Mode-Coupling Theory as a Mean-Field Description of the Glass Transition

doi: 10.1103/PhysRevLett.104.255704

Mode-Coupling Theory as a Mean-Field Description of the Glass Transition

Atsushi Ikeda and Kunimasa Miyazaki

Institute of Physics, University of Tsukuba, Tennodai 1-1-1, Tsukuba 305-8571, Japan

(Received 12 April 2010; revised manuscript received 12 May 2010; published 25 June 2010)

Mode-coupling theory (MCT) is conjectured to be a mean-field description of dynamics of the structural glass transition and the replica theory to be its thermodynamic counterpart. However, the relationship between the two theories remains controversial and a quantitative comparison is lacking. In this Letter, we investigate MCT for monatomic hard-sphere fluids at arbitrary dimensions above three and compare the results with replica theory. We find grave discrepancies between the predictions of two theories. While MCT describes the nonergodic parameter quantitatively better than the replica theory in three dimensions, it predicts a completely different dimension dependence of the dynamical transition point. We find it to be due to the pathological behavior of the nonergodic parameters derived from MCT, which exhibit negative tails in real space at high dimensions.

DOI: 10.1103/PhysRevLett.104.255704 PACS numbers: 64.70.qj, 61.43.Fs, 64.70.pm, 66.30.hh

The nature of the glass transition remains elusive despite decades of discussion. Many theories and scenarios have been proposed to explain the drastic slowdown of dynamics of supercooled liquids, but we still lack a conclusive microscopic understanding of the phenomenon. Among various theories, mode-coupling theory (MCT) [1] and replica theory [2,3] are arguably the only first-principles theories.

On the one hand, MCT describes the slow dynamics of the mildly supercooled liquids using the static structure factor as a sole input. It quantitatively captures the onset of the two-step relaxation of correlation functions, the scaling properties at the intermediate time scale (the β relaxation), and the algebraic increase of the structural relaxation time. MCT, however, predicts a spurious freezing transition at a lower density φ_{MCT} (or higher temperature T_{MCT}) than the experimentally determined glass transition point φ_g (or T_g). On the other hand, the replica theory is a static mean-field description of the glass transition [2]. It predicts that the fluid undergoes a thermodynamic or ''ideal'' glass transition at a higher density φ_K than φ_g (or lower temperature T_K than T_g), characterized by the one-step replica symmetry breaking. The replica theory also predicts that the dynamical transition takes place at $\varphi_d < \varphi_K$ (or $T_d > T_K$) where the phase space or energy landscape starts splitting into numerous metastable states, or basins. MCT is conjectured to be the dynamical counterpart of the replica theory and φ_{MCT} to be identical to φ_d, because the mathematical structure of MCT is equivalent to the dynamical equation of the so-called p-spin spherical model with $p = 3$, a mean-field model for which the relation between the dynamical and ideal glass transition is rigorously established [4,5]. According to this mean-field scenario, the absence of the dynamic transition at φ_{MCT} in real systems is interpreted as the roundoff of the dynamic freezing by activated processes between basins in finite dimensions [6].

Despite the apparent and simple parallelism with spin glasses, the relationship of MCT with replica theory and physical insights from the mean-field treatments have never been fully understood. MCT was originally derived as a generalization of kinetic theories, using the projection operator formalism with numerous uncontrolled approximations [1], whereas the replica theory is based on a purely thermodynamic argument developed for disordered systems. In this Letter, we compare the MCT and replica theory results quantitatively, in order to clarify the relationship between the two theories developed in totally different arenas of physics communities. We especially focus on the dimension dependence of the glass transition point and the nonergodic parameter $f_\infty(q)$, the plateau height of the density correlation function. To simplify the argument, we focus on the monatomic hard-sphere system in d dimensions, for which the sole system parameter is the number density $\rho = N/V$ or the volume fraction $\varphi = V_d\rho$, where V_d is the volume of a single hard sphere. We show that MCT is more quantitative than the replica theory at $d = 3$, which can be largely attributed to the lack of accurate approximation schemes in the replica theory to evaluate the static correlation functions of the replicated liquids. In higher dimensions where the static correlation functions become trivial, discrepancies between the two theories become catastrophic. MCT's dynamical transition point (φ_{MCT}) scales with dimension d differently from the replica counterpart (φ_d). This discrepancy comes from the spurious negative tails of the van Hove correlation function, a generically positive quantity, that MCT predicts in high dimensions. This pathological negative tail is the origin of the non-Gaussian shape of $f_\infty(q)$ and thus the different d dependence of φ_{MCT} from φ_d. These results shed serious doubts about the validity of MCT in higher dimensions and call for reconsideration of MCT as a dynamic theory of the mean-field scenario of the glass transition.

