EXPERIMENTAL INVESTIGATION OF SOLID-LIQUID PHASE CHANGE IN VIBRATED GRANULAR MEDIA AND COMPARISON WITH THEORETICALLY PREDICTED PHASE CHANGE IN HARD SPHERE SYSTEMS

by

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ABSTRACT

KAPIL GAUR. Experimental investigation of solid-liquid phase change in vibrated granular media and comparison with theoretically predicted phase change in hard sphere systems (Under the direction of DR. RUSSELL KEANINI)

Hard sphere systems, for years, have been studied through computer simulations. In the 1950s the work on modern computing was on the rise and computers were being researched for use in every field. Statistical Mechanics was no alien to this and thus came the Monte Carlo and Molecular Dynamics simulation algorithm. The system of hard spheres was one of first Statistical Mechanics problem to be studied using these algorithms. Since then a lot of work has been put in to the computer simulation algorithms and there are much more advance computational methods for calculating these complex problems. Outside of these simulation methods the system of hard spheres have only been studied by using colloidal solutions.

There has, however, almost no work been done to study the system of hard sphere experimentally and gather theoretical data. The main aim here is to use a vibratory polishing machine and gather the PIV (Particle Image Velocimetry) data for the grain motion. Then use the pixel intensity values and the grain velocities to calculate the packing fraction and dimensionless pressure for precisely chosen interrogation areas and use those values to come up with a phase diagram.

The solid liquid phase change diagram has been predicted for hard sphere systems using computer simulation methods to show the effects of increasing pressure and packing fraction of the molecules on the phase change of the material and that is being replicated here experimentally using large granular media to see if it is possible.

DEDICATION

I dedicate this thesis research to my parents and my friends who believed in me.

I also dedicate this thesis research to my sister, Mandakini Gaur who has been a huge motivating factor in my life.

ACKNOWLEDGEMENTS

I would like to thank my advisor Dr. Russell Keanini for presenting me with this amazing research opportunity and having faith in me throughout the whole process. His years of experience and knowledge he has amassed over time proved to be an invaluable asset.

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1.1 Organization of Thesis

Chapter 1 explains the motivation behind choosing this particular topic for research and a brief description of particle simulations and density calculations using PIV.

Chapter 2 describes procedure and calculations done to achieve the results.

Chapter 3 explains the results and conclusions derived from them. It also gives a brief idea of future work that can be done using this as a basis.

1.2 Motivation

Single particle dynamics such as hydrodynamic organization of sub- and near-collision time scale dynamics and near-collision-time scale generalized Langevin dynamics were made accessible through MD simulations. In experiments carried out by R.G. Keanini, Peter Tkacik et al. [1] it is shown that piles of confined, high-restitution grains, subject to low amplitude vibration, can serve as analogs for studying the molecular hydrodynamics of atomic liquids and dense gases. Particle Image Velocimetry (PIV) measurements of short, medium and long-time scale single particle dynamics and long-time scale collective grain hydrodynamics in conjunction with macroscale versions of classical microscale models is used to support the argument that vibrated grain systems can indeed be used as analogs for studying the properties of atomic liquids and dense gases. The same PIV data has been used for this thesis as well to study the solid-liquid phase change in vibrated granular media. The results are compared with the theoretically suggested phase diagram for hard spheres obtained through MC/MD simulation [2]. The experimental setup has been explained in detail in [3], is shown in the Figure 1.1 [1].

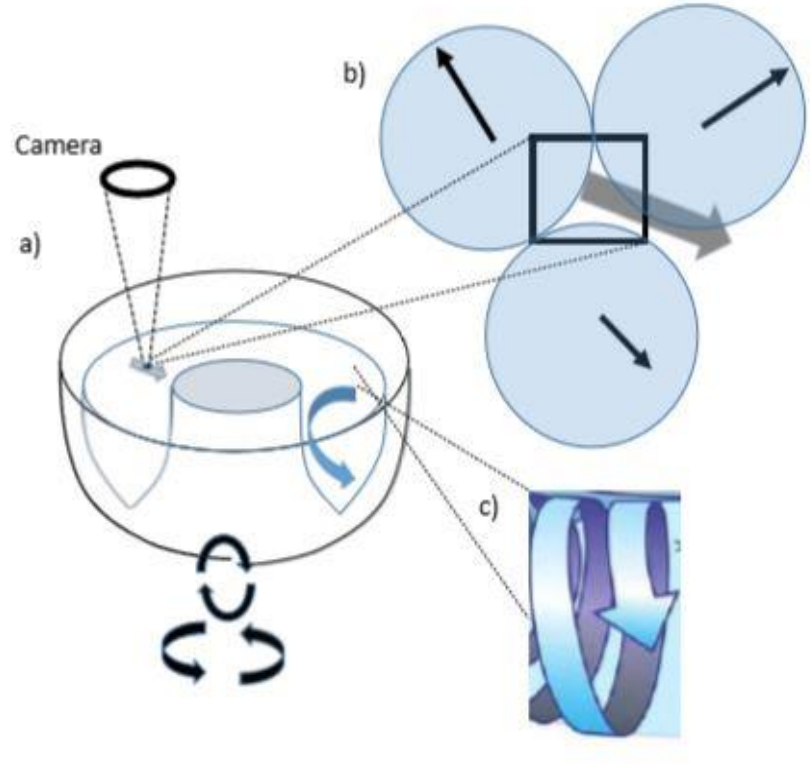


Figure 1.1: Experimental measurement of grain dynamics. a, Grain piles confined to a commercial vibrational finishing bowl undergo three simultaneous modes of single-frequency (29.3 Hz) vibration. Local (interrogation area = variable) and large field-of-view (LFOV, 150 mm X 200 mm) images of grain motion are captured at 500 frames/s at the surface of the vibrating pile; corresponding two-dimensional local and LFOV velocities are determined via PIV. b, The eight grains tested have characteristic dimensions ranging from approximately 10 to 35 mm. Local PIV interrogation area shown as a bold square; local time-average grain (fluid) velocity, v, shown in grey, and local instantaneous random (peculiar) grain velocities relative to v shown in black. c, Time-average grain flows are, for all grains tested, helical. [1]

