres, they found final packing fractions depended on the intensity of vibration. While a one-exponential fit was fair, the results were better represented by a two-exponential fit. An empirical equation with two parameters was used by Knight *et al.* [1] to fit their experimental data. Linz [9] showed how a phenomenological approach to describe the sequential taps provided a difference equation whose approximate solution with two fitting parameters described the experimental data accurately. Saluena *et al.* [10] interpreted the experimental data with a hydrodynamical description based on an assumed glasslike viscosity relation. Gavrilov's [11] recent paper, based on a one-dimensional cluster model, has similarities with the current work. Following cluster fragmentation concepts applied to traffic flow, Gavrilov used a Monte Carlo approach to compute how individual grains dissociated from and reassociated with clusters evolving to hexagonally packed clusters. However, cluster fragmentation (breakage) and aggregation, described by Eq. (2) below, were not considered. Recent work seems generally to agree on the tendency for grains to organize into clusters or ordered domains [12–17].

The present objective is to explore a different approach to density relaxation in granular media. The approach is based on evidence for clustering among grains and recognition that such clusters are distributed in size. We hypothesize that during the relaxation, beginning with a loosely packed medium, the discrete taps cause individual grains to dissociate from or attach to the surfaces of clusters. The clusters may also fragment and aggregate, exposing new surfaces for loosening single grains. The end state of an acceleration period (or tap) is the initial state at the beginning of the next tap. Disregarding the time when the system is quiescent between taps enables one to consider time a continuous variable. Quantifying the evolution of the cluster distributions, both reversible and irreversible time dependence, is a central goal. The kinetics of the cluster processes are represented by population balance equations that explicitly govern the cluster size distribution. Moment methods facilitate the derivation of simple differential equations for the statistical properties of the cluster size distribution.

An advantage of the distribution kinetics (rate) approach reported here is that the moment properties of the size distribution can be evaluated efficiently by solution of differential equations. Averaged particle interactions are represented by rate coefficients, much like intermolecular interactions are averaged to represent crystal growth or chemical reaction rates. This approach is commonly applied in polymerization kinetics to obtain molecular weight distributions and their moments, thus quantitatively describing the significant features of polymer reaction dynamics [6(g)]. Computations and the assumptions upon which they are based are relatively straightforward. This approach is a systematic and versatile method for investigating kinetics and dynamics of systems distributed in size, such as evolving clusters [6]. For an initial condition with a small mass of clusters, a given acceleration Γ will cause irreversible transition to a final steady state. We attribute this irreversibility to the growth of clusters, which, when formed, allow reversible changes for packing density ρ when Γ is either increased or decreased. The process is analogous to a phase transition with S playing the role of supersaturation and Γ representing energy input.

The paper is organized as follows. Beginning with a presentation of the appropriate cluster distribution kinetics, we represent the governing population balance equations for the cluster size distribution and monomer (grain) numbers. A transformation to scaled dimensionless variables provides a minimal set of parameters to determine. The scaled moment equations for number of free grains and clusters and for clus-

ter mass are solved exactly. The solutions are examined for their dependence on fragmentation parameters and on initial conditions. Finally, the results for packing fraction are compared with experimental data for both reversible and irreversible observations.

CLUSTER KINETICS

If $\mathbf{C}(x)$ represents a cluster of mass x and $\mathbf{M}(x_m)$ is a particle (monomer) of mass x_m, we have for concurrent monomer dissociation and attachment

$$\mathbf{C}(x) \underset{k_g}{\overset{k_d}{\rightleftarrows}} \mathbf{C}(x - x_m) + \mathbf{M}(x_m) \qquad (1)$$
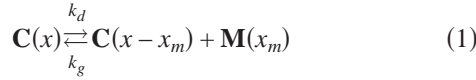
with rate coefficients k_g and k_d for cluster growth (attachment) and dissociation (detachment), respectively. The clusters may also fragment with breakage rate coefficient k_b and aggregate with rate coefficient k_a,

$$\mathbf{C}(x) \underset{k_a}{\overset{k_b}{\rightleftarrows}} \mathbf{C}(x') + \mathbf{C}(x - x'). \qquad (2)$$
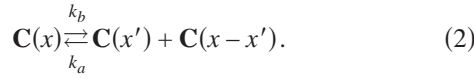
Here we consider that the rate coefficients may depend on the strength of the acceleration, but we ignore any dependence on packed bed depth or cluster size. Although it is obvious how to extend the types of clusters beyond simple forms considered here, we will show that the model of Eqs. (1) and (2) is adequate to explain the observations.