MCT is expressed as a set of nonlinear integro-differential equations for correlation functions such as the intermediate scattering function $F(q,t) = N^{-1}\langle \delta\rho(\vec{q},t)\delta\rho(-\vec{q},0)\rangle$, where $\delta\rho(\vec{q},t)$ is the density fluctuation in reciprocal space at time t. The MCT equation for $F(q,t)$ in d dimension is given by [7,8]

$$\Omega_q^{-2}\ddot{F}(q,t) + F(q,t) + \int_0^t ds M(q,t-s)\dot{F}(q,s) = 0, \quad (1)$$

where $\Omega_q = \sqrt{k_B T q^2/mS(q)}$ is the phonon frequency and $S(q) = F(q,t=0)$ is the static structure factor. The memory function $M(q,t)$ is given by

$$M(q,t) = \int_0^\infty dk \int_{|q-k|}^{|q+k|} dp V(q,k,p) F(k,t) F(p,t). \quad (2)$$

In this expression, $V(q,k,p) = \rho S(q) s_{d-1} J^{d-3} kp\{f_+ c(k) + f_- c(p)\}^2/q^{d+2}(4\pi)^d$ is the vertex function, where $c(q) = \rho^{-1}\{1 - 1/S(q)\}$ is the direct correlation function, s_d is the surface of the d-dimensional unit sphere, $f_\pm = q^2 \pm (k^2 - p^2)$, and $J = \sqrt{4k^2p^2 - (k^2 - q^2 + p^2)}$ is the Jacobian term. MCT predicts a nonergodic transition at φ_{MCT}, beyond which the nonergodic parameter (NEP) $f_\infty(q) \equiv F(q,\infty)/S(q)$ becomes nonzero. NEP can be calculated from the long time limit of Eq. (1),

$$\frac{f_\infty(q)}{1 - f_\infty(q)} = M(q,\infty). \quad (3)$$

The self-part of the intermediate scattering function $F_s(q,t) = \langle \delta\rho_s(\vec{q},t)\delta\rho_s(-\vec{q},0)\rangle$ can also be described by an equation similar to Eq. (1). The set of MCT equations can be solved numerically using $S(q)$ as a sole input.

On the other hand, the replica liquid theory for the structural glass transition has been developed by Mézard and Parisi [2] and recently applied to hard-sphere fluids by Parisi and Zamponi [3]. In this theory, replicated systems with a weak attractive interaction of order ϵ between them are considered. The free energy of the whole system is calculated as a function of intrareplica and interreplica correlations. The relevant physical observables are evaluated by taking the limit $\epsilon \to 0$ at the end of the calculation. The theory predicts a thermodynamical transition characterized by the replica symmetry breaking at which the configurational entropy vanishes. The transition point is often identified with the Kauzmann point φ_K. The theory also predicts a dynamic transition point $\varphi_d < \varphi_K$ at which the free energy splits into numerous metastable basins. The system cannot explore the whole phase space above φ_d because of the infinite free-energy barrier which separates the basins. In the replica interpretation, the interreplica pair density correlation function $\tilde{g}(r)$ plays the role of order parameter and is identified with NEP $\rho\tilde{h}(q)/S(q) = f_\infty(q)$, where $\tilde{h}(q)$ is the wave vector representation of $\tilde{g}(r) - 1$. The NEP is determined from the variational condition of the replicated free energy. In analogy with the p-spin spherical model [5], it is believed that φ_d should be identical to φ_{MCT} and that the NEP calculated from MCT should match that derived from the replica theory at the dynamic transition point.