1.3 Overview of Particle Simulations

1.3.1 Introduction

The use of computer simulations in the field of science began with invention of digital computing. While talking about the development of computer simulation methods a few names stand above others given their contribution to the field. People like von Neumann, Metropolis, Teller, Ulam have huge contributions towards the development of this field in science. Computer simulations do not have a single approach for solving problems. There can be multiple suitable approach for solving same type of problem given what kind of physical properties are being assessed. There are a few benefits of computer simulations such as:

- Validation of theoretical approximations for specific models.
- Giving a clear visualization of complex molecular phenomena.
- Model systems, that can't exist naturally, can be created to give a better understanding of ideal nature of materials.

In this specific thesis, a computationally simulated model is being used as a tool to get the best theoretical approximation. It can be termed as a reverse engineering process as well since usually experimental results are generated first and then perfected using computer simulations. Computer simulations are used for both equilibrium as well as non-equilibrium processes. General plan is to choose a sequence of microstates from equilibrium ensemble of the model through different means available. For example, in Monte Carlo simulation might use the random walk principle while MD simulations will use Newton's equation of motion to achieve the same. Both method, however, serve as excellent examples of a very important statistical and computational physics' technique, importance sampling. Assume that q represents a microstate in a given system where A(q) is a thermodynamic property which is a function of q. In MC simulation q might represent just the position of a particle whereas in MD simulation it will represent both position and momentum. The thermodynamic variable can be potential energy, pair correlation function etc. The simulation primarily focuses on getting the microstates to evolve from a large enough subset of microstates from the equilibrium ensemble so that the average of the thermodynamic variable will approach equilibrium. Thus, it is important to choose large enough number of iterations to give the desired results. Since the simulation can provide us with a finite number of microstates it is important to account for the uncertainty of results. The equilibrium average of the variable A is given by:

$$\langle A \rangle = \langle A \rangle_M \pm \sigma_M$$

The derivation of this equation is given in the appendix. A detail explanation for both MC and MD simulation is given in the next sections.

1.3.2 Monte Carlo Simulation

Monte Carlo simulation give a sample of microstates(q) from equilibrium probability distribution using pseudorandom generators [2]. The program rather than choosing configurations randomly and weighing them with exp (-E/ kT) chooses configuration with a probability of exp (-E/ kT) and weigh them evenly [4]. If the system is able to achieve this then the thermodynamic average can be calculated as simple average as given in the derivation in appendix.

$$P_{\mathrm{eq}}(q) = \frac{\exp(-\beta E(q))}{\sum_{q'} \exp[-\beta E(q')]}.$$

Randomly selected microstates q, that approach equilibrium distribution, are selected from a set of all microstates. Let us assume an initial distribution of probabilities P(q,0) for a canonical ensemble which evolves according to discrete stochastic rate equation: [2]

$$P(q,t+1) = P(q,t) + \sum_{q'} P(q',t) W(q' \to q) - P(q,t) \sum_{q'} W(q \to q'),$$

Where W(q→q') is the rate of transition from one state to another. If this rate of transition obeys the balance condition and the stochastic rate equation can determine that the process of going from one microstate to any other microstate can be completed in a finite number of steps then the probability distribution will reach equilibrium.

$$\sum_{q'} P_{\mathrm{eq}}(q') W(q' \to q) = P_{\mathrm{eq}}(q) \sum_{q'} W(q \to q'),$$

$$\lim_{t \to \infty} P(q,t) = P_{\mathrm{eq}}(q).$$

Since the ratio of $P_{eq}(q')$/ $P_{eq}(q)$ depends only on the energy difference of two microstates $\Delta E = E(q') - E(q)$. The rate of transition for going from one state to next and then from that following state back to the initial state can be related as: [2]

$$W(q \to q') = \exp(-\beta \Delta E)\, W(q' \to q).$$

This whole process verifies that the microstates obtained from this stochastic process is the same as selecting the states by random walk method. The whole process does not depend on the starting configuration.

A variation of this Metropolis Monte Carlo Algorithm uses pseudo-random number generator that returns pseudorandom numbers [2]. As mentioned earlier it uses a computer program that uses pseudorandom number generator rand() returning pseudorandom numbers. Similar to the original MC method choose a starting microstate q, preferably from the equilibrium ensemble as it reduces the computation by reducing the number of steps. [2]

Further info can be found through the paper referenced **[4].**

1.3.3 Molecular Dynamics Simulation

Molecular Dynamics (MD) simulations are used to integrate Newton's equations of motion for a set of particles in the given system [2]. MD has proven to be better at long-time scale dynamics as it predicts(approximately) the time evolution of equation of motion for all the molecules at the same time. The equations of motion used in MD simulations are:

$$\frac{d^2\boldsymbol{r}_i}{dt^2} = \frac{1}{m_i}\boldsymbol{F}_i = -\frac{1}{m_i}\mathbf{r}_i U(\boldsymbol{r}_1, \boldsymbol{r}_2, .., \boldsymbol{r}_N),$$

Where **F**$_i$ is the force on particle **i**. It is a forward in time simulation moving in steps of Δt. [2]

Commonly used integration method is:

$$\boldsymbol{r}_i(t + \Delta t) = 2\boldsymbol{r}_i(t) - \boldsymbol{r}_i(t - \Delta t) + \frac{(\Delta t)^2}{m_i}\boldsymbol{F}_i(t).$$