The cluster size distributions are defined so that $c(x,t)dx$ is the number of clusters having mass in the interval $(x,x+dx)$. Population balances lend themselves to calculations by moments, defined as integrals over cluster mass x,

$$c^{(n)}(t) = \int_0^\infty c(x,t)x^n dx. \qquad (3)$$

The zeroth moment $c^{(0)}(t)$ is the time-dependent number of clusters, and the first moment $c^{(1)}(t)$ is the mass of clusters. The average cluster mass is the ratio $c^{(1)}(t)/c^{(0)}(t) = c^{\mathrm{avg}}(t)$. Although we use only these lower moments for the present treatment of granular materials, measures of cluster polydispersity, such as variance, based on the second moment can also be defined [6(a),6(b)]. The size distribution of the monodispersed grains is $m(x,t) = m^{(0)}(t)\delta(x - x_m)$, in terms of the number of grains $m^{(0)}$.

If the volume per mass of the clusters is v_A, the volume of clusters is $v_A c^{(1)}$. Likewise, the vessel volume occupied by free particles is $v_o x_m m^{(0)}$, where v_o is the volume per mass of the loosely packed particles. The total volume displaced by free particles and particles in clusters is the total mass of particles, $x_m m^{(0)} + c^{(1)}$, divided by the particle mass density d_m. The experiment measures the packing (volume) fraction defined as the ratio of the displaced volume to the total occupied volume,

$$\rho(t) = [x_m m^{(0)} + c^{(1)}]/d_m[v_o x_m m^{(0)} + v_A c^{(1)}]. \qquad (4)$$

It follows that the void fraction among the particles is $1 - \rho(t)$, which decreases as the granular material is compacted.

Consider identical grains of mass x_m that can be either free or aggregated into clusters. The population balance equations that govern the distributions of the clusters, $c(x,t)$, and of the grains, $m(x,t) = m^{(0)}(t)\delta(x - x_m)$, are based on mass conservation [6(a)] for the processes represented by Eqs. (1) and (2):

$$\partial c(x,t)/\partial t = -k_g c(x,t) \int_0^\infty m(x',t)dx' + k_g \int_0^x$$

$$\times c(x - x',t)m(x',t)dx' - k_d c(x,t) + k_d \int_x^\infty c(x',t)$$

$$\times \delta(x - (x' - x_m))dx' - 2k_a c(x,t) \int_0^\infty c(x',t)dx'$$

$$+ k_a \int_0^x c(x',t)c(x - x',t)dx' - k_b c(x,t)$$

$$+ k_b \int_x^\infty c(x',t)\Omega(x,x')dx'. \qquad (5)$$

The particle balance is

$$\partial m(x,t)/\partial t = -k_g m(x,t) \int_0^\infty c(x',t)dx'$$

$$+ k_d \int_x^\infty c(x',t)\delta(x - x_m)dx'. \qquad (6)$$

The Dirac delta distributions of fragmentation products, $\delta(x - (x' - x_m))$ and $\delta(x - x_m)$, represent the monomer removal kernels in Eqs. (5) and (6) [6(g)]. The breakage kernel $\Omega(x,x')$ is the expression of Deimer and Olson [18], which allows N fragments with each breakage, and contributes to the zeroth moment equations as the products $k_b(N-1)$. The choice of rate coefficient expressions is motivated by cluster kinetics representations used previously [6,18]. Here we assume all rate constants are independent of x. The initial condition is a mixture of clusters and free grains,

$$c(x,t = 0) = c_0^{(0)}\delta(x - c_0^{\mathrm{avg}}),$$

$$m^{(0)}(t = 0) = m_0^{(0)}. \qquad (7)$$

For the loosely packed initial state, the mass of clusters is quite small, but not necessarily zero; thus, $c_0^{(1)} \equiv c_0^{(0)}c_0^{\mathrm{avg}} \ll x_m m_0^{(0)}$.

