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Phase coexistence in fluidization

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ABSTACT

The coexistence of granular liquid-like phase (cluster) and gas-like phase (void) in fluidization, a spontaneous symmetry-breaking dissipative state, contributes to excellent mixing behavior in multi-phase reactors. In present study, a universal granular state equation to describe phase coexistence far from critical point is developed, where both the inelastic solid-collision and asymmetrical instability is taken into consideration. Catastrophe theory is applied to find the stable boundary of phase coexistence, and verified by cold-flow experiment with different solid pressure. A phase diagram, based on both theoretical analysis and experimental study, is given as a useful guideline of design and operation of efficient multi-phase reactors.

SIGNIFICANCE

A simple but universal granular state equation, verified by a cold-flow experiment, is developed to describe phase coexistence of granular liquid-like phase (cluster) and gas-like phase (void) in fluidization. Based on nonlinear stability analysis, a phase diagram is provided to find the boundary between homogeneous state and phase coexistence, as a useful guideline of design and operation of efficient multi-phase reactors.

[Graphic Abstract is here]

INTRODUCTION

Granular system, a fundamental idealization of far-from-equilibrium dissipative state, can display three phase similar with molecular media, *i.e.*, solid-like, liquid-like and gas-like phase, classified by different granular volume fraction[1,2]. In gas-solid fluidization, inelastic dissipation from the interparticle collision should be compensated by extra energy input continuously, approaching to static equilibrium[3]. Generally, homogenous state becomes unstable with respect to small density perturbations, that is a granular liquid-like phase (called "cluster") coexistence with granular gas-like phase (called "void")[4,5]. The effective void-cluster interaction plays a key role in the performance of multi-phase reactors, such as excellent fluidity and mixing capability[6-8]. Therefore, the mechanism and stability analysis of phase coexistence in fluidization is required to be carefully investigated.

In statistical physics, gas-liquid coexistence phenomenon can be well described by the classical van der Waals equation when molecular volume and correction of van der Waals attraction is taken into consideration[1]. Similarly, granular matters also exhibit a plethora of spontaneous symmetry-breaking instabilities[9,10]. Both granular hydrodynamics and direct molecular-dynamics simulations[11-13] show that the granular phase coexistence close to the critical point is strikingly similar to the spinodal decomposition of molecular gas-liquid transition. However, both theorical analysis and experiment for phase coexistence in dense fluidization, as an intrinsically system far from critical point, are few. In mathematics, phase coexistence is a typical multiple-roots problem, where the freedom of variables is more than constraints[14-16]. In this case, the homogenous solution is non-unique and cluster and void is represented by another attractive fixed point, respectively. The discussion of phase coexistence in fluidization can be reduced into the stability analysis of multiple roots[17]. As is well known, the catastrophe theory, first proposed by Thom[18], is one of the most appreciated stability analysis of nonlinear processes. Hence, it is a suitable option to capture characteristics of the nonlinear instability, and its simplicity allows for a detailed analytic study of granular phase coexistence.

In present study, the coexistence of cluster and void in gas solids fluidization is investigated by both modeling and experimental study. After introduce solid pressure (p_s), number density (n_s) and temperature (Θ_s), a universal granular state equation is developed where both inelastic particle-particle collision and asymmetric instability are taken into consideration, and catastrophe theory is applied to find the boundary of stable phase coexistence. A cold-flow experiment using Geldart's A particles with 1 to 10 bar pressure is given to verify the granular state equation, where the solid-volume fraction (ε_s) and solid pressure (p_s) is obtained by a dual optical probe and special pressure transducer, respectively. A phase diagram of coexistence between voids and cluster, verified by experimental study, is provided as a useful guideline of operation and design of multi-phase reactors.

MODELING & STABILITY ANALYSIS

Modeling

In gas-solid fluidization, energy input via gas stream from the distributor balances the dissipation from interparticle collisions, so the system reaches a steady state[3,11-13]. Assume the kinetic energy dissipation caused by inelastic collisions will convert to internal energy $I(\mathbf{r}_{jk})$, which are related to the position of particles $\mathbf{r}_i$. Therefore, the partition function of solids, Z_s, is given by

$$Z_s = \frac{1}{N_s!}\frac{1}{(2\pi\hbar)^{3N_s}}\left[\int\prod_i \mathrm{d}^3\,\mathbf{p}_{s,i}e^{-\beta\mathbf{p}_{s,i}^2/2m_s}\right]\left[\int\prod_i \mathrm{d}^3\,\mathbf{r}_i e^{-\beta\left(\sum_{j<k} I(\mathbf{r}_{jk})\right)}\right] \tag{1}$$

