Computer method for modeling the micro-structure of aerogel

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Abstract

We present a variant of the recently developed void expansion method (VEM) to generate random heterogeneous materials with a highly porous micro-structure. A polydisperse mixture of structural and void particles is generated by gradually expanding randomly placed initially point-like objects. Computer simulations revealed that varying the volume fraction of void and structural particles a percolation transition occurs where the critical volume fraction can be tuned by the relative volume fraction of the two components. We achieved critical volume fractions down to 0.05 which enables us to model the structure of aerogels. A detailed analysis of the micro-structure of VEM clusters is presented.

Keywords: porous media, micro-structures

1. Introduction

Aerogels have been in the focus of considerable scientific interest in recent years. This interest was mainly stimulated by its special physical properties. Aerogel is a manufactured material, derived from a gel in which the liquid component of the gel has been replaced with a gas. The result is the lowest bulk density of any known porous solid. Except for this, aerogels exhibit several additional extreme features. In spite of its large-scale porosity it has a considerable mechanical strength, it has very low thermal- and electrical conductivity, it has huge surface-to-volume fraction, it is transparent with almost the same reflection coefficient as air, etc. Due to these extreme properties aerogels are candidates for a large number of potential applications from space investigations through optics, nuclear physics, low-temperature physics and acoustics to microelectronics and electrical engineering [1]. Several experimental techniques have been used to carefully analyze the structure of aerogels of different materials from small angle neutron scattering to positron annihilation lifetime spectroscopy [2, 3]. These investigations revealed that on small length scales aerogels have a fractal structure, where the fractal dimension can be controlled by the fabrication process in the range $1.5 - 2.5$. Based on these studies, aerogels can be conceived as aggregates of blobs which have fractal characteristics. It is a grate challenge for theoretical investigation to reproduce the complex micro-structure of aerogels and understand their mechanical and fracture behavior in terms of the structural properties.

From computational point of view, in the computer modeling of aerogels we face similar problems to the investigation of granular materials. In both fields particle packings have to constructed, however, for granular matter typically high, while for aerogels low packing fraction is desired. The fractal nature of the structure of AG poses additional difficulties. Several different numerical methods have been worked out in the literature for the construction of particle packing which can be classified into two groups: there are physically based method where during the generation process particles interact with each other and the final structure is obtained by computer simulations of the time evolution of the dynamics of the particle ensemble. Other strategies are more formal relaying on mathematical constructions such as Voronoi tessellation and Delaunay tetrahedrization. Investigation of aerogels in the literature are mostly based on the diffusion-limited cluster-cluster aggregation (DLCCA) process [4], modeling the physic-chemical process of gelation. The advantage of the method is that it produces well-controlled fractal structures, however, it does not allow for the tuning of the porosity of the system.

In the present paper we propose an alternative approach for the computational investigation of structural features of aerogels, namely, we extend the void expansion method and explore its capabilities for the modeling of fractal porous structures. The method is physically based in the sense that during the generation process particles interact through contact forces and move according to Newton's law. However, compared to other physical approaches such as DLCCA, our method provides the additional advantage of the flexible control of porosity.

2. Generation process

We propose an extension of the so-called void expansion method (VEM) which was recently introduced to generate the micro-structure of random heterogeneous materials with a controllable porosity [5]. Our final goal is to work out a computer model of aerogels in the framework of which the mechanical response of aerogels can be analyzed by computer simulations.

In our approach a polydisperse mixture of structural and void particles is generated where the two types of spherical particles have two different roles. The final structure is composed by structural particles while the void ones ensure the porosity of the system. Our model system is a cubic simulation box of side length L containing N_S structural particles with radius R_S and N_V void-particles with radius R_V. Three physically relevant parameters characterize the generated structures: the volume fraction of structural particles which can define as

$$\phi_S = \frac{4N_S\pi}{3L^3} R_S^3, \tag{1}$$

the void to structural particle radius ratio

$$q = R_V/R_S, \tag{2}$$

and the void- to structural particle number ratio

$$n = N_V/N_S. \tag{3}$$

During the simulations N_S was fixed and the system size L and the void-particle number N_V were controlled to vary the volume fraction of structural particles ϕ_S and the void- to structural particle number ratio n.