Just like the leap frog and velocity Verlet (1967) algorithms it updates both position and velocity at the same time. The error for this method is of the order of $(\Delta t)^4$. It required the simulation to determine a single instance of force on each particle. This algorithm ensures that the result will be equal to an exact solution of a Hamiltonian nearby thus ensuring long term stability. A starting position and velocity is chosen for each particle and then the algorithm integrates those values forward in time with a time step (Δt) chosen to be smaller than the smallest time scale in Hamiltonian but large enough to ensure that the program remains efficient. Velocity and energy approximation applied are given by:

$$\boldsymbol{v}_i(t) = \frac{\boldsymbol{r}_i(t + \Delta t) - \boldsymbol{r}_i(t - \Delta t)}{2\Delta t},$$

$$E = \sum_{i=1}^{N} \frac{m_i}{2}\left(\frac{\boldsymbol{r}_i(t + \Delta t) - \boldsymbol{r}_i(t - \Delta t)}{2\Delta t}\right)^2 + U[\boldsymbol{r}_1(t), \boldsymbol{r}_2(t), .., \boldsymbol{r}_N(t)].$$

To study a thermodynamic property MD simulation relies on approximation of these properties considered to be moving along the constant energy hypersurface. To calculate equilibrium averages the sampling of all regions on the hypersurface is necessary which can be achieved if the Hamiltonian follows ergodic hypothesis. This ensures that MD time averages can be deemed equal to average over the ensemble.

Lennard-Jones interaction is commonly used for calculating the pair potential of monoatomic gases.

$$u(r) = 4\varepsilon\left(\left(\frac{D}{r}\right)^{12} - \left(\frac{D}{r}\right)^{6}\right),$$

Where D is the diameter of the molecule and ε is the depth of the wall of attraction. The pair potential at long distances is an attractive function while it decays as the van der Waals forces are relevant ($1/r^6$) and to model Pauli repulsion diverges at even shorter distances($1/r^{12}$). Dimensionless parameters are preferred for carrying out these simulations. The fluids that can be classified by Lennard-Jones interaction provide an ease in the calculations as the it reduces the number of variables, all lengths can be measured as functions of D, energies as ε, forces as ε/D, pressure as ε/D^3 etc. [2]

As far as the algorithm for the MD simulation is concerned a brief explanation is provided in the following steps.

- Choose the initial velocities using Maxwell distribution for each component of velocity vector for each particle in the system using:

$$P_{\text{Maxwell}}(v_x(0)) = \frac{1}{\sqrt{2\pi T}} \exp\left(-\frac{v_x^2(0)}{2T}\right);$$

- Use the initial velocities to set the initial positions (after first time step) of the particles using:

$$\boldsymbol{r}_i(\Delta t) = \boldsymbol{r}_i(0) + \boldsymbol{v}_i(0)\Delta t + \frac{1}{2}\frac{(\Delta t)^2}{m_i}\boldsymbol{F}_i(0).$$

- Use:

$$\boldsymbol{r}_i(t+\Delta t) = 2\boldsymbol{r}_i(t) - \boldsymbol{r}_i(t-\Delta t) + \frac{(\Delta t)^2}{m_i}\boldsymbol{F}_i(t).$$

- Use the time steps of $M_{eq}=\tau_{eq}/\Delta t$. As the system moves forward in time with the given time step and a large enough value of τ_{eq} it will reach the equilibrium state.
- Now use the time step of $M= \tau_{avg}/\Delta t$ and calculate the equilibrium average of the required thermodynamic property using the equation given in section 1.3.1. [2]

1.3.4 Simulation of Hard Spheres

This section discusses about the simulation of hard sphere system or molecular system for dense gases and liquids. The results from the hard sphere simulation have been used as basis for the calculations made from PIV data and obtaining experimental results.

Let’s take an example of and N particle system in a periodic box of volume V interacting via a pair potential. Using equipartition theorem the temperature T for a d-dimensional system can be given by [2]:

$$kT = \frac{1}{Nd}\left\langle \sum_{i=1}^{N} m_i v_i^2 \right\rangle.$$

Pressure for the ensemble can be given by virial equation of state [2]:

$$\frac{P}{nkT} = 1 + \frac{1}{NdkT}\left\langle \sum_{i<j} F(\mathbf{r}_{ij}) \cdot \mathbf{r}_{ij} \right\rangle = 1 - \frac{n}{2dkT}\int \frac{du}{dr} r g(r) dr.$$

This equation is derived from the fact that only virial terms, because of forces between pairs of particles, affect the pressure of a d dimensional system. In the particular case of hard spheres pressure is determined by pair correlation function at contact. The hard sphere pressure in one, two and three dimensions are given by [2]:

$$\frac{p^{\mathrm{HS}}}{nkT} = \begin{cases} 1 + \eta g(D^+) & \eta = nD \quad d = 1, \\ 1 + 2\eta g(D^+) & \eta = \frac{\pi}{4} nD^2 \quad d = 2, \\ 1 + 4\eta g(D^+) & \eta = \frac{\pi}{6} nD^3 \quad d = 3, \end{cases}$$

The pair correlation function is given by [2]:

$$g(r) = \frac{2V}{N^2\left(\frac{4\pi}{3}\right)\left[(r+\Delta r)^3 - r^3\right]}\left\langle \sum_{i<j}^{N} \Delta_{\Delta r}(r_{ij} - r) \right\rangle,$$

Where r is the radius of shell of thickness Δr.

Hard sphere model was one of the first one to be studied in MC and MD simulations. As the pair potential lack a finite energy scale temperature becomes an irrelevant factor (energy change is either 0 or infinite). This implies that all thermodynamic properties become independent of temperature or trivially scale with temperature. The density is expressed in terms of packing fraction η (=ЛInD^3/6, for 3 dimensions). The pressure is determined from virial equation of state for hard sphere in one, two and three dimensions given above [2].