The moment equations from Eq. (8) are [6,18]

$$dc^{(0)}/dt = [k_b(N-1) - k_a c^{(0)}]c^{(0)}, \qquad (8)$$

$$dc^{(1)}/dt = x_m[-k_d + k_g m^{(0)}]c^{(0)}, \qquad (9)$$

$$dm^{(0)}/dt = [k_d - k_g m^{(0)}]c^{(0)}. \qquad (10)$$

These moment equations can be deduced from Eqs. (1) and (2) directly, but Eqs. (5) and (6) are necessary if higher moments are to be formulated. By Eqs. (9) and (10), the mass balance is $d[c^{(1)} + x_m m^{(0)}]/dt = 0$, or when integrated with the initial condition and a final condition,

$$c_0^{(1)} + x_m m_0^{(0)} = c_0^{(1)}(t) + x_m m^{(0)}(t) = c_s^{(1)} + x_m m_s^{(0)} \quad (11)$$

where the subscript s denotes a final steady state.

The model evidently meets the condition [19] that the differential equations yield a final end point that retains a dependence on earlier states (a history effect). As seen in the experimental data [1], the differential equations (8)–(10) indicate that a steady state is approached asymptotically as the time derivatives vanish. By Eqs. (9) and (10), the free grains reach the number

$$m_s^{(0)} = k_d/k_g \quad (12)$$

which determines the ratio of rate coefficients in Eqs. (9) and (10), and is similar to a microscopic reversibility condition. According to Eq. (8) the number of clusters also approaches a steady state,

$$c_s^{(0)} = k_b(N-1)/k_a. \quad (13)$$

The force impacting the particles during vibration may depend on the mass of overlying particles. Then the rate coefficients and hence the final state would depend somewhat on the depth in the packed bed, as observed experimentally [1]. Here, we will neglect this position dependence, and assume Eqs. (1)–(13) hold throughout the granular medium.

The number of parameters is minimized if scaled dimensionless variables are defined,

$$C^{(0)} = c^{(0)}/m_s^{(0)}, \quad C^{(1)} = c^{(1)}/(m_s^{(0)} x_m),$$

$$\theta = t k_d, \quad S = m^{(0)}/m_s^{(0)}, \quad \alpha = k_a/k_g, \quad \beta = k_b(N-1)/k_d. \quad (14)$$

Relating each rate term as a ratio allows a comparison of competitive rates of cluster fragmentation or breakage (β), and aggregation (α). It follows from Eqs. (12) and (13) that $\beta/\alpha = c_s^{(0)}/m_s^{(0)} = C_s^{(0)}$. The differential equations (8)–(10), when divided by $k_d m_s^{(0)}$, yield the dimensionless differential equations

$$dC^{(0)}/d\theta = [\beta - \alpha C^{(0)}]C^{(0)}, \quad (15)$$

$$dC^{(1)}/d\theta = (S-1)C^{(0)} = -dS/d\theta. \quad (16)$$

In Eq. (14), if S is different from its steady state value $S(\theta \rightarrow \infty) = 1$, the driving force $S-1$ causes cluster growth or disassociation. If the initial number of free particles were used as the scaling factor in Eq. (22), then $m^{(0)}/m_0^{(0)}$ would start at an initial value 1.0 and evolve to a final value $m_s^{(0)}/m_0^{(0)}$. The definitions in Eq. (14), however, highlight the relationship to supersaturation and crystal growth, and their evolution to equilibrium. The initial conditions for the governing equations for granular compaction [Eqs. (15) and (16)] are

$$S(\theta=0) = S_0, \quad C^{(1)}(\theta=0) = C_0^{(1)}, \quad \text{and } C^{(0)}(\theta=0) = C_0^{(0)}. \quad (17)$$

The symmetry of Eq. (16) gives $d[S+C^{(1)}]/d\theta=0$, and thus the mass balance,

$$S_0 + C_0^{(1)} = S(\theta) + C^{(1)}(\theta) = 1 + C_s^{(1)}. \quad (18)$$

The solution to the logistic equation (15), is

$$C^{(0)} = e^{\beta\theta}[(e^{\beta\theta} - 1)(\alpha/\beta) + (\beta/C_0^{(0)})]^{-1}. \quad (19)$$

