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Global equation of state of two-dimensional hard sphere systems

Stefan Luding
Institute for Computer Applications 1, Pfaffenwaldring 27, 70569 Stuttgart, Germany

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Hard sphere systems in two dimensions are examined for arbitrary density. Simulation results are compared to the theoretical predictions for both the low- and the high-density limit, where the system is either disordered or ordered, respectively. The pressure in the system increases with the density, except for an intermediate range of volume fractions $0.65 \leqslant \nu \leqslant 0.75$, where a disorder-order phase transition occurs. The proposed *global equation of state* (which describes the pressure *for all densities*) is applied to the situation of an extremely dense hard sphere gas in a gravitational field and shows reasonable agreement with both experimental and numerical data.

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A hard sphere (HS) system is a simple and tractable model for various physical phenomena. It was used to examine disorder-order transitions, the glass transition, or simple gases and liquids [1–5] both theoretically and numerically. The theory that describes the behavior of rather dilute hard sphere systems is the kinetic theory [2,3], in which particles are assumed to be rigid and collisions take place in zero time. An extension to Boltzmann's low-density theory was introduced by Enskog [2,3], taking into account excluded volume effects and also momentum transport via collisions. In the limit of high densities, the cage effect, where particles are captured by their neighbors [5], becomes important and a free-volume theory can be formulated [6,7]. There exists no theory, to our knowledge, that is valid for the intermediate densities where the system changes from the disordered to the ordered state, however various theoretical approaches were proposed in recent decades; see Refs. [5,8–10] and references therein.

When dissipation is added to the HS model, one has the simplest version of a granular gas, i.e., the inelastic hard sphere (IHS) model. Granular media represent the more general class of dissipative, nonequilibrium, multiparticle systems [11,12]. Attempts to describe granular media by means of the kinetic theory are usually restricted to certain limits such as small densities or weak dissipation [13,14]. Also in the case of granular media, one has to apply higher-order corrections to successfully describe the system under more general conditions [15–18] or for multiparticle contacts [19]. The result of a kinetic theory approach is, in the simplest case, a set of balance equations for mass, momentum, and energy with constitutive expressions for the transport coefficients, describing stress, viscosity, heat conduction, and energy dissipation. In this Brief Report, we focus on the pressure p, the isotropic part of the stress in a hard sphere gas—or in a granular gas in its elastic limit $r \rightarrow 1$—with the coefficient of restitution r. The model system is periodic and two-dimensional (2D) with volume $V = l_x l_y$, where l_x and l_y are horizontal and vertical size, respectively. It contains N particles with radii a, and masses m that are located at positions $\boldsymbol{r}_i$ with velocities $\boldsymbol{v}_i$. The fraction of the area that is covered by particles is denoted as volume fraction $\nu = N\pi a^2/V$. The kinetic energy is $E = (m/2)\Sigma_{i=1}^{N} \boldsymbol{v}_i^2$, the temperature is defined as $T = E/N$ in 2D, and the energy density is E/V. For low and intermediate densities $\nu < \nu_c$ (with the "crystallization" density ν_c at which order becomes important), the kinetic theory leads to an expression for the equation of state, i.e., the dimensionless excess pressure due to particle interactions,

$$P := pV/E - 1 = 2\nu g(\nu). \tag{1}$$

For an ideal gas with noninteracting particles, one has $pV/E = 1$ so that $P = 0$; for nonzero densities, one has $P > 0$ since the collisions contribute to the momentum transport and thus to the pressure, the viscosity, the heat conductivity, and the dissipation rate. In cases with $r < 1$, the factor 2 can be replaced by $1 + r$. The pair correlation function at contact $g(\nu)$ accounts for the probability that a collision occurs. Typically, $g(\nu)$ is determined via a virial expansion around low densities and one can use

$$g_4(\nu) = \frac{1 - 7\nu/16}{(1-\nu)^2} - \frac{\nu^3/16}{8(1-\nu)^4}, \tag{2}$$

where the subscript 4 indicates that the second term is of order $1/(1-\nu)^4$. The first term in Eq. (2) is the simpler, frequently used version $g_2(\nu)$ introduced by Henderson [13,20,21]. Note that the expression in Eq. (2) is slightly different from the form in Refs. [14,21]. The value of g_4, taken at contact, accounts for the excluded volume effect and the increase of the collision rate with density. At densities larger than $\nu_c \approx 0.7$, an ordered triangular structure is evidenced [22–24].