MD simulation for hard spheres deviates from the standard MD approach considering each particle travelling in a straight line with a constant velocity except from when two particles collide. Since the pair potential is singular the collisions can be time-ordered where both kinetic energy and momentum is conserved allowing to analytically determine the velocities after each collision as well the displacement vector between the centers of two particles at the moment of collision. The relative position and velocity and the change in the velocities of two colliding particles are related by [2]:

$$\Delta \boldsymbol{v}_i = - \Delta \boldsymbol{v}_j = \left. \frac{-(\boldsymbol{r}_{ij} \cdot \boldsymbol{v}_{ij})\, \boldsymbol{r}_{ij}}{D^2} \right|_{|\boldsymbol{r}_{ij}|=D},$$

At low densities or packing fraction the equilibrium phase is liquid whereas at high densities it is solid. An attractive interaction is not required to be incorporated in the calculations for a model to have crystalline phase but it is, however, required to have a liquid vapor coexistence line and this is why the low-density phase in the phase diagram is referred to as fluid phase rather than liquid or vapor phase. The model does not have a liquid-vapor coexistence line but it has a liquid-solid coexistence line which can be seen at $P^*=P_{ls}$. To accurately get the pressure values in the low-density fluid phase the pressure is modeled using Carnahan-Starling equation of state: [2]

$$\frac{P}{nkT} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3},$$

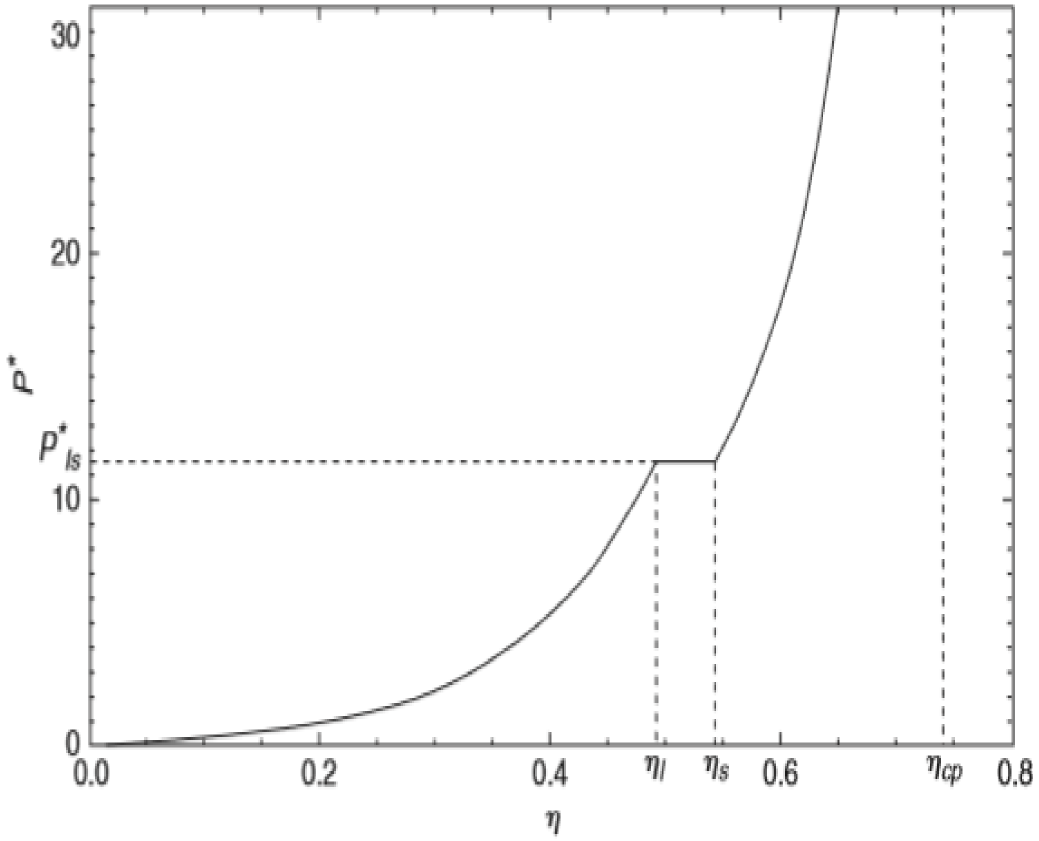


Figure 1.2: Sketch of the equilibrium phase diagram for hard spheres in three dimensions. The horizontal axis is the volume fraction $\eta=\pi n D^3/6$ and the vertical axis is the scaled pressure $P^*=PD^3/kT$ There are two equilibrium phases: a low-density fluid phase for $0 < \eta < \eta_l$ and a high-density solid phase for $\eta_s < \eta < \eta_{cp}$.[2]

1.4 Density Measurement from PIV

The formula for calculating density used here is: [5]

$$\rho(x_c, y_c) \propto \frac{1}{A} \int I(x, y) \mathrm{d}A \propto \sum_{j,k=1}^{N} I(x_j, y_k)$$

The idea here is to determine the density by spatially averaging the intensity fields within the interrogation window. The method has been proven to yield low error values. Variety of averaging methods were used such as using intensity thresholds and pointwise averaging. Pointwise averaging showed large errors in the second order moments and the local averaging of the interrogation window yielded the best results. [5[

CHAPTER 2: PHASE DIAGRAM CALCULATIONS

2.1 General Approach

The first step was to get an idea on how to approach the problem. Thus, a general layout of the problem was created. To start things off interrogation area had to be chosen for grains that are stationary, i.e. frozen into a solid state and for the grains that were moving or in a fluid state. Using these interrogation areas, we had to calculate the total dimensionless pressure (P^*) and the volume fraction (η). The following formulae were used to achieve the aforementioned goals:

$$P^* = \frac{6}{\pi}\frac{I}{I_o}\left[1 + 2\frac{I}{I_o}g(D^+)\right]$$

$$\eta = \frac{\rho_{\mathrm{msd}}}{\rho_{\mathrm{single\ grain}}}$$

$\rho_{\mathrm{msd}} = C_o I$ (from density-intensity correlation function, section 1.4)

Here ‘I’ is the measured intensity for a selected interrogation area and ‘I_o’ is the intensity over the area occupied by a single grain. The value of $g(D^+)$ is constant at 5 (explained later using diagram in appendix). ρ_{msd} represents the measured density for the interrogation window using the intensity values. C_o is the proportionality constant. The derivations of these equations are given in the appendix.