Substituting this into Eq. (16) allows an analytical solution for $S(\theta)$,

$$S(\theta) = 1 + (S_0 - 1)\beta^{1/\alpha}[C_0^{(0)}(e^{\beta\theta} - 1)\alpha + \beta]^{-1/\alpha}. \quad (20)$$

This along with the mass balance is all that is needed to interpret the compaction data. In terms of the scaled variable, the packing ratio Eq. (4) is

$$\rho(\theta) = d_m^{-1}(S_0 + C_0^{(1)})/[v_0 S(\theta) + v_A C^{(1)}(\theta)]. \quad (21)$$

Elimination of $C^{(1)}(\theta) = S_0 + C_0^{(1)} - S(\theta)$ by Eq. (18) and substitution of Eq. (20) into Eq. (21) yields the packing ratio as a function of dimensionless time θ and the parameters α, β, S_0, $C_0^{(0)}$, and $C_0^{(1)}$.

RESULTS

The computations are quite easy and straightforward. We consider the following parameter values [1]: $d_m = 2.4$(g/ml), $\rho(t=0) = \rho_0 = 1/d_m v_0$, thus $v_0 = 1/d_m \rho_0$. The total volume of the initial amorphous cluster is $V_0 = h\pi R^2 = (87 \text{ cm})\pi(1.88 \text{ cm}/2)^2 = 242$ ml. The mass of all particles, and thus the constant total mass of free grains and clusters during any experiment, is $x_m m_0^{(0)} = \rho_0 d_m V_0 = 337$ g. The particles are glass spheres of radius 1 mm, thus $x_m = d_m(4/3)\pi R^3 = 0.010$ g. We assume the clusters have the maximum packing fraction [11] 0.74, for hexagonal packing of spheres. It follows that $v_A = 1/0.74 d_m = 0.56$.

To define the dimensionless quantities and fit the experimental data, one needs $m_s^{(0)}$, which is the solution to Eqs. (4) and (11) at the steady state value ρ_s. The initial state consists almost entirely of free grains, $m_0^{(0)} = 33\,700$, so $S_0 = 1.94$ for $\Gamma = 4.5$. The clusters are assumed very small in the initial, loosely packed system, $c_0^{(1)} = 0.02 \text{ g} \ll x_m m_0^{(0)}$. These tiny clusters act as seeds (heterogeneous nuclei) for cluster growth. The number of clusters, $c_0^{(0)}$, decreases with aggregation to the final steady state value $c_s^{(0)}$. Mass balances are ensured by the moment equations (15) and (16) and their solutions. The relationships for the final, steady state clusters, $S_s = 1$ and $C_s^{(0)} = \beta/\alpha$, are satisfied automatically by the differential equations.

Figures 1(a)–1(c) show the impact of the three parameters α, β, and $C_0^{(0)}$ on the evolution of density with time. Both the transition time and the final steady state are affected. Decreasing α or increasing β enhances the breakup of clusters and hence raises the curves to earlier times. The initial condition $C_0^{(0)}$ significantly influences the evolution of density. The final condition must obey the mass balance, and thus the initial number of free grains, together with the rate constants, influences the packing fraction.

Linz [9] defined a dimensionless group, the compaction ratio $a(t)$, that conveniently allows comparison with the Knight *et al.* [1] experimental data,