The first integral term on the right of Eq.(1) is kinetic energy which has a similar format of molecular system and the second term is dissipation from particle-particle interaction. In order to obtain integral calculation, the Mayer function g_{jk} is defined as

$$g_{jk} = g(\mathbf{r}_{jk}) = \exp[-\beta I(\mathbf{r}_{jk})] - 1 \tag{2}$$

In the dense fluidization, it is reasonable to neglect quadratic terms in Mayer function where interaction between only two adjacent particles is taken into account. Consider a granular medium that begins in homogenous state with Maxwellian distribution of velocities. The dissipation from inelastic particle collisions results in deviation from initial state, including (i) a reduction in the relative velocity of particles, accounted by a coefficient of restitution (e), and (ii) deviation from Maxwellian distribution of velocities, described by radial distribution function G[19,20]:

$$G = \left[1 - \left(\frac{\varepsilon_s}{\varepsilon_{s\max}}\right)^{\frac{1}{3}}\right]^{-1} \tag{3}$$

where $\varepsilon_{s\max}$ is maximum solid-volume fraction which corresponds to “packed-state” of particles ($\varepsilon_{s\max} = 0.636$)[20].

Here, we define solid temperature Θ_s, like in molecular fluids, to be proportional to the kinetic energy per particle. The partition function Z_s can be expressed as a convenient form of free energy F_s based on thermodynamics law[1]:

$$p_s = -\frac{\partial F_s}{\partial V} = \frac{k_B \Theta_s}{V - b} - \frac{a}{V^2} \tag{4}$$

where

$$a = 8(1-e^2)Gr_0^3 \frac{(k_B\Theta_s)^{3/2}}{\pi^{3/2} m_s^{1/2}}$$
$$b = \frac{2}{3}\pi r_0^3 \tag{5}$$

Obviously, the constant of a and b represent to the inelastic dissipation and the particle volume, respectively. After the introduction of solid number density n_s, the Eq. (4) can be rewritten as a granular state equation, *i.e.*, the relationship among solid number density n_s, solid pressure p_s and temperature Θ_s:

$$\left(p_s + a n_s^2\right)\left(\frac{1}{n_s} - b\right) = k_B \Theta_s \tag{6}$$

When there is no inelastic collision (e = 1) and particle volume can be neglected (r_0 =0), the granular state equation will be reduced to the form of ideal-like state equation, where no phase coexistence will occur.

Stability analysis

The hydrostatic problem of phase coexistence in fluidization can be fully described by two parameters: a and b, and the nonlinear characteristics of granular state equation in three-dimensional space belongs to cusp-type catastrophe. Therefore, the critical point from phase coexistence to homogeneous state is determined by the following two conditions:

$$\left(\frac{\partial p_s}{\partial n_s}\right)_{\Theta_s} = 0 \tag{7}$$

$$\left(\frac{\partial^2 p_s}{\partial n_s^2}\right)_{\Theta_s} = 0$$

In this case, those two governing parameters (*a* and *b*) can be well expressed with respect of variables in the critical state:

$$a = \frac{27}{64}\frac{k_B \Theta_{sc}}{p_{sc}}$$

$$b = \frac{k_B \Theta_{sc}}{8 p_{sc}} \tag{8}$$

where Θ_{sc}, and p_{sc} is the solid temperature and pressure at the critical point. Therefore, the Eq. (6) can be re-written as the following dimensionless universal granular state equation

$$(p_s^* + 3n_s^{*2})\left(\frac{3}{n_s^*} - 1\right) = 8\Theta_s^* \tag{9}$$

where

$$p_s^* = \frac{p_s}{p_{sc}},\quad n_s^* = \frac{n_s}{n_{sc}},\quad \Theta_s^* = \frac{\Theta_s}{\Theta_{sc}} \tag{10}$$

[Figure 1 is here]

For a certain gas solids fluidization, the coefficients will depend on the boundary and granular characteristics. Nevertheless, a precise knowledge of those values is not necessary to deduce the cusp-type normal form. Here, we construct the nonlinear surface of solid pressure as illustrated in Figure 1(a), where the x- and y-axe is p^*_s and Θ^*_s, respectively. On this topological surface, with the decrease of solid pressure, the granular system may change from homogeneous state to phase coexistence, passing by folding section. As shown in the Figure

1(b), when $p_s > p_{sc}$, fluidization prevails at homogeneous state (only one root) where the contribution from inelastic collision is suppressed due to limited space. The granular system evolves thereafter with the decrease in granular pressure until phase coexistence, where $p_s < p_{sc}$. Importantly, there are three roots of nonlinear granular state equation, which is called as *multiple steady state*, implying non-uniqueness of the steady-state solutions of Eq. (9), and it paves the way to symmetry-breaking state.

