COMPUTATION OF COMPLEXITY FOR THE STRUCTURAL GLASS TRANSITION USING THE REPLICA FIELD APPROACH

Trideep Rajbhar[1], Raj Kumar Gupta[1], Prakash Vardhan[2*]

Abstract

We investigate the microscopic replica field theory for the unquenched disordered system. A scenario of spontaneous ergodicity breaking is used to analyse the abrupt decrease in configurational entropy of a many-particle system, in which the free energy landscape of the system divides into many basins of local minima. We make use of the nonlocal free energy functional of Ramakrishnan and Yussouff's DFT that takes the cubic order of density fluctuation into account. In the present paper, we compute complexity S_c of the deep supercooled liquid state using the replica field theory of Parisi and Monasson. The Kauzmann point η_k is obtained from decline of S_c with increasing density. The model's calculated Kauzmann point, η_k, agrees with prior studies.

[1]Sardar Vallabhbhai Patel College, Bhabua, Department of Physics,Veer kunwar Singh University, Ara 282004, Bihar, India
[2*]Visiting faculty, SVP College, Bhabua, Khaimur, Bihar, al091188@gmail.com (Dated: May 22, 2023)

Corresponding Author: Prakash Vardhan
*Visiting faculty, SVP College, Bhabua, Khaimur, Bihar, al091188@gmail.com (Dated: May 22, 2023)

I.INTRODUCTION

Decades of theoretical and experimental research have been focused on understanding the non-ergodic state and entropy paradox that frequently occur in spin glass [1] and structural glass systems [1-4]. It has remained difficult to really understand how a metastable liquid turns into an amorphous solid with rigidity. Above the freezing point T_m the disordered liquid phase has single global free energy minima. As we decrease the temperature (or density) well below T_m, the free energy landscape fragments into many states so called metastable states. The supercooled liquid get trapped in a deep minima of the free en-ergy. Such transformation in supercooled liquid leads to sponataneous breaking of ergodicity.

In this paper, we employ replica field theory to understand behaviour of sluggish liquids via sponataneous breaking of ergodicity and complexity of the metastable liquids. As we increase density (packing fraction), viscosity increases rapidly results in diverging relaxation time and a dynamic crossover is seen [4]. In the present work, we computed the complexity of metastable liquids. As we go below the freezing point, a strong correlation developed between the metastable liquids. We demonstrate how ergodicity spontaneously breaks down and complexity declines as density rises in the context of a hard sphere system. We extrapolate complexity S_c to zero in order to determine the Kauzmann point η_k [8,9].

II.REPLICA FIELD MODEL

In the present work, we consider three dimensional hard sphere liquid of particles in a volume V. In a continuum field-theoretic description, the minima corresponding to the various FEL basins are specified in terms of the function space of density field $\rho(z)$. The system's equilibrium free energy is calculated as a functional integral over ρ:

$$\mathcal{F}(T) = -k_B T \ln \int \mathcal{D}\rho(z) e^{-\frac{\mathcal{H}[\rho]}{k_B T}} . \quad (1)$$

H represents the microscopic Hamiltonian as a functional of density field ρ. By introducing an externally quenched pinning field $\psi(z)$ [6,7] coupled to $\rho(z)$ with a coupling $g > 0$, the free-energy values at the bottom of the associated valley are picked up. The corresponding free energy [2] is then obtained as:

$$\mathcal{F}_\psi[g,T] = -k_B T \ln \int \mathcal{D}\rho(z) \exp\left\{ -\frac{\mathcal{H}[\rho]}{k_B T} - \frac{g}{2} \int [\psi(z) - \rho(z)]^2 dz \right\} . \quad (2)$$

An equilibrium state is provided by the derivative of the free energy functional with respect to the density field $\rho(z)$. According to the assumptions [1,2], ergodicity breaking happens as long as crystallisation is avoided at fairly high densities c below the freezing point of liquids. Ergodicity breakdown causes the underlying FEL to split up into numerous local minimas for metastable states. Through the groundbreaking work of Monasson [2], it is possible to count how many minima that $\rho(x)$ provides contribute to the system's partition function. With a coupling constant term g, a symmetry breaking field $\psi(z)$ is related to $\rho(z)$ quadratically. When $\psi(z)$ is equal to the configuration $\rho(z)$, the free energy functional F is at its lowest value. Take into account a system of n replicas of the original system, which is denoted by $\{\rho^k\} = \{\rho^1\}\{\rho^2\}\{\rho^3\}\cdots\{\rho^n\}$. The contribution from minima of various metastable states in the FEL is picked up by spanning the ρ's function space. The relevant free energy results from treating F as a Hamiltonian as:

$$\mathcal{F}(mT) = -k_B T \lim_{g \to 0^+} \ln\left[\int \prod_{a=1}^{n} \mathcal{D}\rho^a(z) \exp\left\{ \beta \sum_{a=1}^{n} \mathcal{H}[\rho^a] - \frac{g}{2n} \sum_{a<b} \int \{\rho^a(z) - \rho^b(z)\}^2 dz \right\} \right] . \quad (3)$$

at a certain temperature nT, where n is a positive integer. The coupling term g drives all replicas to stay in the same meta-stable minima of the FEL, which eventually results in the glass phase after putting $g \to 0$. The corresponding internal energy at temperature nT is, $\mathcal{U}(n,T) = \frac{\partial}{\partial n}\{n\mathcal{F}[n,T]\}$, treating T as a constant and n being variable. In the limit $n \to 1$, the complexity of the metastable liquid can be obtained as: $S_c = T^{\frac{\partial^2}{\partial n^2}} F[n,T]|_{n=1}$

III. CALCULATION OF COMPLEXITY

In the n identical replica space, the two-point correlation matrix is defined as: $G_{ab}(x - y) = <\delta\rho^a(x)\delta\rho^b(y)>$. Direct matrix G is built in replica space using diagonal and offdiagonal components, for example, $G^{ab} = (G-F)\mathbf{I_{aa}} + F\mathbf{E_{ab}}$. $\mathbf{I_{aa}}$ is an identity matrix of size n by n, and $\mathbf{E_{ab}}$ is a matrix whose elements are all of the same size and equals to unity. We derived a two-point correlation function in polynomial expansion form by using free energy functional in addition to an external field ξ, follows as:

$$\mathcal{H}_\xi[\Phi] = \frac{1}{2}\sum_{1,2}\mathcal{G}_0^{-1}(12)\Phi(1)\Phi(2) + \frac{1}{3}\sum_{1,2,3}B(123)\Phi(1)\Phi(2)\Phi(3) - \sum_1\xi(1)\Phi(1)$$
. 4)

where we denote field $\Phi(1) \equiv \delta\rho^k(z)$, with $k = 1$, to n, and spatial point x_1 denoted by 1. The Gaussian matrix, and symmetrized cubic vertex $B(123)$ are obtained in terms of the direct correlation functions $c^{(2)}(12)$ and $c^{(3)}(123)$, using Ramakrishnan-Youssouff free energy functional [6]. Ramakrishnan-Youssouff [6] free energy functional is used to derive the Gaussian matrix $\mathcal{G}_0^{-1}$ and symmetrized cubic vertex $B(123)$ in terms of the direct correlation functions c^2 and c^3. The

correction to zeroth order correlation function G_0 is provided by non-linear term and replicated Schwinger Dyson's equation is obtained as, $\mathcal{G}^{-1\,ab} = \mathcal{G}_0^{-1\,ab} - \Sigma_{ab}$. In the n replica space, Σ has similar structure to matrix G, with Σ_G and Σ_F denoting diagonal and off diagonal elements respectively. Comparing the SchwingerDyson's eqn with direct matrix G in the limit $n \to 1$ leads to self consistent off diagonal correlation function,

$$F(k) = G(k) - \kappa(k) \tag{5}$$

$$G(k) = \left[G_0^{-1}(k) - \Sigma_G(k)\right]^{-1} \; and, \tag{6}$$

$$\kappa(k) = \overset{i-1}{\underset{h}{\Big[}}G^{-1}(q) + \Sigma_F(q) \tag{7}$$

Using the isotropic property of the system, we obtained the off diagonal self energy Σ_F with θ_{12} being angle between vectors $\vec{k}$ and $\vec{q} - \vec{k}$ as:

$$\Sigma_F = \int\left\{\left(\frac{1}{\rho_0^2} + c^{(3)}(|\vec{k}|, |\vec{q} - \vec{k}|, \cos\theta_{12})\right)^2 \times F(k)F(|\vec{q} - \vec{k}|)\frac{d^3\vec{k}}{(2\pi)^3}\right. \tag{8}$$

Further, we calculated the replicated free energy $F(n)$ and configurational entropy S_c and , which are as follows.

$$\mathcal{F}(n) = \frac{1}{\beta}\frac{1}{n}\left[\operatorname{Trln}\quad \mathcal{G}^{-1} + \operatorname{Tr}(\Sigma\mathcal{G})\right] \tag{9}$$

$$S_c = \frac{1}{2}\sum_k\left[(F(k) - G(k))\Sigma_F(k) + \ln(1 + \Sigma_F(k)G(k))\right]. \tag{10}$$