$$a(t) = [\rho(t) - \rho_\infty]/[\rho_0 - \rho_\infty]. \quad (22)$$

The packing fraction $\rho(t)$ is defined by Eq. (7), and its initial ($t=0$) and equilibrium ($t\rightarrow\infty$) values are written with sub-
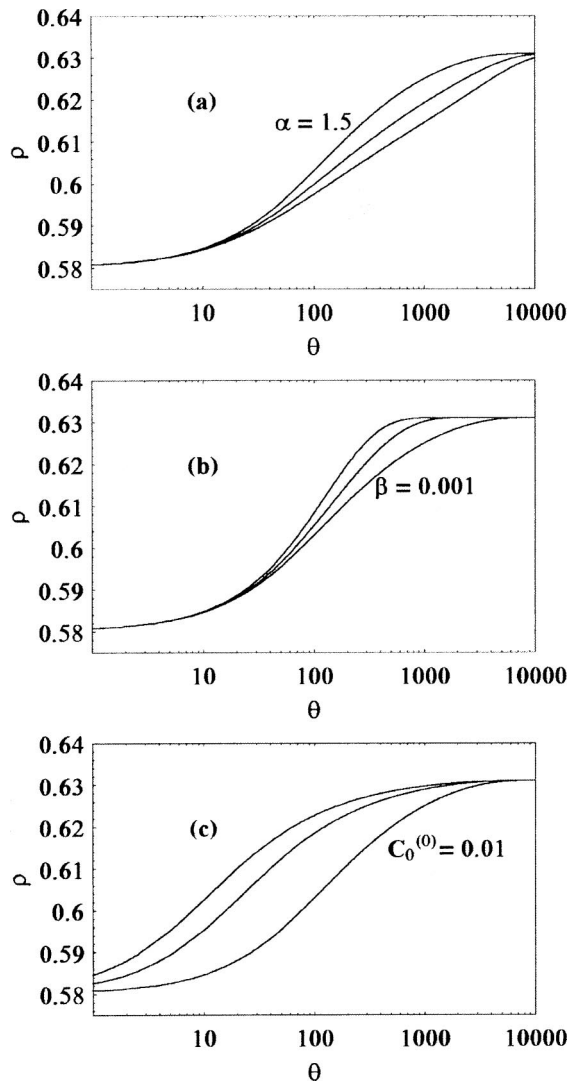
FIG. 1. Effect of (a) $\alpha = 1.5$, 2.5, and 3.5; (b) $\beta = 0.001$, 0.005, and 0.01; and (c) $C_0^{(0)} = 0.01$, 0.05, and 0.1, on the time evolution of the packing fraction ρ. The other parameters are the same as in $\Gamma = 1.8$ in Table I.
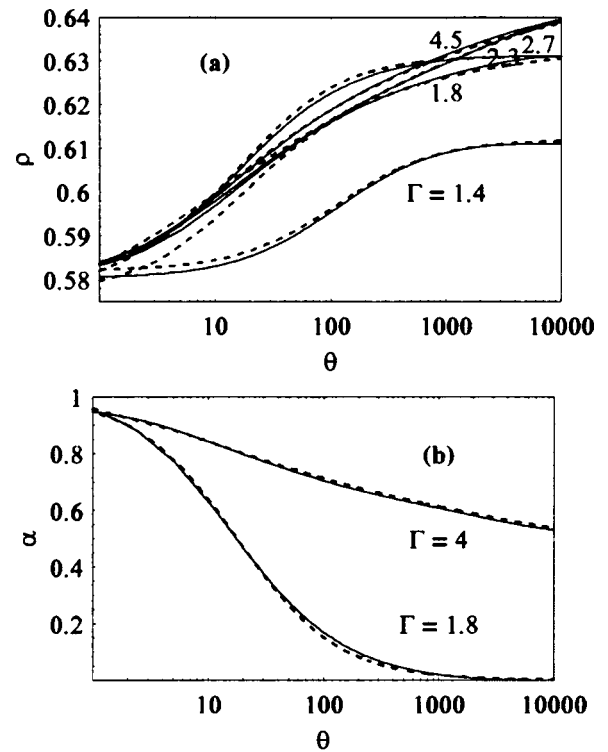

FIG. 2. Comparison of ρ versus time for the model (solid lines) with (a) the experimentally based equations of Knight *et al.* [1] (dotted lines) and (b) of Linz [9] (dotted lines). The parameters used in the model are given in Table I.

scripts 0 and ∞, respectively. Linz derived a difference equation for the compaction process, which yielded a solution that represented the experimental data,

$$a(t) = \{1 + C\nu[\Psi(t + 1 + \nu) - \Psi(1 + \nu)]\}^{-1} \qquad (23)$$

where time has integer values, $t = 0, 1, 2, \ldots, \infty$. The digamma function $\Psi(x)$ is the logarithmic derivative of the gamma function. Linz gave values for the parameters C and ν at two conditions: 10 000 and 0.056 for $\Gamma = 1.8$, and 1.3 and 0.077 for $\Gamma = 4$. The Knight *et al.* [1] empirical equation, expressed in terms of $a(t)$ defined by Eq. (22), is

$$a(t) = [1 + B \ln(1 + t/\tau)]^{-1}. \qquad (24)$$

The two equations (23) and (24) yield results in close agreement. Verifying the current model is particularly convenient by comparison with Eqs. (23) and (24).