A simple but universal state equation, after scaling the variables, yields the cusp-type normal form, and the catastrophe theory allows us to understand the physical mechanism of phase coexistence.

EXPERIMENTAL & MEASUREMENT

Experiment unit

In order to verify our theoretical analysis of granular state equation, a cold-flow experiment is carried out in a fluidized bed as shown in Figure 2(a), which consists of a stainless-steel column (800 mm in height and 100 mm in diameter) and an internal filter on the top to continuously return entrained particles to the solids bed. A plate distributor (fractional free area is 0.2%) is used to ensure gas solids uniformity at the wide range of gas velocity from 0.051 to 0.136 m/s. The fluidized bed is operated at ambient temperature and the operating pressure ranged from 1 to 10 bar. Four axial positions: 0, 150, 300, and 450mm above the distributor are located to measure both local solid pressure (p_s) and solid-volume fraction (ε_s). The solids is industrial FCC catalyst with a particle density of 1400 kg/m^3 and a Sauter mean diameter of 75 μm.

[Figure 2 is here]

Measurement of solid pressure

The solid pressure (p_s) is measured using a differential pressure transducer made by FLOTU, which is capable of resolving the solid pressure independently of gas pressure. As shown in the Figure 2(b), the front of diaphragm experiences both gas and solid pressure. Since a small passage with mesh admits gas but no solids, the back of diaphragm experiences only gas pressure. Thus, the net deflection of the diaphragm reflects the solid pressure[20]. Figure 2(b) indicates that the solid pressure (p_s) non-linearly increases with total operating pressure (p_o) in the range of measurement.

Measurement of solid-volume fraction

A dual-optical density probe made by FLOTU is used to obtain the transient signals of solid-volume fraction (ε_s) in the fluidized bed. The front tip of probe is 2×2 mm^2 ensuring that the measurements reasonably represent the passing solids without causing much disturbance. Because of the nonlinear relationship between the output signal and the solid-volume fraction, a reliable calibration is required as shown in the Figure 2(c). The measurement frequency is 200 Hz with 120 s sampling time after the fluidized bed reaches steady-state condition. The details of calibration can be referred in our recent work[8].

RESULTS & DISCUSSION

The effect of solid pressure on phase co-existence

Figure 3(a) illustrates the transient signals of solid-volume fraction under different operating pressure. In the 1 bar operating pressure, the transient signals of solid-volume fraction contain evidence of phase coexistence: the signals mainly reside at a high value, indicating the cluster phase dominates the flow, but a small amount of steep decrease of signals can be observed as well implying voids are passing by the front of optical probe. In comparison, there is nearly no signal fluctuations in the homogeneous state when the operating pressure is to 10 bar. It reflects that fluidization prevails at homogeneous state, where only one ordered granular liquid-like structure occurs.

[Figure 3 is here]

The normalized probability distribution function (PDF) curve of solid-volume fraction signals is shown as the Figure 3(b) under operating pressure of 1 and 10 bar, respectively. The bimodal distribution for normalized PDF at 1 bar operating pressure is consistent with the previous findings[4,7]. The first peak locates low solid-volume fraction with a long tail, indicating that voids are characterized by dispersed gaseous phase with low solids fraction. And the second peak is characterized with much higher solid-volume fraction and a roughly self-symmetrical shape, indicating that clusters are characterized by a continuous dense solid density. In the homogeneous state (10 bar operating pressure), however, the statistical law of the transient signal is totally different from that of the phase coexistence state. There is just one peak in the normalized PDF curve and its peak broadening is significantly suppressed, illustrating that no phase coexistence occurs and fluidization under such high operating pressure gain a special ordered uniformity.

