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Physica A 330 (2003) 189–194

PHYSICA A

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Glasses and local packings

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Abstract

A cell theory for glassforming liquids, amorphous solids and granular packings, is developed by combining geometrical properties of local packings with the ideas of inherent structures and free volume theory. We show that for hard-spheres the present theory reproduces well the equation of state, the approach to zero of the configurational entropy and the divergence of large relaxation times following both the Vogel–Tammann–Fulcher behavior and the Adam–Gibbs relation.

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PACS: 05.20.-y; 61.43.Fs

Keywords: Glasses; Supercooled liquids; Granular matter; Sphere packings

1. Introduction

Glasses have been described by several valuable theories based on free volume [1], cooperative rearrangements of particles [2], inherent structures approach [3–5], mode coupling theory [6], replica theory [7]. Here we present a novel approach (which combines some of the features of free volume [1] and the inherent structures approach [3]) to derive the structural and dynamical properties of large systems of interacting particles from the local geometrical properties of space-filling sets of cells.

A useful concept in glass theory based on the idea of energy landscape has been introduced by Goldstein in 1969 and developed by Stillinger and Weber [3] in 1982. The energy landscape is associated to potential energy $U(\{\mathbf{r}_i\})$ as function of the $3N$ particles coordinates. The idea is that in supercooled liquids this energy landscape is characterized by deep minima and at low temperatures the particles vibrates around

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these deep minima with some jumps from one minimum to another. In molecular dynamics simulations these minima are called “inherent structures” [3]. If the minima are labeled by the index α and F^α is the free energy relative to the metastable state α , the partition function Q can be written as $Q = \sum_\alpha e^{-\beta F^\alpha} = \sum_F \Omega(F) e^{-\beta F}$. Here, $\Omega(F)$ is the number of states with free energy F and it is related to the configurational entropy $S_{conf}(F) = \ln \Omega(F)$ with the equilibrium condition given by $\beta = \partial S_{conf}(F) / \partial F$. Theoretical studies [8] and molecular dynamics techniques [5,8] show that at low temperature S_{conf} is a decreasing function of the temperature and it can be extrapolated to zero at a temperature T_K , as expected by the Kauzmann’s argument.

An interesting connection between kinetics and thermodynamics has been provided by Adam and Gibbs, by introducing the concept of cooperatively rearranging regions. According to this phenomenological theory, at low temperature, relaxation can only occur if an entire region of minimum size undergoes a cooperative rearrangement. Since this minimum size can be related to the inverse of the configurational entropy, it follows that the relaxation time τ can be expressed as $\tau \sim A \exp(B/Ts_c)$, where $s_c = S_{conf}/N$ is the configurational entropy per particle and A and B are constants. If s_c goes linearly to zero at the Kauzmann temperature T_K one recovers the Vogel–Tammann–Fulcher relation [9] $\tau \sim A' \exp(B'/(T - T_{VF}))$, with $T_{VF} = T_K$. In this way the Adam–Gibbs theory predicts that if there is a thermodynamical transition where the configurational entropy goes to zero, then at this temperature the relaxation time—or the viscosity—diverges according to the Vogel–Tammann–Fulcher relation, as found in many glass formers and in agreements with recent experiments in colloid systems [10].

2. Cell theory

Let us first identify the set of positions $\{\mathbf{r}_1^\alpha, \mathbf{r}_2^\alpha, \dots, \mathbf{r}_N^\alpha\}$ in which the probability to find the particles is a local maxima. This set of positions is a *point* in the $3N$ -dimensional configuration space. Let us now identify a region \mathcal{B}^α around this point which corresponds to the region of small displacements around the metastable equilibrium positions. The partition function for the N particles in a volume V can be written as

$$Q = \sum_\alpha e^{-\beta F^\alpha} = \sum_\alpha \frac{1}{N! A^{3N}} \int \dots \int_{\mathcal{B}^\alpha} e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)} d\mathbf{r}_1 \dots d\mathbf{r}_N \quad (1)$$

where $A = h/(2\pi m k_B T)^{1/2}$ and $\beta = (k_B T)^{-1}$, with T the temperature, m the particle-mass. Note that, if the regions \mathcal{B}^α do not overlap and if the $3N$ -dimensional configurational space is entirely tiled by the set of \mathcal{B}^α , then Eq. (1) is an *exact* way to write the configurational integral.

For a given α , we divide the volume V into N cells $C_1^\alpha, \dots, C_N^\alpha$ constructed around the positions $\mathbf{r}_1^\alpha, \dots, \mathbf{r}_N^\alpha$. In this way we associate to each state α a cellular space-partition which reflects the structure of the metastable configurations. Each cell C_i^α is characterized by a set of parameters \mathbf{n}_i^α which carry the complete information about its geometrical and topological properties (size, shape, etc). The volume of cell C_i^α is $v(\mathbf{n}_i^\alpha) = \int_{C_i^\alpha} 1 d\mathbf{r}$ and the total volume is: $V = \sum_i v(\mathbf{n}_i^\alpha)$. We find that, for two-body

interactions and under an Hatree-like approximation (see [11]), the expression for F^α can be written in terms of the local properties of the cells C_i^α