Initially the particles are point-like so that they can be placed into the simulation box in a completely random manner. The particles are then slowly blown up which might cause interaction between them. The particles can move in the simulation box, and during their motion they touch each other and overlap. To capture of the finite size of the particles a repulsive force was introduce between overlapping particles

$$\vec{F}_{ij}^{pp} = -k_n(R_i + R_j - r_{ij})\vec{n}_{ij} = -k_n\vec{f}_{ij}^{pp}, \tag{4}$$

where k_n is the normal stiffness of the particles, R_i, R_j and r_{ij} are the radii and the distance of the touching particles respectively, and the superscript pp refers to the particle-particle contact. The force is parallel to the line $\vec{n_{ij}}$ connecting the particles i and j. The void-particles are much softer than the structural ones ($10k_{n,V} = k_{n,S}$) in our simulations. Energy dissipation was treated using a damping force

$$\vec{F}_i^d = -\alpha_i\vec{v}_i, \tag{5}$$

where $\vec{v}_i$ is the velocity of particle i and α_i is the drag coefficient. The mass of both type of particles is set to unity. No further forces like shearing stiffness or gravity were implemented. The value of the parameters α and k_n were chosen to prevent large velocities and large overlaps of structural particles. The time evolution of the system was followed by solving numerically the following equations of motion of particles

$$\frac{d^2\vec{r}_i}{dt^2} = -\alpha_i\frac{d\vec{r}_i}{dt} - \sum_{r_{ij}<R_i+R_j} k_n\vec{f}_{ij}^{pp}, \tag{6}$$
$$i = 1, \ldots, N_S + N_V$$

The molecular dynamics steps were performed by a fifth order Predictor-Corrector method [6].

The initial state was constructed by random packing of the particles inside the cubic simulation box generating the particle coordinates by a uniform distribution. In order to keep low the value of repulsive forces due to the overlap, the initial particle radius was small $R_S^0 = R_S/m_S$ and $R_V^0 = R_V/m_V$ where $m_S = 200$ and $m_V = 300$. After the preparation of the initial state three generation steps are applied: (i) the radius of structural particles were gradually blown-up: at each time step the particle radius was increased with its initial value R_S^0, and after each incrementation molecular dynamics steps were performed taking into account the repulsive force arising between overlapping particles and the damping force. This procedure is repeated until the structural particle radius reaches the desired value. Thus $m_S - 1$ is the number of incrementation steps and its value ensure slow gradual inflation.(ii) at the beginning of second section $R_V << R_S$, then the same procedure is applied for blowing-up the void-particles, gradually rearranging the whole structures. (iii) in the final stage of simulation the system undergoes a further relaxation process minimizing the overlap and getting to an equilibrium where no further changes occur. A side view of the simulation box is presented in Fig. $1(a)$ for the final state of the generation process where the structural and void particles are indicated by red and blue colors. It can be observed that our algorithm results in a highly heterogeneous particle packing as it is expected.

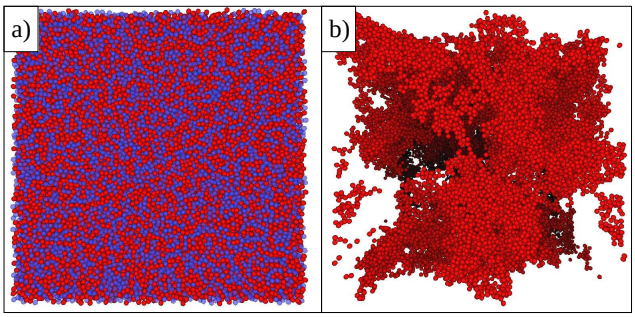

Figure 1: (a) The mixture of structural (red) and void (blue) particles at the end of the construction process. (b) The percolating cluster of structural particles obtained using periodic boundary conditions in all the three directions. Note that the cluster is fully connected even if it has large holes inside.

As the final step of the generation process, void particles are removed from the system so that the micro-structure is built up from only the structural particles. Simulations are carried out in a three dimensional box of cubic shape applying periodic boundary conditions in all three directions. In order to reduce the computation time we used Verlet-table method, i.e. we store the interacting partners of each particle in a neighborhood list, which is then updated after several molecular dynamics steps. In this way the CPU time requirement of the generation process becomes proportional to less than second power of the particle number, so that we could simulate 200.000 particles in reasonable time on a PC. While the generation of the structure needs much more CPU time than the its evaluation, the two procedures were executed by independent programs.