First we consider the irreversible density relaxation experiments [1]. Figures 2(a) and 2(b) show the fit of the

present model with the experimental data [1] for five accelerations ($\Gamma = 1.4$, 1.8, 2.3, 2.7, and 4.5). Parameter values are recorded in Table I. The computations show that if $\beta = 0.001$ is fixed, the fitted value of α varies between 1.0 and 3.4. Figure 2(a) is a comparison with Eqs. (22) and (24), and Fig. 2(b) is a comparison with Eq. (23) for the two data sets presented by Linz [9]. For $\Gamma = 1.4$, 1.8, and 2.3, steady state values of density are reached within 10 000 taps. For the more intense vibrations, $\Gamma = 2.7$ and 4.5, ρ was still climbing slightly at 10 000 taps. Good agreement was found for the comparison of model and data with values of α that increased from 1.1 to 3.4, as shown in Table I. The increasing values of α indicate the greater agitation of the more forceful taps. The extreme condition of severe cluster disruption (liquefaction or fluidization) would cause the grains to end up in a low-density amorphous state, much like the initial condition for the described experiments. The number of clusters, $c_0^{(0)}$, starts out at the assumed value 1500, and decreases with aggregation to the final steady state value $c_s^{(0)}$, which is of order of magnitude 10. Fitted values of $c_0^{(0)}$ were 1500 except at $\Gamma = 1.4$, where $c_0^{(0)} = 260$ was required for a satisfactory agreement with data. The reason for the anomalous value for the initial cluster number at $\Gamma = 1.4$ is unclear, but may be due to a decreased formation of nuclei (cluster seeds) at the weaker tapping intensity. As Γ increases, the steady state number of free grains, $m_s^{(0)}$, decreases, and thus S_0 increases. Correspondingly, the steady state number of clusters $c_s^{(0)}$ decreases and their mass $c_s^{(1)}$ increases such that the average cluster mass increases. The model thus is a realistic

TABLE I. Parameters for Knight *et al.* [1] experimental data with $\beta = 0.001$. The initial cluster mass $c_0^{(1)}$ is constant for all runs at 0.020 g.

Γ	ρ_s	$10^{-4} m_s^{(0)}$	S_0	α	$C_0^{(0)}$	$c_0^{(0)}$	$10^5 C_0^{(1)}$	$10^5 C_s^{(0)}$	$c_s^{(0)}$	$C_s^{(1)}$	$c_s^{(1)}$ (g)
1.4	0.611	2.60	1.29	1.1	0.01	260	7.80	90.9	23.6	0.296	142
1.8	0.631	2.14	1.57	1.2	0.07	1500	9.30	83.3	17.8	0.575	140
2.3	0.631	2.14	1.57	2.25	0.07	1500	9.30	44.4	9.51	0.575	123
2.7	0.639	1.96	1.71	2.8	0.076	1500	10.0	35.7	7.01	0.716	123
4.5	0.640	1.94	1.73	3.4	0.077	1500	10.3	29.4	5.71	0.736	76.9

representation of the irreversible experiments [1].