2.2 PIV Data and Selection of Interrogation Area

The PIV data was chosen form experiment that meets the specific requirements i.e. where the media stagnates near a flat plate and flows around to give a good mix of both solid and fluid states with the least possible shadow region. Although it has been made clear that media of different shapes, sizes and densities could serve as analogs for the hard sphere simulations. [1] Spherical grains were specifically chosen here to give a better idea of the analogy and for the ease of use. The PIV data had been collected for ~10 seconds with 5059 time stamps.

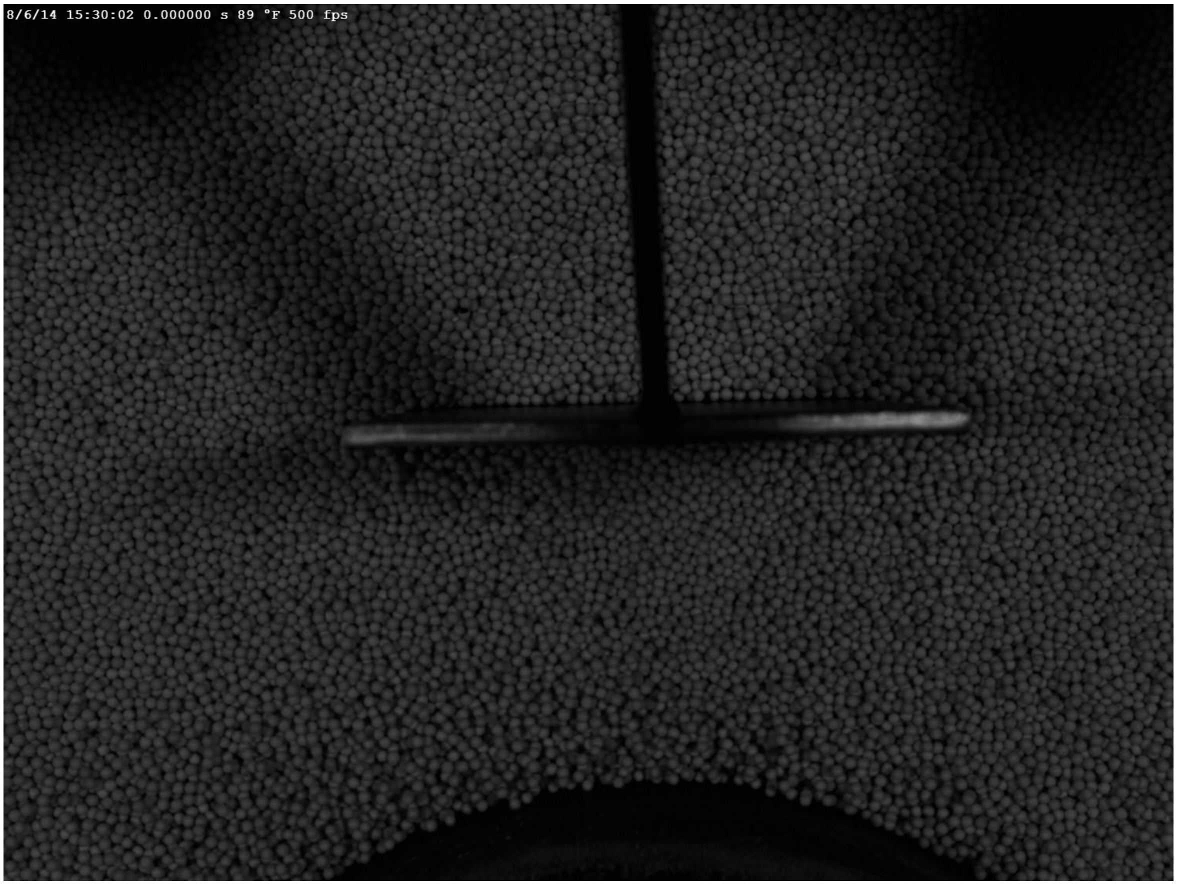


Figure 2.1: Image of part of the bowl taken during the experiment by high speed camera during the PIV data collection. The horizontal plate at the center if the obstruction used. It is suspended from the top of the bowl using the vertical rod, a part of which is seen in the image.

The interrogation area for the stagnation phase was chosen directly from the velocity plots obtained by PIV where the instantaneous grain velocities were the lowest (v<<<1). For this purpose, the area near the center of the plate provided the best velocity readings. The grains at the end of the plate are near stagnation but still are still moving inwards towards the center of the plate. The area was chosen such that it is good enough to give a good average of velocity and intensity values while not being large enough to average the significant changes. Three areas were chosen for the stagnation (solid) region.

For the fluid state, the interrogation area was chosen from the instantaneous velocity plots as well. The areas were chosen where the grains were freely moving and such that the velocities do not vary significantly. Several different areas were chosen around the flat plate (to give a decent solid-liquid phase interaction) and away from the plate. The interrogation areas were chosen to give a good average of pressure and density in that general area. As visible from **Figure 2.1** the fluid region is much larger than the stagnation region, more number of fluid values were averaged over the whole region to give a better understanding of the fluid phase.

2.3 Calculations

The data was processed using matlab. Vector coordinates corresponding to the interrogation areas were used to gather the specific intensity data for all the 5059 time stamps. The intensity values were then time averaged over the ~10 second window.