One of the unsolved problems concerning an application of the balance equations to a specific boundary-value problem is the limited range of validity of Eq. (2). Under realistic conditions with $r < 1$, the volume fraction can take values $\nu > \nu_c$ [25] so that a solution based on Eqs. (1) and (2) can be correct up to ν_c only. This is even worse, since the "virial" $\nu g(\nu)$ also occurs in all the other transport coefficients. For the same reason, fortunately, a generalization of the pressure P to all densities will thus enter all the other transport coefficients. This is why we examine the equation of state at *all densities* and propose a *global equation of state* that is then tested by a comparison with simulation and experiment.

For the numerical modeling of the system, an event-driven (ED) method [25,26] is used. A change in velocity can occur only at a collision when the standard interaction model, based on momentum and energy conservation, is used [12]. The postcollisional velocities $\boldsymbol{v}'$ of two collision partners, in their center-of-mass reference frame, are given in terms of the precollisional velocities $\boldsymbol{v}$, by $\boldsymbol{v}'_{1,2} = \boldsymbol{v}_{1,2} \mp [(\boldsymbol{v}_1 - \boldsymbol{v}_2) \cdot \hat{\boldsymbol{n}}]\hat{\boldsymbol{n}}$, with the unit vector $\hat{\boldsymbol{n}}$ pointing along the line connecting the centers of the colliding particles. This model can also be extended to the more general case of dissipative particles with rough surfaces [12,13].

The stress tensor inside a test volume V (whose isotropic part is the pressure p) has two contributions, one from the convectional transport of mass and thus momentum and the other due to collisions and the related momentum transport; for details see Refs. [23,25] and references therein. The mean pressure is obtained from simulations with different volume fractions ν in the following.

The equation of state in the dense, ordered phase has been calculated by means of a free-volume theory [6,22,27], which leads in 2D to the reduced pressure $P_{\text{fv}} = c_0/(\nu_{\max} - \nu) - 1$, with $c_0 \approx 1.8137$ as obtained from our numerical data. Based on the simulation results, we propose the corrected high-density pressure

$$P_{\text{dense}} = \frac{c_0}{\nu_{\max} - \nu} h_3(\nu_{\max} - \nu) - 1, \tag{3}$$

where $h_3(x)$ is a fit polynomial $[1 + c_1 x + c_3 x^3]$ of order 3, with $c_1 = -0.04$ and $c_3 = 3.25$ [28].

What remains to be done is to merge the low-density pressure P_4 and the high-density expression (3). To our knowledge, no theory exists that connects these two limiting regimes, besides the Maxwell construction [10]. For various approaches concerning the melting and freezing transition, see Refs. [8,9,22,27,29,30]. Therefore, we propose the *global equation of state*

$$Q = P_4 + m(\nu)[P_{\text{dense}} - P_4], \tag{4}$$

with an empirical merging function

$$m(\nu) = \frac{1}{1 + \exp[-(\nu - \nu_c)/m_0]} \tag{5}$$

that selects P_4 for $\nu \ll \nu_c$ and P_{dense} for $\nu \gg \nu_c$, with the width of the transition m_0. The parameters $\nu_c = 0.7006$ and $m_0 = 0.0111$ lead to qualitative agreement between Q and the simulation results, by far better than 1% for the purely ordered and disordered regimes, and still within about 3% in the interval $0.65 \leqslant \nu \leqslant 0.75$ [31].

When plotting P against the volume fraction ν with a logarithmic vertical axis in Fig. 1, the results for the different simulations cannot be distinguished from the theoretical prediction P_4 for $\nu \lesssim 0.65$. For larger volume fractions, one obtains crystallization around $\nu_c \approx 0.70$ and the data clearly deviate from P_4. In the transition regime, the coexistence of fluid and solid phases can be obtained. The pressure is strongly reduced due to the enhanced free volume in the ordered phase. The reduced pressure data eventually diverge at the maximum packing fraction in 2D, $\nu_{\max}^{\text{mono}} = \pi/(2\sqrt{3})$. Note that one has to choose the system size such that a triangular lattice fits perfectly in the system, i.e., $l_y/l_x = \sqrt{3}h/2w$ with integer w and even h, otherwise the maximum possible volume fraction can be smaller. Since our simulations are already set up on a perfect triangular lattice, the maximum density is approached for $\nu \rightarrow \nu_{\max}$. If, instead, the volume fraction is increased by increasing the particle size [24,26] and the simulations are started from random, low-density configurations, $\nu_{\max}$ is not reached due to defects in the 2D crystal [27,29]. Thus our global equation of state represents the high-density, small compression-rate limit.