Nowak *et al.* [2] presented data for both irreversible and reversible transitions during granular compaction. As discussed earlier, the compaction process is slow, approaching the steady state logarithmically with time. In the experiments [2], after a steady state is reached within 10 000 taps, the acceleration Γ is increased and a new steady state is achieved. At a critical value $\Gamma^* \approx 3.3$, subsequent increases and decreases of Γ led to reversible transitions between steady states. To simulate these experimental data, values for α and β were taken from Table I so that the transition would occur within 10 000 taps. Given the experimental steady state density ρ_s, and knowing $c_s^{(1)}$ by the mass balance [Eq (11)] one calculates $m_s^{(0)}$ by Eq. (4). The ratio of rate constants, α/β, gives $C_s^{(0)}$ and hence $c_s^{(0)}$. The values of $m_s^{(0)}$, $c_s^{(0)}$, and $c_s^{(1)}$ become $m_s^{(0)}$, $c_0^{(0)}$, and $c_0^{(1)}$ for the succeeding computation. If $S_0 < 1$ then the density ρ decreases, analogously to crystal dissolution in an undersaturated condition. Figure 3 shows the simulation of the data [2] for irreversible and reversible transitions. The parameters used in the model are given in Table II. For the model, the variation of $C_s^{(0)}$ and $C_s^{(1)}$ with Γ mirrors the variation of the steady state value of density ρ_s with Γ from the experiments (Fig. 3). The analogy with the crystal growth phase transition [6(a)–6(d)] from a supersaturated solution is helpful in understanding granular

FIG. 3. The steady state values of experimental packing fraction ρ [2] (solid lines) and computed reduced cluster mass $C_s^{(1)}$ (dashed lines) at different accelerations Γ showing reversible and irreversible behavior. The parameters used in the model are given in Table II.

compaction, albeit imperfect given the absence of crystal surface (Gibbs-Thomson) energy [6(f)]. When the supersaturation S is greater than 1.0, crystals will irreversibly grow from seeds (heterogeneous nuclei). Crystal growth in a supersaturated solution or dissolution in an undersaturated solution proceeds irreversibly to equilibrium. For granular compaction, after Γ has reached the critical acceleration Γ^*, the clusters grow or shrink, respectively, if S is greater than or less than unity. Thus, according to the cluster hypothesis, the history effect and the reversible/irreversible behavior are explained by clusters growing irreversibly to a critical size, from which size they can then reversibly grow or reduce.

CONCLUSION

Our approach is consistent with the concept [3] that vibrational relaxation of a powder is a combination of independent-particle and collective excitations. According to the present view, the excitations are dynamic processes of single particles and of clusters. Free particles interact with the clusters by association and dissociation rate parameters representing, respectively, cluster growth and dissolution, k_g and k_d. The clusters may fragment or coalesce through rate parameters for cluster breakup and aggregation, k_b and k_a. The kinetics of the cluster size distribution $c(x,t)$, are expressed as a population dynamics equation. The model is thus statistical, with the rate coefficients accounting for the details of particle interactions in an overall average manner. In agreement with Barker and Mehta [3], the behavior is only weakly affected by details of particulate shape and surface and is to a far greater extent dependent on cluster packing behavior. Unlike the Monte Carlo simulation [3], however, the current approach yields uncomplicated differential equations for the moments (average properties) of the cluster size distributions. The extension of the model to describe measured density fluctuations in vibrated granular materials was not attempted here.

The model suggests that granular compaction is similar to a liquid-solid phase transition (here with surface energy effects neglected). Free particles are analogous to a liquid phase and clusters to the crystalline phase. The desirability of explaining granular flow behavior based on a system of differential equations has been discussed [19]. We have attempted to meet this condition by demonstrating that a cluster kinetics approach yields differential equations for the moments of the cluster size distribution and free particle con-
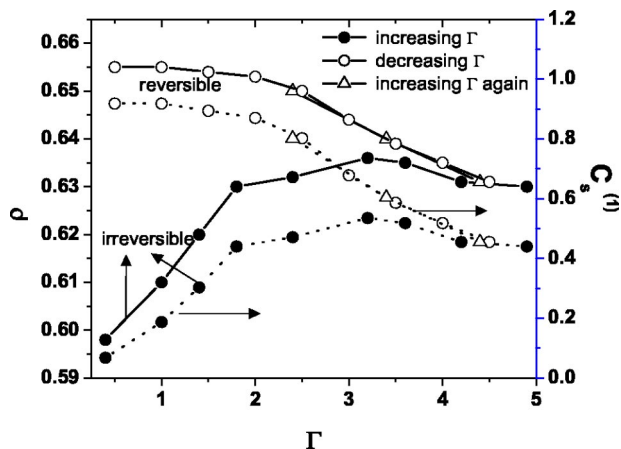
TABLE II. Parameters for modeling the experimental data of Nowak *et al.* [2].