In order to check the validity of this conjecture, we numerically compare the results of both theories for φ_{MCT}, φ_d, and $f_\infty(q)$ for $d \geq 3$. First, we look at a $d = 3$ hard-sphere system. MCT for three-dimensional hard spheres was studied by Götze and co-workers [9]. On the other hand, the quantitative accuracy of the replica theory sensitively depends on the approximation scheme employed to calculate the free energy of replicated liquids. The small cage expansion technique is known to be a good approximation near the Kauzmann point, but it does not describe the dynamic transition in low dimensions [2,3]. Therefore, we use another scheme, the replicated hypernetted chain (RHNC) approximation [2], the only method at present which captures the dynamic transition in finite dimensions. RHNC consists of a set of closure equations for both interpair and intrapair density correlation functions, $\tilde{g}(r)$ and $g(r)$, given by

$$\ln g(r) = \beta v(r) + \int \frac{d\vec{q}}{(2\pi)^d} e^{i\vec{q}\cdot\vec{r}} \frac{\rho h^2(q)}{1 + \rho h(q)},$$
$$\ln \tilde{g}(r) = \int \frac{d\vec{q}}{(2\pi)^d} e^{i\vec{q}\cdot\vec{r}} \left\{ \frac{\rho h^2(q)}{1 + \rho h(q)} - \frac{\rho[h(q) - \tilde{h}(q)]^2}{1 + \rho[h(q) - \tilde{h}(q)]} \right\}. \quad (4)$$

Here, $\rho h(q) = S(q) - 1$ and $v(r)$ is the interaction potential. The first equation is the HNC equation of a simple liquid [10], and the second equation describes the interreplica coupling. The dynamic transition point φ_d is defined as the volume fraction beyond which $\tilde{h}(q)$ becomes nonzero. We solve the MCT equation, Eq. (3), and the RHNC theory, Eq. (4), for the monatomic hard-sphere system. For MCT calculation, we employ the HNC equation to evaluate $S(q)$ in order to make the comparison consistent. The dynamic transition points thus obtained are $\varphi_{\mathrm{MCT}} = 0.523$ (which is slightly larger than 0.515 obtained from Percus-Yevick closure) and $\varphi_d = 0.612$ [11]. $f_\infty(q)$ calculated from MCT at φ_{MCT} and the replica theory at φ_d are shown in Fig. 1. The quantitative difference between the shape of the NEP from the two theories is obvious. Since it is well established that MCT's $f_\infty(q)$ agrees very well with simulation [9] and experimental results [12], this discrepancy could be mainly due to poor performance of the replica theory. However, it is not clear whether this is attributed to the inherent inconsistency of MCT with replica theory or solely to a lack of accuracy of the RHNC approximation.

In order to give the two theories a more stringent test, we discuss the dimension dependence of quantities near the dynamic transition point. We start with $d = 4$–8 and solve Eq. (3) to evaluate φ_{MCT} and $f_\infty(q)$. An algorithm by Baus and Colot [13] is used to evaluate $S(q)$. φ_{MCT} thus obtained is listed in Table I along with φ_K reported in Ref. [3]. Note

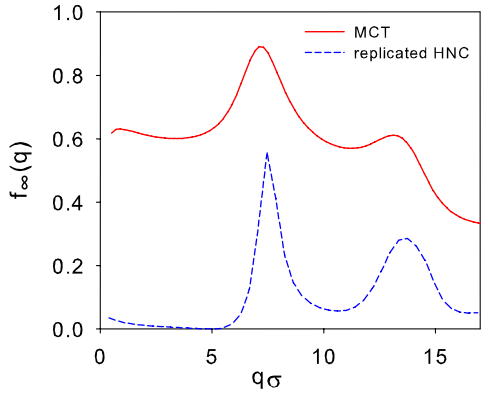

FIG. 1 (color online). $f_\infty(q)$ evaluated from MCT (solid line) and the replica theory (dashed line) at φ_{MCT} and φ_d, respectively. q is scaled with the diameter of a sphere σ. $S(q)$ from HNC closure is used for MCT calculation.

that φ_{MCT} is smaller than φ_K in lower dimensions, but the gap narrows with increasing dimension, and at $d = 8$ φ_{MCT} *exceeds* φ_K.

