Distribution function analysis of the structure of depleted particle configurations

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We present an analysis of the n-particle distribution functions of a material constructed via random depletion of an arbitrary quenched state (of an equilibrium or nonequilibrium system). We show that the structure, as measured by the distribution functions $g^{(n)}(\mathbf{r}_1,\mathbf{r}_2, \ldots,\mathbf{r}_n;\rho)$, is unchanged by the depletion process. Low-density configurations can thus be created with nontrivial spatial correlations inherited from a higher-density fluid. We show that this leads to an enhanced void volume and discuss implications to an irreversible adsorption process. [S1063-651X(97)50208-X]

PACS number(s): 68.10.Jy, 02.50.−r. 05.20.−y

Recently, considerable interest has been expressed in idealized materials consisting of immobile particles [1]. Quenches from an equilibrium configuration or a nonequilibrium sequential addition process represent means of realizing such systems. Physical examples include porous materials formed by a quick freeze of a gel-like liquid and systems of irreversibly adsorbed particles such as proteins and colloids. Depleting these systems of some of the constituent particles is possible through desorption or dissolution. As the resulting structure of this lower-density system is expected to differ from that of a system quenched at the lower density, depletion allows for the realization of materials with new structural characteristics.

The structure of a system of N identical particles is fully characterized by the set of n-particle density functions $\rho^{(n)}(\mathbf{r}_1,\mathbf{r}_2, \ldots,\mathbf{r}_n;\rho)$ representing the joint-probability density of finding n unspecified particles, among the N particles composing the system, at the positions $\mathbf{r}_1,\mathbf{r}_2, \ldots,\mathbf{r}_n$ where ρ is the particle number density [2]. These are related to the distribution functions $g^{(n)}(\mathbf{r}_1,\mathbf{r}_2, \ldots,\mathbf{r}_n;\rho)$ by $\rho^n g^{(n)}(\mathbf{r}_1,\mathbf{r}_2, \ldots,\mathbf{r}_n;\rho)=\rho^{(n)}(\mathbf{r}_1,\mathbf{r}_2, \ldots,\mathbf{r}_n;\rho)$. Considerable effort has been made to obtain exact or approximate expressions for the distribution functions of equilibrium and nonequilibrium fluids. In the former, knowledge of the $g^{(n)}$'s allows for the determination of all the thermodynamic properties of the fluid. In the latter, the $g^{(n)}$'s may be useful in determining void volumes or transport properties. Additionally, as $g^{(2)}$ is often experimentally available via scattering techniques, its determination can give physical insight into the intermolecular potential or the formation history of the material.

In this Rapid Communication, we present an analysis of the distribution functions of a particle configuration obtained by depletion of a higher-density quenched fluid. Physical examples of depletion include desorption in two dimensions and partial dissolution in three dimensions. We show that the structure, as measured by $g^{(n)}$, is unchanged by a uniform random depletion process and we use this result to predict an enhanced void volume in an irreversible adsorption process.

Depletion is a process that results in the removal of a fraction of the particles from an initial quenched configuration at a density ρ_1 and proceeds until a final density ρ_2 is achieved. During the depletion process, the remaining particles do not move in space and their density evolves according to

$$\frac{d\rho}{dt} = -\rho/\tau, \qquad (1)$$

where τ is the characteristic time of the depletion process. Therefore, if the particles are removed at random, the pair density function evolves according to

$$\frac{\partial\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\rho)}{\partial t} = -2\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\rho)/\tau, \qquad (2)$$

where the factor 2 results from the removal of a particle at either position $\mathbf{r}_1$ or position $\mathbf{r}_2$. We emphasize that Eq. (1) involves no assumption other than first-order kinetics while in Eq. (2) no explicit dependence on intermolecular interaction is given. It follows from these two equations that

$$\frac{\partial\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\rho)}{\partial\rho} = \frac{2}{\rho}\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\rho). \qquad (3)$$

The above equation can be re-expressed as

$$\frac{\partial[\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\rho)/\rho^2]}{\partial\rho} = \frac{\partial[g^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\rho)]}{\partial\rho} = 0, \qquad (4)$$

which means that the pair distribution function $g^{(2)}(\mathbf{r}_1,\mathbf{r}_2;\rho)$ is conserved along the depletion process (but not the pair density function). More generally, the n-particle density functions evolve as

$$\frac{\partial\rho^{(n)}(\mathbf{r}_1,\mathbf{r}_2, \ldots,n,\rho)}{\partial\rho} = \frac{n}{\rho}\rho^{(n)}(\mathbf{r}_1,\mathbf{r}_2, \ldots,n,\rho), \qquad (5)$$

where n corresponds to the n possibilities of removing one particle among n particles. This leads to ga conservation of the distribution functions and, therefore, of the correlations in the system, so long as the particles are removed randomly. A similar line of reasoning can be applied to show that the

distribution functions of a multicomponent quenched mixture are unchanged by a random depletion of all species or by a random depletion applied only to some of the species.