After getting the average intensity values a separate set of intensity values were calculated for a new area of 2mm X 2mm. The idea here is that in an interrogation are of the given dimension, at any given time, can be occupied by one sphere only. Thus, if the time averaged intensity averaged over the interrogation area 'I_o' is used to calculate density it will be equal to the density of one sphere, which is a known quantity. This can be used to calculate the constant of proportionality 'C_o' for the density-intensity correlation function.

Now since both ‘I’ and ‘I_o’ are known the pressure corresponding to the packing fraction for a given interrogation area can easily be modeled using these values.

The average intensity values were then used with the density-intensity correlation function to get the measured density and then it was divided by the known grain density to get the volume fraction. The results were then plotted to get the phase diagram.

CHAPTER 3: RESULTS AND CONCLUSION

3.1 Results

After going through the calculations explained above values for η and P^* were tabulated and plotted to get the graph below. Important thing to be kept in notice here is that the results are completely preliminary and the reduced pressure has been neglected here. The main purpose was to generate initial results based available data and check if it was at all possible to replicate the phase diagram using huge granular media.

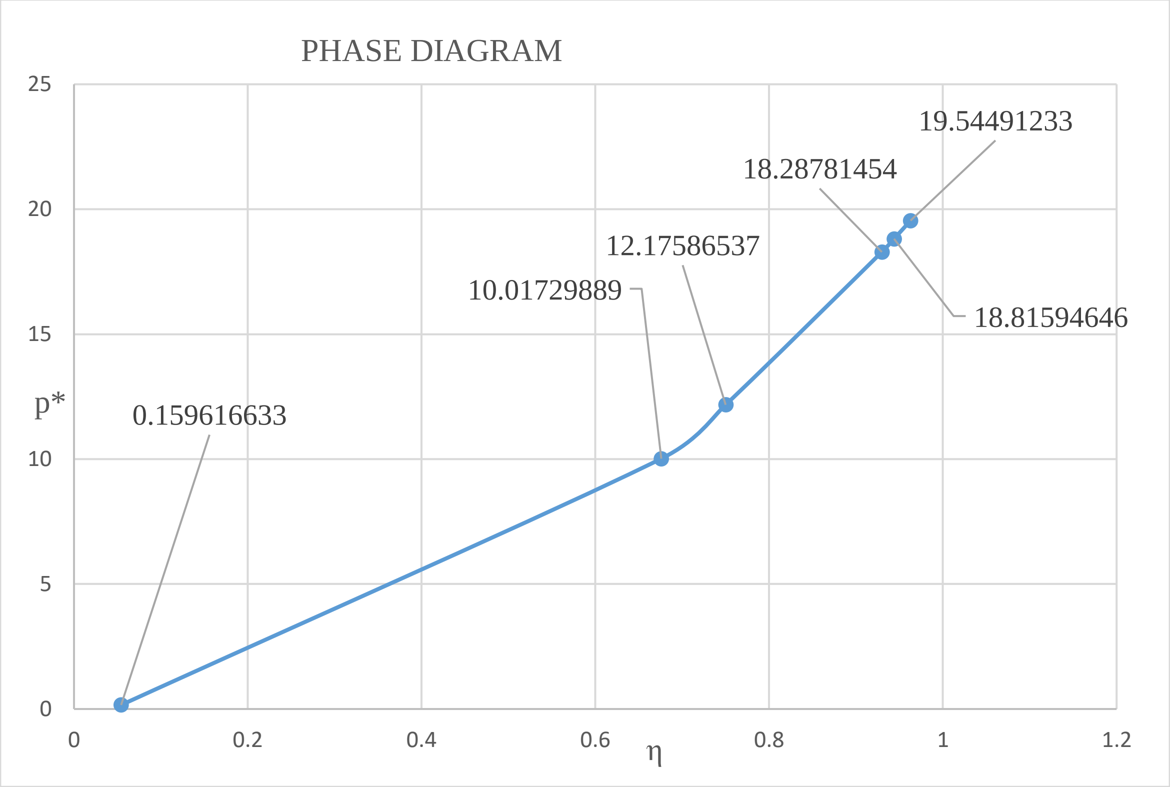
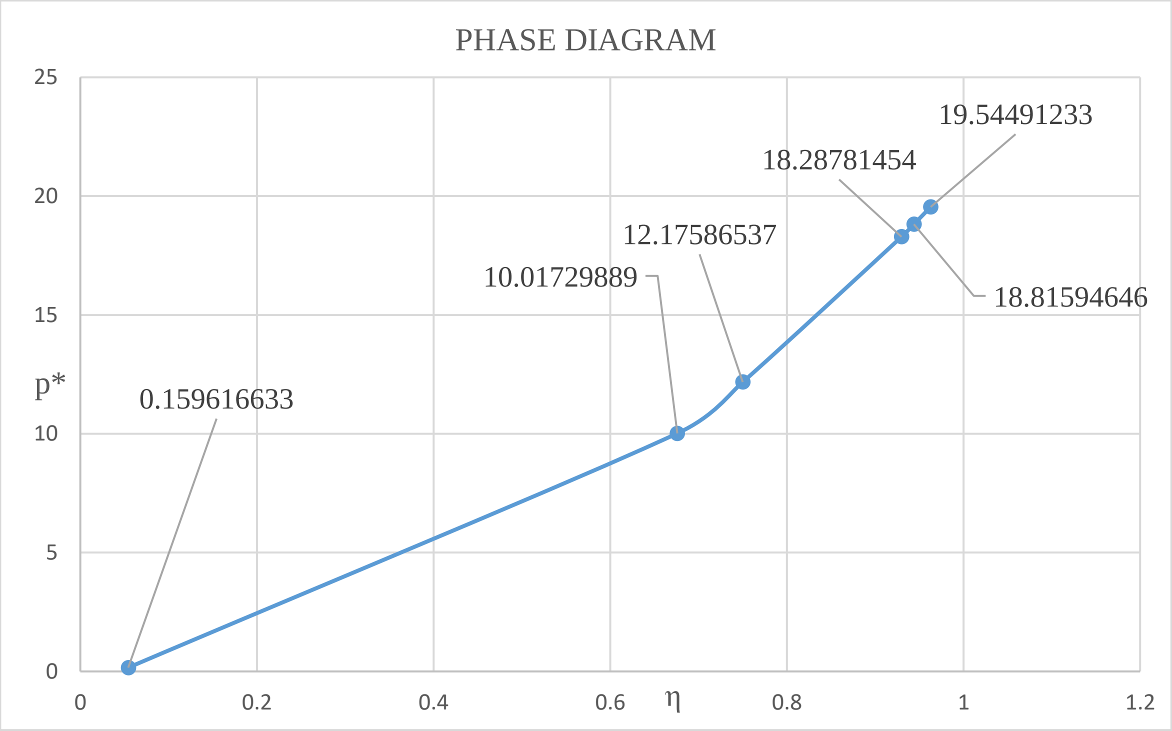