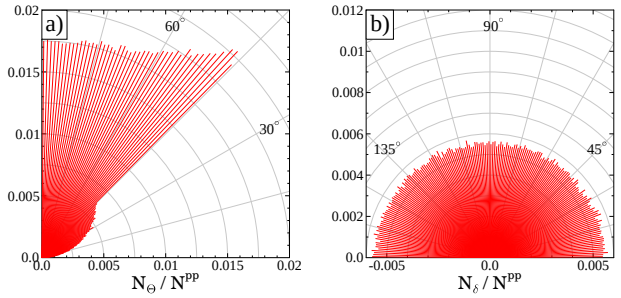

Figure 2: (a) Distribution of the angle θ between $\vec{n}_{ij}$ and a unit vector pointing along a side of the simulation box. (b) The azimuth angle δ of the projection of $\vec{n}_{ij}$ on the plane perpendicular to the unit vector chosen for the measurement of θ.

To test the quality of the random packing generated by the above algorithm we analyzed the angular distribution of the contact vectors $\vec{n}_{ij}$ of touching particle pairs. For simplicity, this calculations were performed in such a way that void and structural particles had the same size $q = 1$ and their number was also equal to each other $n = 1$. We determined the angles θ and δ between $\vec{n}_{ij}$ and two orthogonal unit vectors pointing along the sides of the simulation box. It can be observed in Fig. 2 that the distribution of the azimuth angle δ is uniform over the entire range, while the most values of the angle θ measured perpendicular to this plane is larger than 45^o due to geomatrical reasons, but the distribution is otherwise almost uniform. These results demonstrate the good quality isotropy of the packing structure in agreement with the expectations for this particular parameter settings.

3. Structural properties

3.1. Controllable percolation

Large number of computer simulations were carried out which revealed that three parameters have relevant influence on the structure: the volume fraction ϕ_S of structural particles, the relative size q and the relative number n of void and structural particles. Simulations revealed that from structural point of view the system has two distinct phases: At low value of the volume fraction of structural particles ϕ_S the expansion of void particles results in small independent clusters of connected structural particles which could move freely after the removal of the voids. On the contrary, at high concentration almost all particles form a single connected cluster which spans the simulation box. All other clusters of structural particles are orders of magnitude smaller than the spanning one. The transition between the two phases occurs in a narrow range of ϕ_s similarly to percolation [7]. A representative example of the spanning cluster is presented in Fig. $1(b)$. The fully connected spanning cluster is a good candidate for the computational modeling of aerogel's micro-structures. It has to be emphasized that during the construction phase no lattice is used, i.e. the particles move continuously in the three-dimensional space. It has the consequence that the system shows interesting analogies to percolation, however, it is different from both lattice and continuous percolation as well [7]. In the following we explore the detailed structural features of the system.

In order to determine the percolation threshold ϕ_S^*, we carried out a large number of simulations varying the parameters ϕ_S, n and q is a broad range. The critical concentration ϕ_S^* was obtained as the arithmetic average of those ϕ_S values where the spanning cluster first occurred.

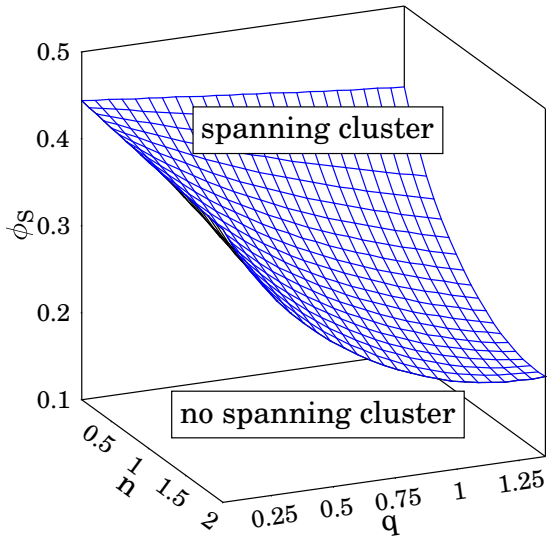

Figure 3: Phase diagram of the system. It can be observed that the percolation threshold can be controlled by varying n and q. In the parameter range above the surface a spanning cluster exists, while below it in the sub-critical phase the system is composed of a large number disconnected small sized clusters.