An application of this result is to two-dimensional systems of adsorbed particles. If disk-shaped particles adsorb sequentially, without overlap, at random positions on a surface [i.e., the random sequential adsorption (RSA) model [3]], the kinetics obey the following law:

$$\frac{\partial \rho}{\partial t} = k_a c \Phi(\rho), \qquad (6)$$

where $k_a c$ is the adsorption rate constant and $\Phi(\rho)$ is the fractional available surface function given by [5,6]

$$\Phi(\rho) = 1 + \rho \int d2 \ f_{12} + \frac{1}{2} \int d2 \ d3 f_{12} f_{13} \rho^{(2)}(2,3,\rho)$$

$$+ \frac{1}{3!} \int d2 \ d3 \ d4 f_{12} f_{13} f_{14} \rho^{(3)}(2,3,4,\rho) + \cdots, \qquad (7)$$

where the f's are Mayer f functions. For an RSA process onto an initially empty surface, to obtain a third-order density expansion of Φ, $g^{(2)}$ and $g^{(3)}$ are needed to first and zeroth order, respectively, i.e. [4],

$$g^{(2)}(1,2;\rho) = [1 + f_{12}]\left[1 + \tfrac{2}{3}\rho \int d3 f_{13} f_{23}\right], \qquad (8)$$

$$g^{(3)}(1,2,3;\rho) = (1 + f_{12})(1 + f_{23})(1 + f_{13}). \qquad (9)$$

Our result indicates that if adsorption initially proceeds to ρ_1, followed by a desorption stage to ρ_2 (for instance, by replacing the protein solution by a buffer solution), the available surface function $\Phi(\rho|\rho_1)$ during the desorption step is obtained by inserting $g^{(2)}(1,2;\rho_1)$ from Eq. (8) into Eq. (7):

$$\Phi(\rho) = 1 + \rho \int d2 f_{12} + \frac{1}{2}\rho^2 \int d2 \ d3 \ f_{12} f_{13}(1 + f_{23})$$

$$+ \frac{1}{3}[\rho^3 + \rho^2(\rho_1 - \rho)] \int d2 \ d3 \ d4 \ f_{12} f_{13} f_{34} f_{24}$$

$$\times (1 + f_{23}) + \frac{1}{6}\rho^3 \int d2 \ d3 \ d4 \ f_{12} f_{13} f_{14}(1 + f_{23})$$

$$\times (1 + f_{24})(1 + f_{34}) + O(\rho^4)$$

$$= \Phi_{\mathrm{RSA}}(\rho) + A\rho^2(\rho_1 - \rho), \quad \rho_1 \geq \rho \geq \rho_2. \qquad (10)$$

In Eq. (10), Φ_{RSA} denotes the available surface function for an RSA process starting with an initially empty surface and A has a known value of $64/(3\pi^2)[\pi\sqrt{3} - 9/2]$ [4]. Thus, to third order in density, the fractional available surface for a particle to adsorb is just that of the standard RSA process plus a correction term that is itself third order in density ρ. Figure 1 shows $\Phi(\rho)$ before and during the desorption step. We note that the fractional available surface area is larger after the desorption step than it was at the same density during the initial adsorption phase. This is a consequence of the structure being inherited from a higher-density configuration.
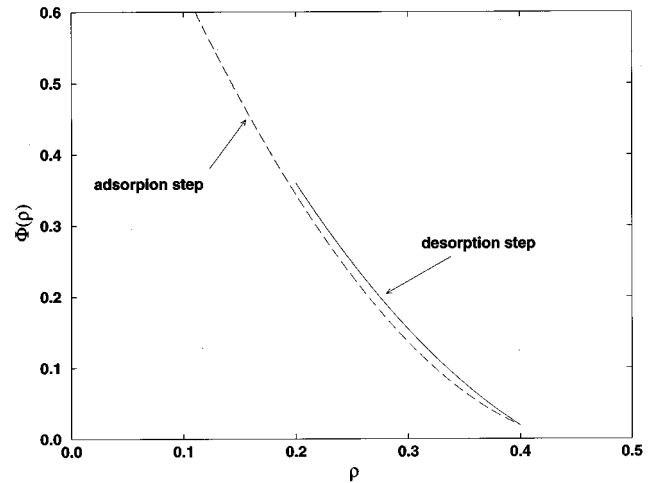

FIG. 1. The fractional available surface $\Phi(\rho)$ versus ρ. The dashed curve corresponds to adsorption process up to $\rho = 0.4$ and the full curve to a uniform desorption process beginning at $\rho_1 = 0.4$.

We point out that void volume enhancement would also occur if the original configuration were obtained by a quench of an equilibrium fluid.

An interesting implication of this work is the possibility of realizing disordered materials at one density whose spatial correlations are those of a material at a much higher density. For example, configurations of hard spheres at a (low) density ρ_2, where $g^{(2)}(r)$ would normally be near unity for $r \geq \sigma$, can be realized with a $g(r)$ reminiscent of a (high) density ρ_1, i.e., with a large contact value and appreciable second and third peaks. Similarly, by depleting an RSA configuration near its saturation (jamming) limit, one could obtain a very low-density state with a $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \rho)$ that diverges at contact. This enhanced structure at low density is consistent with a greater fraction of void space. As it is known that the diffusivity of a mobile phase in a porous medium is very sensitive to void volume, even the small changes seen in Fig. 1 could give rise to a largely different mobile phase mobility.

Our result implies that if particles desorb randomly, then one knows the structure of the depleted configuration. This can serve as the starting point for an approximate theory of the ensuing kinetics when the adsorption process is restarted. The enhanced void volume achieved during the removal step leads to a more efficient filling of space when more particles are added during a second addition step. An enhancement in the final saturation coverage is predicted using such an approach and this is confirmed by numerical simulations [7]. This is consistent with recent experiments showing enhanced surface filling following a desorption step [8]. Conversely, if the correlations of the depleted (quenched) configurations are unchanged after partial desorption, one can conclude that the desorption is random.

Use of this result potentially allows a greater flexibility in calculating $g^{(2)}(r)$ from configurations generated by a simulation or obtained from an image analysis of adsorbed configurations. Typically, one averages over both the particles within a given configuration as well as over independent

configurations. We show here that one is not required to use all particle coordinates in a given configuration. It may be advantageous to use more independent configurations, selecting at random only a fraction of particles from each.

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