Figure 3.1: Chart representing the phase diagram obtained experimentally using PIV data from Vibratory Polishing experiment using huge granular media (D=2mm).

A comparison with the theoretical results obtained through MD simulation is also given below.



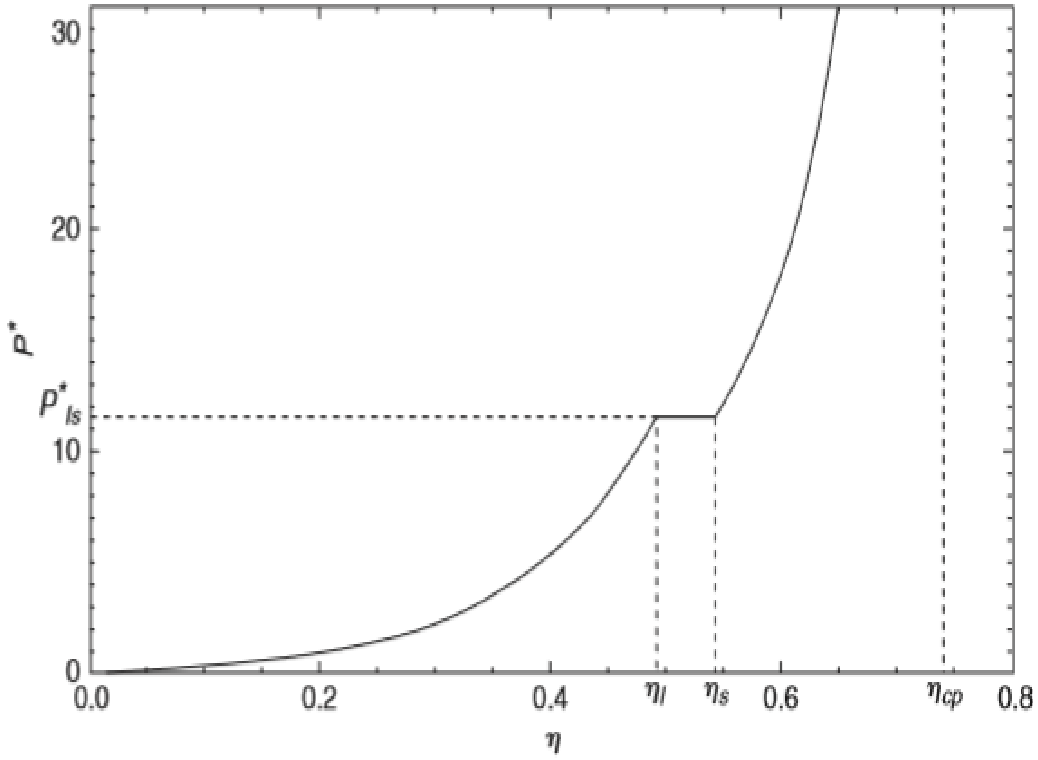


Figure 3.2: Comparison of experimental and theoretical results.

3.2 Conclusion

As mentioned above these are just preliminary results for the purpose of confirming if it was, even slightly, possible to study the hard sphere systems and with extension, if not all, some of the statistical mechanics problems using the granular media in a vibratory polishing machine. The results are promising as the experimental results follow the general trend of the theoretically predicted phase diagram. As we can observe there is a steady rise from the region of low pressure and then as the packing fraction increases and goes beyond 0.6 we see that the rise in pressure is much steeper. There are no major anomalies when it comes to the P* and η values. The results obtained fall within the same region and show a huge potential of even following the phase diagram closer than expected. Once a few things such as modeling the lower densities of the fluid phase separately are incorporated a better idea can be given for that stage.

For now, the main observation is the absence of the solid liquid coexistence line and that can be attributed to the usage of same formula for the calculation of both states. As it can be observed from the theoretical results the two phases can be neatly characterized using η as $\eta < \eta_l$ being the fluid phase and $\eta > \eta_s$ being the crystalline or solid phase. There is a possibility that if a different set of equations are used to model the pressures for both the phases separately there might be no need to go directly for a solid-liquid coexistence line. Rather than going directly for the coexistence line in a single curve a different approach can be used to go for the individual phases and plot the different curves together.

3.3 Future Work

To model the reduced density fluid phase:

$$\frac{P}{nkT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}$$

This is also known as Carnahan-Starling equation of state [2]. Here nkT is nothing but random averaged kinetic energy. To calculate which the velocity values for the interrogation area can be time averaged over the 10 second window and the average velocity values can then be subtracted from the instantaneous velocity values from the PIV data for the interrogation area for each 5059 time stamps to get the random velocities which will give the random kinetic energies. The random kinetic energy values again need to be time averaged to get the final random average kinetic energy value (KE_{avg}).