$$F^\alpha \simeq \sum_i \varepsilon(\mathbf{n}_i^\alpha) - k_B T \left[\ln \frac{u(\mathbf{n}_i^\alpha)}{A^3} - \ln \mathcal{P}(\mathbf{n}_i^\alpha) \right] \tag{2}$$

with $\varepsilon(\mathbf{n}_i^\alpha)$ the energy contribution from a particle in the cell C_i^α , $u(\mathbf{n}_i^\alpha)$ the ‘free volume’ [11,12] associated with the cell C_i^α and with $\mathcal{P}(\mathbf{n}_i^\alpha)$ the probability of finding cell ‘ i ’ singly occupied. Note that the free energy depends only on the distribution $N^\alpha(\mathbf{n})$: the number of cells, in the space-partition α , characterized by the set of geometrical and topological parameters \mathbf{n} . Therefore, we have $F^\alpha = F(\{N^\alpha(\mathbf{n})\})$. It follows that the sum over the states α in Eq. (1) can be written as a sum over the space-partitions $\{N^\alpha(\mathbf{n})\}$ associated with these states

$$Q = \sum_\alpha e^{-\beta F(\{N^\alpha(\mathbf{n})\})} = \sum_{\{N(\mathbf{n})\}} \Omega(\{N(\mathbf{n})\}) e^{-\beta F(\{N(\mathbf{n})\})}, \tag{3}$$

where $\Omega(\{N(\mathbf{n})\})$ counts the number of distinct space-partitions made with the set $\{N(\mathbf{n})\}$. A rough approximation gives

$$\Omega(\{N(\mathbf{n})\}) \simeq \frac{N!}{\prod_{\mathbf{n}} N(\mathbf{n})!}, \tag{4}$$

which is an upperbound for Ω , since some of these combinations do not generate space-filling assemblies and others might be associated with overlapping regions in the phase-space.

The typical distribution $N^*(\mathbf{n})$ can now be evaluated by minimizing the free energy

$$\frac{N^*(\mathbf{n})}{N} = \frac{u(\mathbf{n})}{A^3 \mathcal{P}(\mathbf{n})} \exp[-\beta \varepsilon(\mathbf{n}) - \theta v(\mathbf{n}) - \lambda]. \tag{5}$$

Here, the two parameters λ and θ are Lagrange multiplier which are fixed by the two constraints: $\sum_{\mathbf{n}} N^*(\mathbf{n}) = N$ and $\sum_{\mathbf{n}} v(\mathbf{n}) N^*(\mathbf{n}) = V$.

Using this distribution, the saddle-point estimation of the free energy is

$$\frac{\ln Z}{N} = -\beta \sum_{\mathbf{n}} \frac{N^*(\mathbf{n})}{N} \left[\varepsilon(\mathbf{n}) - kT \left(\ln \frac{u(\mathbf{n})}{A^3 \mathcal{P}(\mathbf{n})} - \ln \frac{N^*(\mathbf{n})}{N} \right) \right]. \tag{6}$$

3. Hard spheres

From Eqs. (5) and (6) it is clear that the thermodynamical properties of the system can be retrieved from local geometrical properties only: (1) the volume $v(\mathbf{n}_i)$; (2) the free-volume $u(\mathbf{n}_i)$; (3) the caging-probability $\mathcal{P}(\mathbf{n}_i)$. ($\varepsilon(\mathbf{n}_i) = 0$ for hard spheres). We identify the cell C_i^α , with the Voronoi cell (also known as Wigner–Seitz cell or Dirichlet region) generated by bi-setting with planes the segments between the center of sphere ‘ i ’ and the centers of its neighboring spheres [16]. We explore extensively the attainable local configurations by generating more than 10^6 compact local configurations with one central sphere and a number of neighboring spheres between $5 \leq n \leq 16$ placed disorderly (but avoiding overlapping) at equal distance h_0 from the central one. Then

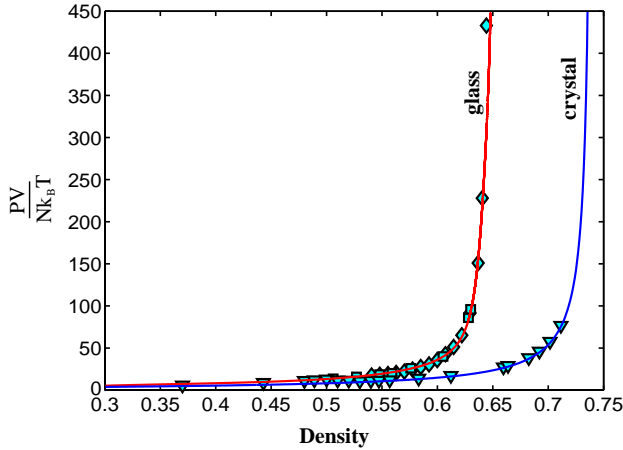


Fig. 1. Comparison between $PV/Nk_B T$ from molecular dynamics simulations for the ordered-FCC branch [13] (triangles down), the disordered-glassy branch [13] (squares) [14] (lozenges) and the predictions from the present theory (full-lines).

we generate larger cells by uniformly expanding the compact ones from h_0 to $\sqrt{2}h_0$. The distance h_0 is a measure of the geometrical frustration [15–17] and it has been fixed at $h_0 = 1.058d$ (with d the sphere-diameters).