Next, we study the d dependence in even higher dimensions, where the static properties of the liquid and the replicated liquid become insensitive to the approximation schemes. Therefore, it is possible to check the relationship between the two theories without obscuration from approximations for the static inputs. In the high d limit where the diagrammatic expansions of the free energy is given by a simple function of the Mayer function $e^{-\beta v(r)} - 1$, exact analytical expressions for static correlation functions are available. For the hard-sphere system, the direct correlation function $c(q)$ is simply given by $c(q) = -(2\pi/q\sigma)^{d/2} J_{d/2}(q\sigma)$, where $J_l(x)$ is the lth Bessel function of the first kind and σ is the diameter of a sphere. Recently, accurate replica theory calculations of the free energy in high dimensions was carried for the monatomic hard-sphere system, using this $c(q)$ as an input and the cage expansion method [3]. The dynamic transition point was shown to scale with d as

$$\varphi_d = 4.8 \times 2^{-d} d \tag{5}$$

and the Kauzmann point as $\varphi_K = 2^{-d} d \ln d$ in the high dimension limit $d \to \infty$ [3]. We solve the MCT equation with the same $c(q)$, keeping the convergence of discretization error and the numerical accuracy of the Bessel function under control. In Fig. 2, φ_{MCT} is shown as a function of d. We find that φ_{MCT} scales as $\varphi_{\mathrm{MCT}} = 0.22 \times 2^{-d} d^2$, in stark contrast with the replica prediction for φ_d, Eq. (5).

TABLE I. Values of φ_{MCT} and φ_K from $d = 4$ to $d = 8$. φ_K is from Parisi and Zamponi [3].

d	4	5	6	7	8
φ_{MCT}	0.3652	0.2542	0.1736	0.1159	0.0751
φ_K	0.4319	0.2894	0.1883	0.1194	0.0739

We also calculate the NEPs from MCT and find that their q dependence are non-Gaussian shaped in high d. In low dimensions below $d = 8$, decay of $f_\infty(q)$ at $q\sigma \gtrsim 10$ and $f_{s,\infty}(q)$ are well fitted by a Gaussian form, but in higher dimensions they decay faster than Gaussian at large q's (not shown). Different d dependence of φ_{MCT} from φ_d originates from this non-Gaussianity. This can be shown by solving Eq. (3) assuming that $f_\infty(q)$ and $f_{s,\infty}(q)$ both have a Gaussian shape, i.e., $f_\infty(q), f_{s,\infty}(q) \approx e^{-Rq^2/2d}$. Here, we assume that $f_\infty(q) \approx f_{s,\infty}(q)$, the so-called vineyard approximation [10]. Substituting this Gaussian form in Eq. (3), we obtain a self-consistent equation for R,

$$\frac{1}{R} = \frac{\rho s_d}{2d^2(2\pi)^d} \int_0^\infty dq q^{d+1} c^2(q) S(q) e^{-Rq^2/d}. \tag{6}$$

This expression is strikingly analogous to the equation for the density field for the amorphous solid obtained using Gaussian approximation in the framework of the density functional theory [14]. Solving Eq. (6), we find that the equation has a finite solution for R above a volume fraction $\varphi_{\mathrm{MCT}}^{(G)}$ that behaves in high d as [15]

$$\varphi_{\mathrm{MCT}}^{(G)} = 8.27 \times 2^{-d} d. \tag{7}$$

Though the prefactor differs, it retrieves the same d dependence as the replica theory, which ascertains the origin of discrepancies between MCT and the replica theory.