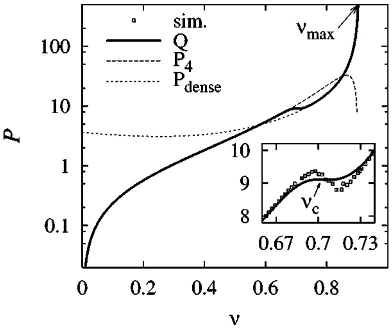

FIG. 1. Global, dimensionless equation of state Q, plotted against the volume fraction ν with logarithmic vertical axis. The dashed and dotted lines correspond to P_4 and P_{dense}, respectively, see Eqs. (1), (2), and (3). In the inset, simulation data ($N = 1628$, $r = 1$) are compared with Q.

The transition by itself is also interesting, since we obtain a hysteresis loop when the density is increased and decreased with a finite rate [7,25,30]. Especially in the transition region, the relaxation time is very large, and the inflection in the data (see the inset in Fig. 1) can be due to either the finite relaxation time, the finiteness of the system, or the initial and boundary conditions [30,31]. Note that the analytical expression Q allows for a straightforward numerical integration of the density profile (see below), since the fit parameters are chosen such that the slope of Q is always positive. This is a compromise between the quality of the fit on the one hand and the numerical treatability of the function on the other hand; instabilities are avoided but also memory effects are disregarded.

For a HS system in a gravitational field with the acceleration g in the negative vertical direction, both density and pressure gradient have to be taken into account. In the following, we compute analytically the density profile for an ideal HS gas ($\nu < 0.65$); the profile for the extremely dense gas is computed numerically using the global equation of state and is found to be in excellent agreement with the numerical ED simulations, where a horizontal wall at $z = 0$ is introduced in a periodic, two-dimensional system of width $L = l_x/(2a)$ and infinite height. The number density $n = n(z) = N/V$ is related to the volume fraction by $n = \nu(z)/(\pi a^2)$. Here, we briefly sketch how to obtain an analytical solution for the density profile, valid at least for low and intermediate densities [14,23,32].

Given the equilibrium of forces, the force $-L dp$ due to the pressure gradient at height z compensates the weight

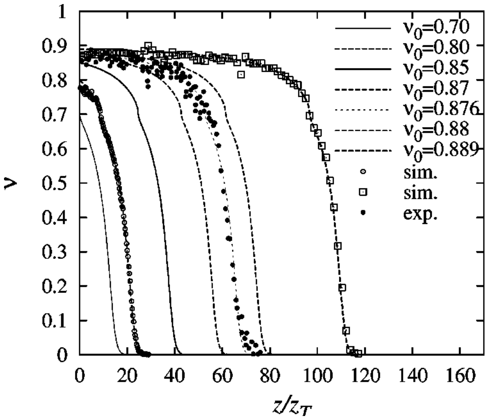

FIG. 2. Volume fraction of the hard sphere gas as a function of the rescaled height z/z_T for different ν_0 values as given in the inset. Lines are the theoretical predictions with increasing bottom density, from left to right, open symbols are two simulations, and the solid dots are the experimental data from Ref. [34].

$nmgLdz$ of the particles in a layer with height dz, so that the differential equation $dp/dz=-nmg$ has to be solved. In the simplest case, the equation of state of an ideal dilute gas $p=nT$, separation of variables, and the assumption of a constant temperature lead to an exponentially decreasing density profile $\nu(z)=\nu_d \exp[-(z-z_0)/z_T]$, with $\nu<\nu_d:=\nu(z_0)$ and $z_T=T/(mg)$. In a closed system, the particle number N is conserved so that integration of n over z determines the volume fraction at the bottom $\nu_d=N\pi a^2/(z_T L)$ in the dilute limit.