To model the high density solid phase:

$$\frac{P}{nkT} = \frac{3}{1 - \eta^*} - 0.5921\left(\frac{\eta^* - 0.7072}{\eta^* - 0.601}\right)$$

$$\eta^* = \frac{\eta}{\eta_{cp}} \qquad (\eta_{cp}=0.7405)$$

The value of η_{cp} has been calculated theoretically and need to be validated experimentally. The resulting graph will have two separate curves for the two phases and the pressure from these different curves can be used to determine the start and end of each phase and by extension the coexistence line. In other words, there will be an η in both solid phase and liquid phase for which the value of pressure will be the same and that will give the coexistence line.

There is a bit more work that can be done to improve upon the results. The interrogation window has been chosen manually and whether it follows the continuum hypothesis can’t be validated. There can be a slight chance that real changes have been averaged or the interrogation area is smaller than it should be. Another set of calculations can be done to incorporate this wherein all the values at each time stamp for the chosen interrogation area can be collected and can be plotted to see the change and verify that the interrogation area chosen is perfect. Next time and experiment is being carried out the sole purpose should be to predict the phase diagram so that the intensity and the barrier can be adjusted to give the best results. It can be adjusted so that the stagnation region is larger and can give a better approximation of that area.

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APPENDIX: DERIVATIONS

- Equilibrium Average Formula

To calculate the equilibrium averages for any given thermodynamic property is given by:

$$\langle A \rangle = \langle A \rangle_M \pm \sigma_M$$

Where $[A]_M$ is the simulation average and σ_M is the uncertainty. These are calculated using the following:

$$\langle A \rangle_M = \frac{1}{M} \sum_{j=1}^{M} A(q_j),$$

$$\sigma_M = \frac{\sqrt{\langle A^2 \rangle_M - \langle A \rangle_M^2}}{\sqrt{M/(2\tau + 1)}},$$

$$\langle A^2 \rangle_M - \langle A \rangle_M^2 = \frac{1}{M} \sum_{j=1}^{M} [A(q_j) - \langle A \rangle_M]^2.$$

Here τ is the correlation time which directly proportionally affects the correlation in the values of $A(q_j)$. The microstates q_j are generated using the simulation as we set an initial microstate and subsequently get the rest. But this means that these microstates are close to each other so the values of thermodynamic property in question which is a function of these microstates are also close and thus highly correlated. The correlation time can be calculated using:

$$\phi_{AA}(t) = \frac{\langle A(t)A(0)\rangle - \langle A(t)\rangle \langle A(0)\rangle}{\langle A^2\rangle - \langle A\rangle^2},$$

$$\tau = \sum_{t>0} \phi_{AA}(t).$$

- P^* Formula

$$\frac{P^{HS}}{nkT} = [1 + 2\eta g(D^+)]$$

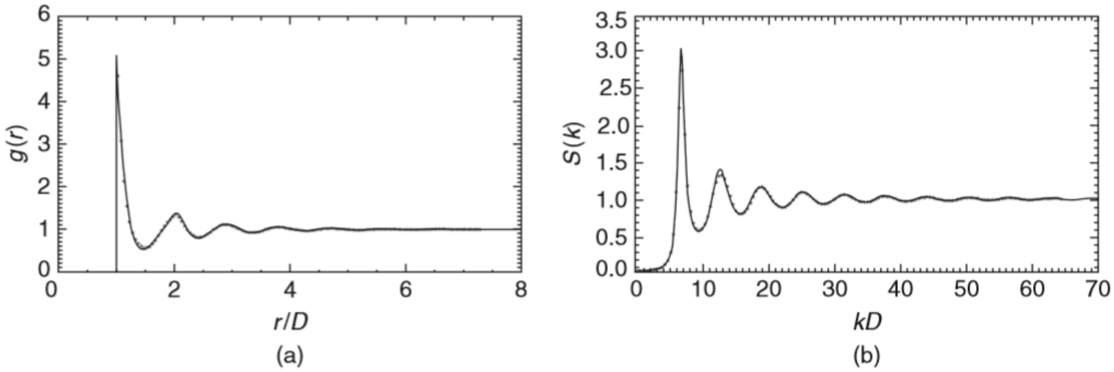
Where $[1 + 2\eta g(D^+)]$ is for 2-dimensional system as explained in section 1.3.4.

$$\frac{1}{2}m(vx^2 + vy^2) = kT$$

But,

$$nkt = \frac{nm}{2}[vx^2 + vy^2]$$

$$P^{HS} = \frac{\rho}{2}[vx^2 + vy^2][1 + 2\eta g(D^+)]$$



(a)

(b)

Figure A.1: a.) g(r) is the pair correlation function and b.) S(k) is the structure factor for a system of hard sphere at a volume fraction of 0.49. [2]

$$g(D^{+}) \cong 5 \text{ (using figure A.1 a)}$$

$$\eta = \rho_{\text{msd}} / \rho_{\text{single grain}}$$

$$P^{*} = \frac{P^{HS} d^{3}}{kT}$$

Where d is the diameter of the grain k is the Boltzmann constant.

Substituting the values of P^{HS} in the above equation:

$$P^{*} = \frac{6}{\pi} \eta [1 + 2\eta g(D^{+})]$$

$$\eta = \frac{C_o \mathrm{I}}{\rho_{grain}} = \frac{C_0 I}{C_0 I_o} = \frac{I}{I_o}$$

where C_o is the proportionality constant for density intensity correlation function and I_o is the intensity in the area covered by a single grain.

Thus,

$$P^* = \frac{6}{\pi}\frac{I}{I_o}\left[1 + 2\frac{I}{I_o}g(D^+)\right]$$

- Volume fraction formula

$$\eta = \frac{volume\ of\ solid}{total\ volume} = \frac{mass\ of\ solid}{total\ volume}\ X\ \frac{volume\ of\ solid}{mass\ of\ solid} = \frac{\rho_{msd}}{\rho_{grain}}$$