Negative compressibility in granular media

As shown in the Figure 4(a), as operating pressure increases from 1 to 10 bar, both cluster (continuous phase with high solid-volume fraction) and void (dispersed phase with small solid-volume fraction) approaches towards to the same point. According to the stability analysis, this point (7 bar) is the boundary between homogeneous state and phase coexistence, and the critical solid pressure (p_{sc}) can be obtained here. In the case of high operating pressure (> 7 bar), there is just one self-symmetrical peak in the normalized PDF curve, a homogenous state characterized by a uniform distribution of solid-volume fractions. The phase coexistence, which normalized probability density function has two peaks located at positions of dense and dilute section respectively, is observed in the condition of low operating pressure (< 7 bar). Here, it is noted that negative compressibility phenomenon occurs in granular media: the peak of cluster phase decreases from 0.54 to 0.42 as the operating pressure (p_o) increases from 5 to 7 bar. Since cluster phase dominates gas-solid multiphase flow, negative compressibility phenomenon, *i.e.*, the solid density (ρ_s) decreases with the increasing of solid pressure (p_s), is detected. Generally, it is difficult to measure negative compressibility phenomenon in molecular system due to its instability. While, the obvious and stable state with negative compressibility in the granular media provides a useful idealization of metastable state, contributing to a deep understanding of phase transition in dissipative system.

[Figure 4 is here]

Phase diagram

Here, 1×10^9 numbers of particles with diameter of 75 μm are chosen to calculate the granular free energy F_s. Here, the coefficient of restitution (e) is 0.995[20] and the critical solid pressure (p_c) is 250 Pa measured by the experiments. In this case, the critical solid temperature can be calculated as $k_B\Theta_{sc}/m_s$=1.04 (m/s)^2. Figure 4(b) illustrates a phase diagram in granular system based on Eq.(6). Graphically, the red solid curve in the Figure 4(b) passing through the co-existence points of the isotherms constructs the binodal curve (also called coexistence curve). The binodal curve can be obtained using method of Maxwell's construction, where the chemical potential of voids and clusters should be equal. In mathematics, the binodal line originates from the section which is nonlinearly unstable although linearly stable. The bule dot curve in Figure 4(b) passing through the inflexion points of the isotherms constructs the spinodal curve. A negative compressibility implies mathematically that, within the spinodal region, the state is unstable with respect to small amplitude long-wavelength perturbations[11-13]. Those two branches (binodal and spinodal curve) in the (p_s, ε_s) plane merge into one point, which is the critical point (p_{sc}, ε_{sc}) between homogenous state and phase coexistence. Close to the critical point, the Maxwell's construction is well proved in previous studies[12,13]. With significant inelastic energy loss, *i.e.* far from critical point, stability analysis based on catastrophe theory can predict unsymmetrical ratio of the spinodal and binodal lines, in disagreement with what the normal van der Waals equation predicts. Hence, qualitative and quantitative agreement is observed between the granular state equation and experimental study, even in the state far from critical point. It provides a novel version to understand abundant characteristics in granular media such as gas-solid bifurcation[9] and hysteresis[10].

CONCLUSION

In present study, phase coexistence of void and cluster in fluidization is investigated through both theoretical analysis and experimental study. The conclusion is as follows:

1. A granular state equation is developed to describe phase coexistence in the state of far-from critical point where both inelastic collision and asymmetric instability are taken into consideration.

2. The phase coexistence is reduced to stability analysis of multiple roots where the catastrophe is applied to calculate the critical point.

3. A cold-flow experiment is carried out to verify theoretical analysis and negative compressibility in granular media is detected.

4. By identifying the mechanism responsible for phase coexistence, a phase diagram of dense fluidization is obtained.

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NOTATION

Roman letters

a = constant of granular state equation (-)

b = constant of granular state equation (-)

e = coefficient of restitution (-)

F_s = free energy of solids (J)

$g(\mathbf{r}_{jk})$ = Mayer function (-)

G = radial distribution function (-)

$I\,(\mathbf{r}_{jk})$= internal energy (J)

k_B = Boltzmann constant (J/K)

m_s = mass of solids (kg)

n_s = solid number density (-)

n_{sc} = critical solid number density (-)

N_s = the number of particles (-)

$\mathbf{p}_{\mathbf{s},i}$ =the momentum of the i particle (kg·m/s)

p_s = solid pressure (Pa)

p_{sc} = critical solid pressure (Pa)

p_o = operating pressure (bar)

$\mathbf{r}$ = position of particle (-)

r_0 = radius of particle (m)

V = volume (m^3)

Z_s = partition function of solids (-)

Greek letters

ρ_s = density of solids (kg/m^3)

ε_s = solid-volume fraction (-)

ε_{smax} = maximum solid-volume fraction (-)

Θ_s = solid temperature (K)

Θ_{sc} = critical solid temperature (K)

Superscripts

* = dimensionless value

Abbreviations

FLOTU = Fluidization Laboratory of Tsinghua University

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