Γ	ρ_s	$10^{-4}m_0^{(0)}$	$10^{-4}m_s^{(0)}$	S_0	α	$c_0^{(0)}$	$10^4C_0^{(0)}$	$c_0^{(1)}$ (g)	$C_0^{(1)}$	$c_s^{(0)}$	$10^4C_s^{(0)}$	$c_s^{(1)}$ (g)	$C_s^{(1)}$
0.4	0.598	3.37	3.16	1.07	1.0	31.6	10.0	31.6	0.001	31.6	10.0	21.3	0.068
1.0	0.610	3.16	2.84	1.11	1.1	31.6	11.1	21.3	0.075	25.8	9.09	53.0	0.187
1.4	0.620	2.84	2.59	1.10	1.1	25.8	9.98	53.0	0.205	23.5	9.09	78.4	0.303
1.8	0.630	2.59	2.34	1.11	1.2	23.5	10.0	78.4	0.335	19.5	8.33	103	0.440
2.4	0.632	2.34	2.29	1.02	1.2	19.5	8.51	103	0.450	19.1	8.33	108	0.471
3.2	0.636	2.29	2.20	1.04	1.2	19.1	8.70	108	0.491	18.3	8.33	117	0.535
3.6	0.635	2.20	2.22	0.99	1.2	18.3	8.24	117	0.529	18.5	8.33	115	0.518
4.2	0.631	2.22	2.32	0.96	1.2	18.5	7.99	115	0.497	19.3	8.33	106	0.455
4.9	0.630	2.32	2.34	0.99	1.2	19.3	8.25	106	0.451	19.5	8.33	103	0.440
4.5	0.631	2.34	2.32	1.01	1.2	19.5	8.42	103	0.445	19.3	8.33	106	0.455
4.0	0.635	2.32	2.22	1.04	1.2	19.3	8.69	106	0.475	18.5	8.33	115	0.518
3.5	0.639	2.22	2.12	1.04	1.2	18.5	8.71	115	0.541	17.7	8.33	125	0.586
3.0	0.644	2.12	2.01	1.06	1.2	17.7	8.82	125	0.620	16.7	8.33	136	0.678
2.5	0.650	2.01	1.87	1.07	1.2	16.7	8.95	136	0.728	15.6	8.33	150	0.802
2.0	0.653	1.87	1.80	1.04	1.2	15.6	8.65	150	0.832	15.0	8.33	157	0.870
1.5	0.654	1.80	1.78	1.01	1.2	15.0	8.44	157	0.881	14.8	8.33	159	0.894
1.0	0.655	1.78	1.76	1.01	1.1	14.8	8.44	159	0.905	16.0	9.09	161	0.918
0.5	0.655	1.76	1.76	1.00	1.1	16.0	9.09	161	0.918	16.0	9.09	161	0.918
2.4	0.650	1.76	1.87	0.94	1.2	16.0	8.54	161	0.862	15.6	8.33	150	0.802
3.4	0.640	1.87	2.10	0.89	1.2	15.6	7.42	150	0.714	17.5	8.33	127	0.604
4.4	0.631	2.10	2.32	0.91	1.2	17.5	7.56	127	0.548	19.3	8.33	106	0.455

centration that finally arrive suitably at a steady state end point and yet have a dependence on past history, i.e., a prior state. Since Maxwell's comment that the past state of a granular system would influence its dynamics (reported by Gudehus [20]), the effect of system history or "memory" has been a concern. Our proposal is that the number and size of dense clusters, through their evolution to equilibrium, indeed affects the time dependence during compaction. Starting from a low density with very small seed clusters, the clusters grow irreversibly to their steady state size and number. Changing to a new vibrational intensity allows a reversible transition to a new cluster steady state. By the differential equations for the cluster size distribution moments, the evolving state can be established at any time after an initial time if the rate coefficients are known. Any state after $t=0$ could be chosen as an initial condition and the subsequent states on the way to steady state will be determined uniquely by the governing equations and parameter values.

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