Once obtained $v(\mathbf{n}_i)$, $u(\mathbf{n}_i)$ and $\mathcal{P}(\mathbf{n}_i)$, we derive the distribution of cells from Eq. (5) and therefore the free energy from Eq. (6), from which the equation of state: $P = k_B T (\partial \ln \Omega / \partial V)_{N,T}$. The comparison with data from molecular dynamics simulations for hard spheres [13,14] is shown in Fig. 1.

Within the framework of the present theory we can also investigate the crystalline case. This case is simpler to treat analytically because only identical rhombic-dodecahedral cells are involved. We have

$$\frac{PV}{k_B NT} = \frac{1}{1 - ((\sqrt{18}/\pi)\rho)^{1/3}}. \quad (7)$$

The comparison with the molecular dynamics simulation data is also shown in Fig. 1.

Using the distribution $N^*(\mathbf{n})$ we calculate the escaping probability $\langle \mathcal{P}_{esc} \rangle = \sum_{\mathbf{n}} (N^*(\mathbf{n}) / N) \mathcal{P}_{esc}(\mathbf{n})$, where $\mathcal{P}_{esc}(\mathbf{n}) = 1$ or 0 depending on whether the configuration of the cell \mathbf{n} is such that the external spheres allow or not the sphere inside the cell to escape. We observe that the relaxation time $\tau = \langle \mathcal{P}_{esc} \rangle^{-1}$ has a behavior vs. density which is well described with a Vogel–Tammann–Fulcher equation: $\tau \sim A \exp(B/(\rho_{VF} - \rho))$ with $\rho_{VF} = \rho_K \simeq 0.65$ (Fig. 2a). We have also calculate the configurational entropy per particle $s_c = \ln \Omega / N$ which goes to zero at the Kauzmann density $\rho_K \simeq \rho_{VF} \simeq 0.65$ (Fig. 2b). Moreover, we verify that the definition of s_c is consistent with the definition of the configurational entropy as the difference between the entropies of the glass and crystalline phases (Fig. 2b). We finally observe that the Adam–Gibbs relation: $\tau \sim A' \exp(B'/(Ts_c))$ is followed (Fig. 2a).

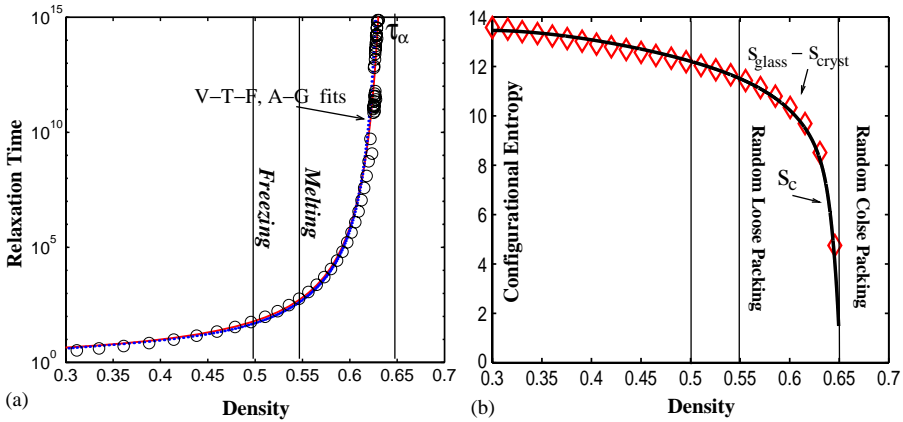


Fig. 2. (a) Semi-log plots of the characteristic relaxation time τ_α vs. ρ . The lines are fits with Vogel–Tammann–Fulcher and Adam–Gibbs behaviors (full- and dotted-lines); (b) configurational entropy vs. ρ (line) and the difference between the entropies of the disordered and crystalline phases (lozenges).

4. Conclusions

We have presented a theory which combines some of the features of the free volume and inherent structures approach. Its application to hard spheres system, in spite of some approximation involved, gives results in very good agreement with molecular dynamics data. Moreover, the theory reproduces well the Voghel–Fulcher–Tamman law, the Adam–Gibbs relations and the Kauzmann’s behavior for the configurational entropy.

We point out that the main approximation in this work is the identification of the number of possible configurations with the combinatorial factor $N! / \prod_{\mathbf{n}} N(\mathbf{n})$. This approximation ignores geometrical frustration and overlaps in the configuration-space. To obtain a better approximation one should go beyond the single cell and consider a larger group of cells as a basic unit (supercell). The larger the supercell the better would be the approximation.

Acknowledgements

We would like to dedicate this paper to Shlomo Havlin, who has made so many contributions in the field of complex and disordered systems. This work has been partially supported by the European TMR Network-Fractals No. FMRXCT980183, by INFM PRA-HOP 99 by MURST PRIN-2000 and by MIUR FIRB-2002.

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