Figure 3 presents the percolation threshold ϕ_S^* as a function of n and q, which can also be considered as the phase diagram of the system. Note that the percolation threshold ϕ_S^* can vary in a broad range from 0.12 to 0.53 when adjusting the parameters n and q. Above the surface a spanning cluster exists which dominates the behavior of the system, while below it in the sub-critical phase the system is composed of a large number of small sized disconnected clusters. Simulations revealed that the presence or absence of the spanning cluster in a given system is mainly determined by the relative concentration of the components $\phi_r = \phi_V/\phi_S$, because the space available for structural particles is decreased by the volume of void ones. Close to $\phi_r = 1$ where our simulations are performed only the total volume of void particles plays a crucial role, so varying n and q^3 has the same effect. It follows that the key parameter of the construction is $\phi_r = nq^3$.

To give a quantitative characterization of the structural transition, we analyzed the strength of percolation P_∞ defined as the fraction of particles belonging to the spanning cluster. $P_\infty(\phi_S)$ is the order parameter of the percolation transition with the properties $P_\infty = 0$ for $\phi_S < \phi_S^*$ and $P_\infty > 0$ for $\phi_S \geq \phi_S*$. It is a very important feature of the transition that in the vicinity of the percolation threshold the strength of percolation P_∞ exhibits a power law behavior as a function of the distance from ϕ_S^*. Figure $4(a)$ shows P_∞ as a function of $\phi_S - \phi_S^*$ in the range $\phi_S > \phi_S^*$ for three different values of q. The remarkable feature of the numerical results is that a power law functional form is obtained

$$P_\infty \sim (\phi_S - \phi_S^*)^\beta, \tag{7}$$

where the exponent β is independent of the value of q. The best fit was obtained with the exponent $\beta = 0.6 \pm 0.053$. The average cluster size $\langle S \rangle$ is defined as the ratio of the second and first moment of the cluster size distribution

$$\langle S \rangle = \frac{\sum_S S^2 n_S(\phi_S)}{\sum_S S n_S(\phi_S)}, \tag{8}$$

where n_S is the number of clusters of size S. We found that $\langle S \rangle$ has a significant peak at $\phi_S^*(q)$ for all values of q. Fig. $4(b)$ presents that the average cluster size has also a power law dependence on both sides of the critical point

$$\langle S \rangle \sim |\phi_S - \phi_S^*|^{-\gamma}, \tag{9}$$

which defines the γ exponent of the transition. It is important to emphasize that the value of $\gamma = 1.224 \pm 0.027$ is independent of the construction parameter q. Simulations showed that the cluster size distribution n_S, i.e. number of clusters containing S particles has also a power law functional form in the vicinity of the transition point $n_S \sim S^{-\tau}$ (not presented here for brevity), where the numerical value of the exponent was obtained by fitting $\tau = 2.185 \pm 0.085$.

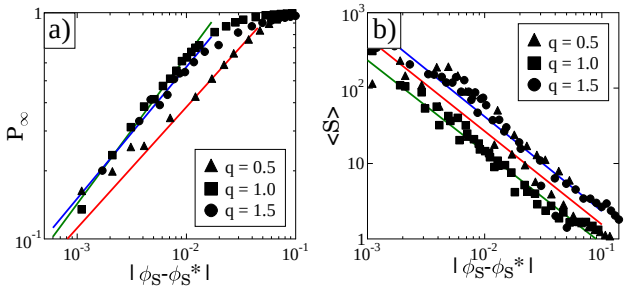

Figure 4: (a) The strength of percolation P_∞ as a function of $\phi_S - \phi_S^*$ on a double logarithmic plot at different q values. (b) The average cluster size $\langle S \rangle$ as a function of the distance from the critical point. Good quality power laws are obtained for both quantities, where the exponents are independent of the value of q.

Our analysis showed that the critical exponents characterizing the percolation transition in our porous system are different from the standard exponents of continuous percolation in three dimensions [7]. It is an important feature of the exponents that they fulfill the well-known scaling relation $\tau = 2 + \beta/(\beta + \gamma)$ within the error bars.