The diagonal correlation function G and off-diagonal correlation function F of renormalized liquid is shown in Fig 1. Using density dependence of S_c, we fit S_c with power-law formula as shown in Fig 2. The form of power fit is $A(\eta - \eta_K)^\gamma$. Thus, the Kauzmann point η_K is obtained.
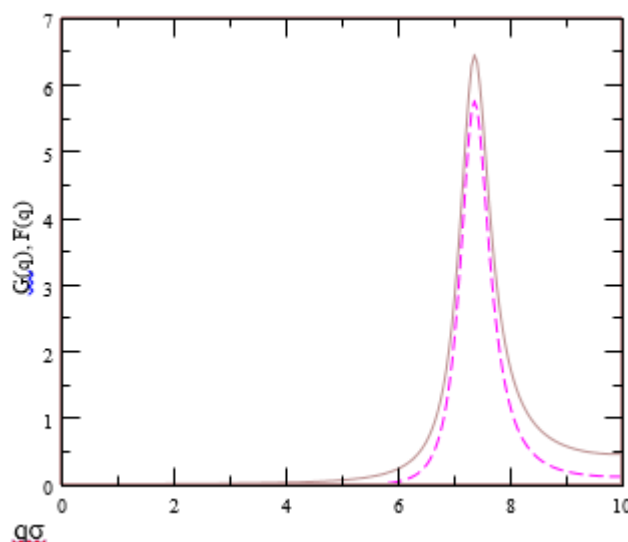
FIG. 1: The structure factor $G(q)$(solid), $F(q)$(dashed) vs. $q\sigma$ for $\eta = 0.602$.

Discussion

In conclusion, following field theoretic model plays a significant role in identifying transition when analysing super-cooled liquid utilising DFT free energy functional with the inclusion of three body correlation. Additionally, a replica approach is employed to explain the entropy crisis based on the uniform liquid's structure data. Below ergodicity breaking transition point, we obtain a off-diagonal correlation function, F, which denotes overlap of different replicas *a* and *b*. Inclusion of two and three body correlation function generate the sufficient frustration between the particles that establish the overlap between two different replicas. With further increasing density, the overlap between the replicas become so strong that they remain likely to stay close to each other, is indeed the main key in the formation of glass. Alternatively, we can say that these replicas condense in the same quite deep minima of the free energy of the system, and causes the formation of glassy phase. A sharp fall of S_c in a first principle calculation is calculated and therefore, we obtained the Kauzmann transition point η_k.
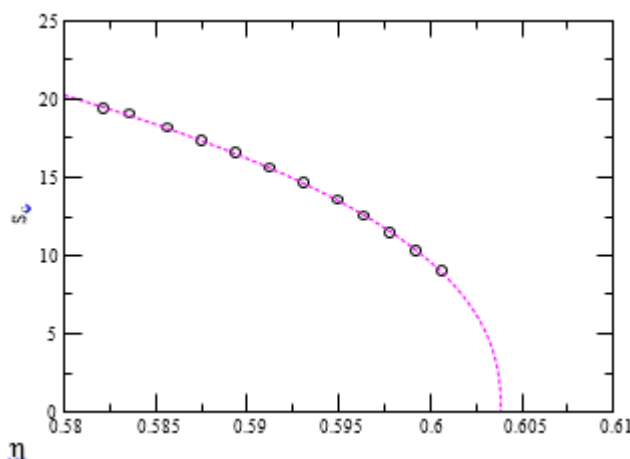

FIG. 2: Complexity S_c vs. packing fraction η, for input structure factors from Roger-Young Hard sphere. Power law fits extrapolating to zero at exponent $\gamma = 0.450$.

References

1. M. Mezard, et. al., J. Physique 45, 843-854 (1984).
2. R. Monasson, Phys. Rev. Lett. 75, 2847(1995).
3. T. R Kirkpatrick, D. Thirumalai, J. of Phys.A, Math and Gen,22, L149-155(1989).
4. S. P. Das, Stat. Phys. of Liquids at Freezing and Beyond, Cambridge Univ. Press, NewYork, (2011).
5. H. Jacquin and F. Zamphoni, J. of Chem. Phys, 138, 12A542 (2013).

6. W. Kauzmann, Chemical Physics, 43, 219 (1948).
7. T.V. Ramakrishnan, and M. Youssouff. Phys. Rev. B, 19, 2775 (1979).
8. Prakash. Vardhan, Shankar P. Das, Phys. Rev. E, 105, 024110 (2022).
9. Prakash Vardhan, Shankar P. Das, Journal of Non-Crystalline Solids, 2022, 121744.