This non-Gaussian shape of the NEP that MCT predicts in high dimensions is the compelling evidence that MCT breaks down. Analyzing the van Hove correlation function $G_s(r, t)$, which is the real space representation of $F_s(q, t)$, makes this breakdown clear. $G_s(r, t)$ is a distribution function of the distance for one particle to explore during the time interval t, $G_s(r, t) = \langle \delta[r - |\vec{R}_i(t) - \vec{R}_i(0)|] \rangle$, where $\vec{R}_i(t)$ is the position of the ith particle at time t. By definition, the van Hove function is a non-negative quantity. In Fig. 3, we plot $G_{s,\infty}(r) \equiv G_s(r, t = \infty)$ derived from MCT for several dimensions. Following the standard convention a multiplicating factor $s_d r^{d-1}$ is used. In high dimensions, it exhibits a negative dip whose depth be-

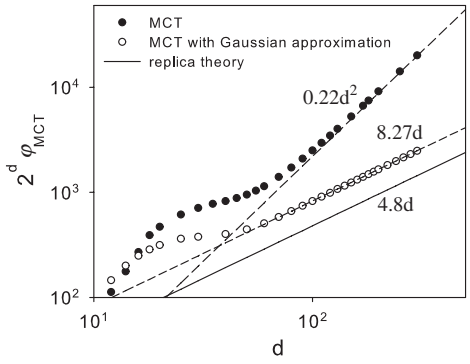

FIG. 2. φ_{MCT} as a function of d. Filled circles are the numerical solution of Eq. (3) and empty circles from MCT with Gaussian approximation, Eq. (6). Solid line is the prediction from the replica theory.

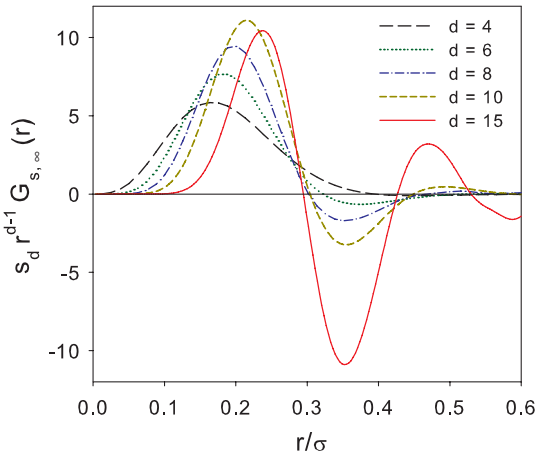

FIG. 3 (color online). The van Hove function $G_{s,\infty}(r)$ evaluated using MCT in several dimensions. From left to right, $d = 4, 6, 8, 10, 15$.

comes larger as dimension increases. We checked that $f_{s,\infty}(q)$ retrieves the Gaussian shapes if the negative dips are absent.