3.2. Porous structure

Our main goal is to use the void expansion method for the computational investigation of aerogels. At a given parameter set, after removing the void particles the system may be composed of a large number of disconnected clusters. To ensure the connected structure for the modeling of aerogels, we select only the percolating cluster which spans between opposite walls of the sample, i.e. for aerogels we only use the supercritical phase of VEM. To be able to make comparison to real aerogel structures - assuming that particle arches are responsible for the mechanical stability of aerogels - those particles which are not important from this point of view are removed from the percolating cluster.

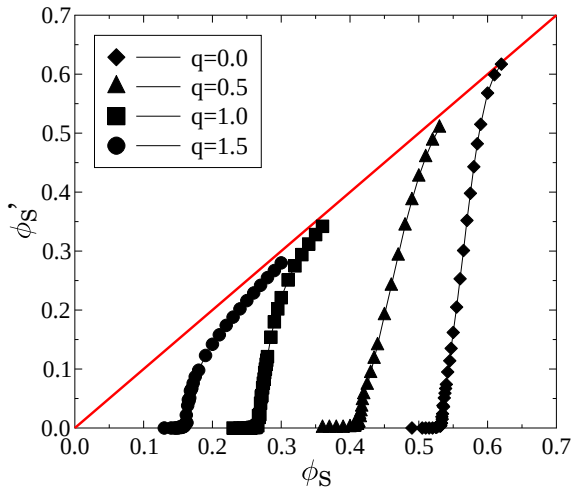

Figure 5: The volume fraction ϕ_S' of the truncated system as a function of initial volume fraction ϕ_S. It can be seen that if ϕ_S is close to the percolation threshold but above it the value of ϕ_S' can be very low as in real aerogels [1, 2, 3]. The continuous red line has slope 1.

These are single particles or tail-like particle chains (dangling ends) which have only one connection to the main body of the spanning cluster. Figure 5 shows the volume fraction ϕ_S' of the truncated cluster as a function of the initial volume fraction before removing dangling ends. It is interesting to note that this way volume fractions can be obtained close to the measured characteristics of real aerogels ~ 0.05 [1, 2, 3] showing the capabilities of the approach to model structures of vary large porosity. Note that in Fig. 5 all the curves obtained at different values of q tend to the continuous red line which has slope one. This indicates that at higher volume fraction the truncation implies less and less change in the volume fraction of the spanning cluster.

In order to get a more detailed quantitative characterization of the truncated structure we calculated its fractal dimension by means of the sand-box method: we calculated the average number of particles M of the cluster falling inside spheres of radius R which are centered on the particles. In Figure 6 the function $M(R)$ is presented for several values of ϕ_S. The functional form of $M(R)$ can be well described by power laws

$$M(R) \sim R^D, \tag{10}$$

where the exponent D defines the fractal dimension of the system. We found that on length scales larger than $2R_S + 2R_V$, far from the critical volume fraction but above, the percolating cluster is nearly space-filling $D = 3$. However, close to the critical point the system has a fractal structure characterized by a fractal dimension $D = 2.24 \pm 0.07$ lower than the dimension of the embedding space d, see Fig. 6. At ϕ_S below the critical point there is no spanning cluster so the $M(R)$ function goes to saturation.

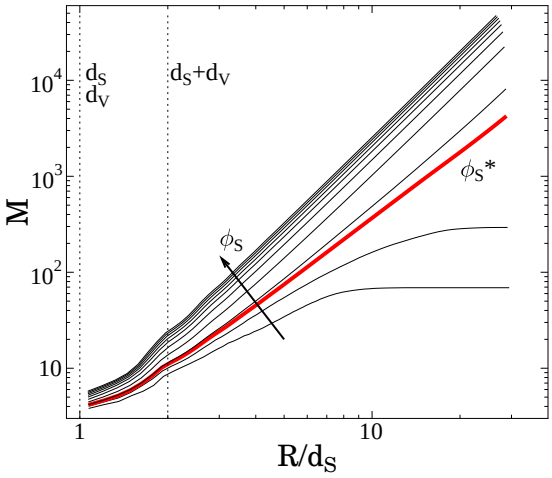

Figure 6: The number M of particles falling inside spheres of radius R which are centered on the particles. $M(R)$ has a power law behavior above the particle size scale. At high concentration the slope of the function is 3 showing the space-filling nature of the cluster, however, close to the critical point ϕ_S^* the cluster proved to have a fractal structure. Here d_S and d_V denotes the diameter of the structural and void particles.