In denser situations $(0<\nu<0.65)$ the pressure can be expressed as $p=nT[1+2\nu g_2(\nu)]$ [we do not use $g_4(\nu)$ in order to keep the analysis simple], and integration leads to an implicit definition of $\nu(z)$:

$$\frac{z-z_0}{z_T}=\ln\frac{\nu_0}{\nu}-\frac{7}{8}\ln\frac{1-\nu_0}{1-\nu}+2[g_2(\nu_0)-g_2(\nu)] \qquad (6)$$

with the unknown volume fraction ν_0 at z_0, again determined by the integral over the density. This leads to a third-order polynomial for ν_0, which can be solved analytically [33], and has at least one real solution. When the theoretical density profile in Eq. (6) is compared with numerical simulations, one obtains perfect agreement for $\nu<0.65$ [23]. Since the functions $g_2(\nu)$ and $g_4(\nu)$ are wrong at larger densities ν, one cannot expect that the pressure and the density profile are correct.

Using the global equation of state, Q, from Eq. (4) instead of $2\nu g_2(\nu)$, one has to integrate the differential equation $dp/dz=-nmg$ numerically with $p=nT(1+Q)$ under the constraint that the particle number is a constant. In Fig. 2, the volume fraction ν is plotted against the rescaled height z/z_T for both theory and simulations. Simulation parameters are $N=1000$, $L=10$, and $z_T/(2a)=5.85$ (open circles) or $N=3000$, $L=50$, and $z_T/(2a)=0.508$ (open squares). In addition, we present experimental results from vibrated two-dimensional arrays of small spheres [34] (solid dots), neglecting the fact that this situation is weakly dissipative. Both the qualitative and the quantitative behavior of the density profile are well reproduced by the numerical solution using the global equation of state. All solutions belong to one master curve and can be rescaled by a horizontal shift. The averaging result is somewhat dependent on the averaging procedure; we evidence strong coarse-graining effects in the dense, ordered regime with densities $\nu>0.70$. Using two methods, one tailored for the ordered regime and the other for the disordered regime, however, we obtain consistent results.

In summary, we tested existing predictions for the equation of state of a 2D hard sphere gas of arbitrary density via comparison with numerical simulations and experimental data. In the dilute case, the particle correlation at contact and the collision frequency (and thus the equation of state) are nicely predicted by the kinetic theory expressions up to intermediate densities $\nu\approx 0.65$. In the dense case, the free volume theory for 2D systems can be applied to systems with densities larger than $\nu\approx 0.75$. Finally, a merging function is proposed, which connects the low- and high-density regimes, resulting in a differentiable *global equation of state* for the 2D hard sphere gas for arbitrary density.

The equation of state is used to compute analytically and numerically the density profile of an elastic, monodisperse HS gas in a gravitational field. For maximum densities below ν_c, the analytical solution works perfectly well. For higher densities, we used a numerical solver (MAPLE). The strange shape of the density profile as obtained from simulations is nicely reproduced by our theory based on the global equation of state, including a wiggle at $\nu\approx\nu_c$. We remark that the ED simulation method parallels the Monte Carlo (MC) method [30] concerning the particle-particle interactions, but in contrast to MC it allows for a definition of time and thus for the examination of the dynamics.

The presented results are obtained from homogeneous, elastic systems of arbitrary density. The range of applicability, however, is much wider. Since already weak dissipation can lead to strong inhomogeneities in density, temperature, and pressure, the global equation of state is a necessary tool to treat effects such as clustering, surface waves, pattern formation, or phase transition and coexistence by means of a continuum theory. In a freely cooling ''granular gas,'' for example, clustering leads to *all* densities between $\nu\approx 0$ and $\nu\approx\nu_{\max}$ [25].

The proposed global equation of state is based on a limited amount of data from ED simulations. Initial checks of whether our global equation of state still makes sense for different particle-size distribution functions are promising, however the crystallization effect vanishes for strong enough polydispersity [23]. What remains to be done is to find similar *global* expressions for other transport coefficients such as the viscosity and the heat conductivity, and, furthermore, to extend the presented approach to three-dimensional systems.

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