These results suggest that MCT in its present form is not consistent with replica theory and that, moreover, MCT suffers from serious deficiencies. The validity of the dimension dependence $\varphi_{\mathrm{MCT}} \sim d^2/2^d$ that MCT predicts is suspicious because it originates from the pathological behavior of the NEP. It is noteworthy that the non-Gaussian shape of $f_\infty(q)$ and the negative tails of $G_{s,\infty}(r)$ already appear in $d = 8$, below the upper-critical dimension $d_c = 8$ of the glass transition [16,17]. Assuming a Gaussian shape for $f_\infty(q)$ in MCT recovers the linear dimension dependence of $2^d\varphi_{\mathrm{MCT}}$ [see Eq. (7)], but the prefactor still does not match with the replica theory prediction. This fact implies that a quick remedy is unlikely to fix the problem. In hindsight, a convincing reason to conjecture that two theories are related is lacking, except for their apparent mathematical similarity with the p-spin spherical mean-field model of spin glasses. The deceptively similar structure between Gaussian-approximated MCT, Eq. (6), and the equation for the density profile derived in the mean-field analysis of the density functional theory [14] also hints that MCT is a mean-field-like theory, but a small yet non-negligible difference between these equations leaves us with a nagging suspicion about MCT's validity. One of the routes to resolve these problems is to reformulate MCT in a field theoretic language in which parallels and differences with the mean-field theory of spin glasses and the dynamic liquid theory are highlighted. Efforts in this direction have suffered from a series of difficulties associated with consistencies with the fluctuation-dissipation theorem [18], the double-counting problem of the potential interactions, and the reconciliation between the dynamic and static liquid theories. Although it is not clear if the replica theory and the density functional theory correctly describe the dynamic transition, at least our results clearly indicate that reconsideration and revision of MCT from the ground up are in order. We conjecture, however, that prospective revisions leave general mathematical properties of the MCT equation intact. It is argued that MCT should be seen as a Landau theory in a sense that critical behavior and scaling properties that MCT describes near the dynamical transition point are universal [19]. Indeed, a recent numerical study indicates that MCT works better for critical behaviors in high dimensions [8].

We thank D. R. Reichman, F. Zamponi, G. Biroli, J.-P. Bouchaud, and P. Charbonneau for stimulating discussions. A. I. is supported by the JSPS and K. M. by KAKENHI No. 2154016 and Priority Areas "Soft Matter Physics."

Note added.—As this Letter was being finalized for submission, we became aware of an article by Schmid and Schilling [20]. They have solved the MCT equation for $d \geq 10$ and shown the same dimension dependence of φ_{MCT} as reported in Fig. 2 and non-Gaussian shape of $f_\infty(q)$.

[1] W. Götze, *Complex Dynamics of Glass-Forming Liquids* (Oxford University Press, Oxford, 2009).
[2] M. Mézard and G. Parisi, Phys. Rev. Lett. **82**, 747 (1999).
[3] G. Parisi and F. Zamponi, J. Chem. Phys. **123**, 144501 (2005); Rev. Mod. Phys. **82**, 789 (2010).
[4] T. R. Kirkpatrick and D. Thirumalai, Phys. Rev. Lett. **58**, 2091 (1987).
[5] T. Castellani and A. Cavagna, J. Stat. Mech. (2005) P05012.
[6] G. Biroli and J.-P. Bouchaud, arXiv:0912.2542.
[7] M. Bayer *et al.*, Phys. Rev. E **76**, 011508 (2007).
[8] P. Charbonneau, A. Ikeda, J. A. van Meel, and K. Miyazaki, Phys. Rev. E **81**, 040501(R) (2010).
[9] G. Foffi, W. Götze, F. Sciortino, P. Tartaglia, and Th. Voigtmann, Phys. Rev. E **69**, 011505 (2004).
[10] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 2006).
[11] A. Velenich, A. Parola, and L. Reatto, Phys. Rev. E **74**, 021410 (2006).
[12] W. van Megen and S. M. Underwood, Phys. Rev. Lett. **70**, 2766 (1993).
[13] M. Baus and J.-L. Colot, J. Phys. C **19**, L643 (1986).
[14] T. R. Kirkpatrick and P. G. Wolynes, Phys. Rev. A **35**, 3072 (1987).
[15] The prefactor of Eq. (7) as well as (6) differs from that in Ref. [14] by a factor of 2.
[16] G. Biroli and J.-P. Bouchaud, J. Phys. Condens. Matter **19**, 205101 (2007).
[17] G. Biroli, J.-P. Bouchaud, K. Miyazaki, and D. R. Reichman, Phys. Rev. Lett. **97**, 195701 (2006).
[18] K. Miyazaki and D. R. Reichman, J. Phys. A **38**, L343 (2005).
[19] A. Andreanov, G. Biroli, and J.-P. Bouchaud, Europhys. Lett. **88**, 16 001 (2009).
[20] B. Schmid and R. Schilling, Phys. Rev. E **81**, 041502 (2010).