The fractal dimension is a global characteristics of the cluster's structure. In order to understand the mechanical stability of the cluster, a more detailed microscopic analysis is needed. For this purpose we determined the average coordination number of the particles, i.e. the average number of contacts of the particles $\langle CN \rangle$. During the truncation process the tail-like parts were removed from the spanning cluster, hence, there are no particles without neighbors $CN = 0$ or with only one neighbor $CN = 1$. Simulations revealed that close to the critical point most of the particles have 2 or 3 neighbors, however, at higher initial volume friction the coordination number has a broader scatter.

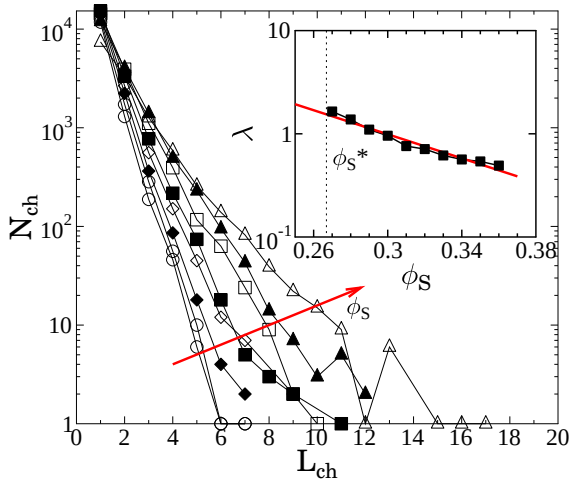

Figure 7: Probability distribution of the chain length on a semi-logarithmic plot. The straight line shows that the functional form is exponential, where the slope depends on the volume fraction ϕ_S. Inset: The coefficient λ is an exponentially decreasing function of ϕ_S for the regime $\phi_S > \phi_S*$.

The low value of average coordination number of the particles inside the spanning cluster shows that the system is built up

from short particle chains in agreement with experimental findings on aerogels [1, 2]. A chain can be defined in such a way that inside a chain all particles have two contacts and the chain is closed by two particles with more than two connections. We define the chain length L_{ch} as the number of those particles which have coordination number $CN = 2$, i.e. the junctions are not members of the chain. It can be observed in Fig. 7 that the probability distribution of chain length $N_{ch}(L_{ch})$ has an exponential decay

$$N_{ch}(L_{ch}) \sim \exp\left[-L_{ch}/\lambda\right], \tag{11}$$

where λ is a scale parameter being proportional to the average chain length. The figure shows that the value of λ depends on the initial volume fraction ϕ_S, i.e. increasing ϕ_S longer chains more frequently emerge in the system because they are able to bridge larger distances between voids. The inset of the figure presents that λ decreases as an exponential function of ϕ_S above the percolation threshold. This chainy structure is one of the main source of the high porosity of the structure. It is interesting note that the chains are not straight because they are formed along the curved surface of void particles. This way our construction method can naturally account for arching of the particles which is important for the structural stability of the system again mechanical loading.

4. Summary

Aerogels are solid materials with the lowest volume fraction. They exhibit a broad spectrum of unique features which make them candidates for a multitude of future applications. Experimental investigations performed during the last decade have accumulated a large amount of information on the micro-structure, mechanical response, chemical, and electro-magnetic features, however, theoretical explanations are still lacking.

For the computer modelling of aerogels it is crutial to work out numerical methods which are able to reproduce the key features of the structure. In the present paper we demonsrated that using the void expansion method it is possible to generate porose structures with a controllable volume fraction. We showed that when changing the paramegters of the construction a structural transition emerges in the system similar to percolation. We carried out a detailed analysis of the percolation transition and showed that it is different from continuous percolation characterized by unique values of the critical exponents. Calculations revealed that the spanning cluster above the critical point is a good candidate to model aerogels with a controllable volume fraction falling in the range of experimental values.

We demonstrated that the underlying mechanism behind the high level of porosity is the chaining of the particles, i.e. the particles form chains whose length can span broad range. The length distribution proved to be exponential.

The results serve as input for future investigations of the mechanical properties of aerogels, where between the particles we introduce appropriate introductions.

Acknowledgments

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