

# Insight into Molecular Dynamics and Thermodynamics in a Simple Ellipsoidal Model near the Glass Transition via Invariants of Density Scaling

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Since the beginning of this century, the density scaling idea has attracted a lot of interest as bearing hallmarks of universality in the study of the glass transition and related phenomena [1]. The primary advantage of this idea relies on a simple link between macroscopic phenomena near the glass transition and a simple effective short-range intermolecular potential mainly dependent on the inverse power law (IPL) of intermolecular distances. What is important, the IPL exponent is related to the scaling exponent  $\gamma$ , which enables to scale onto one master curve different dynamic quantities  $X$ , for instance structural relaxation time and viscosity, as a function of the single variable  $\rho^\gamma/T$  (where  $\rho$ -density,  $T$ -temperature), and can be found from the density scaling criterion,

$$\log_{10}\rho = \gamma\log_{10}T + \text{const}(X) \text{ at } X=\text{const} \quad (1)$$

Despite many achievements of this approach, there are some unsolved fundamental problems with its theoretical grounds. The crucial flaw of the most popular theoretical explanation of the density scaling behavior, called the isomorph theory, is its phenomenological character based on many simulation experiments carried out in simple isotropic models based on the Lennard-Jones potential. However, the real molecular shapes are anisotropic in the vast majority, and the anisotropic force fields seem to be much more adequate to model physicochemical properties of such materials. Guided by this premise, very recently we have successfully employed a well-known Gay-Berne (GB) model earlier parametrized to achieve a supercooling and glass transition at zero pressure [2] in order to find the glass transition points and investigate volumetric and dynamic properties in the supercooled liquid state at elevated pressure [3]. In this way, we have been able to explore the density scaling fundamentals in the GB model characterized by the well-defined anisotropy in both the molecular shape and the intermolecular potential. Among other things, we have confirmed that Eq. (1) provides the best method for evaluating the scaling exponent  $\gamma$ , which enables to scale both translational and rotational relaxation times of the supercooled GB liquid (Fig. 1), while the isochoric virial - potential energy correlation promoted by the isomorph theory is not useful in the anisotropic case. Moreover, we have argued that the reduced units of the isomorph theory should not be used to analyze the vast majority experimental data measured in isobaric or isothermal conditions, because these units are not applicable in the isobaric-isothermal statistical ensemble.

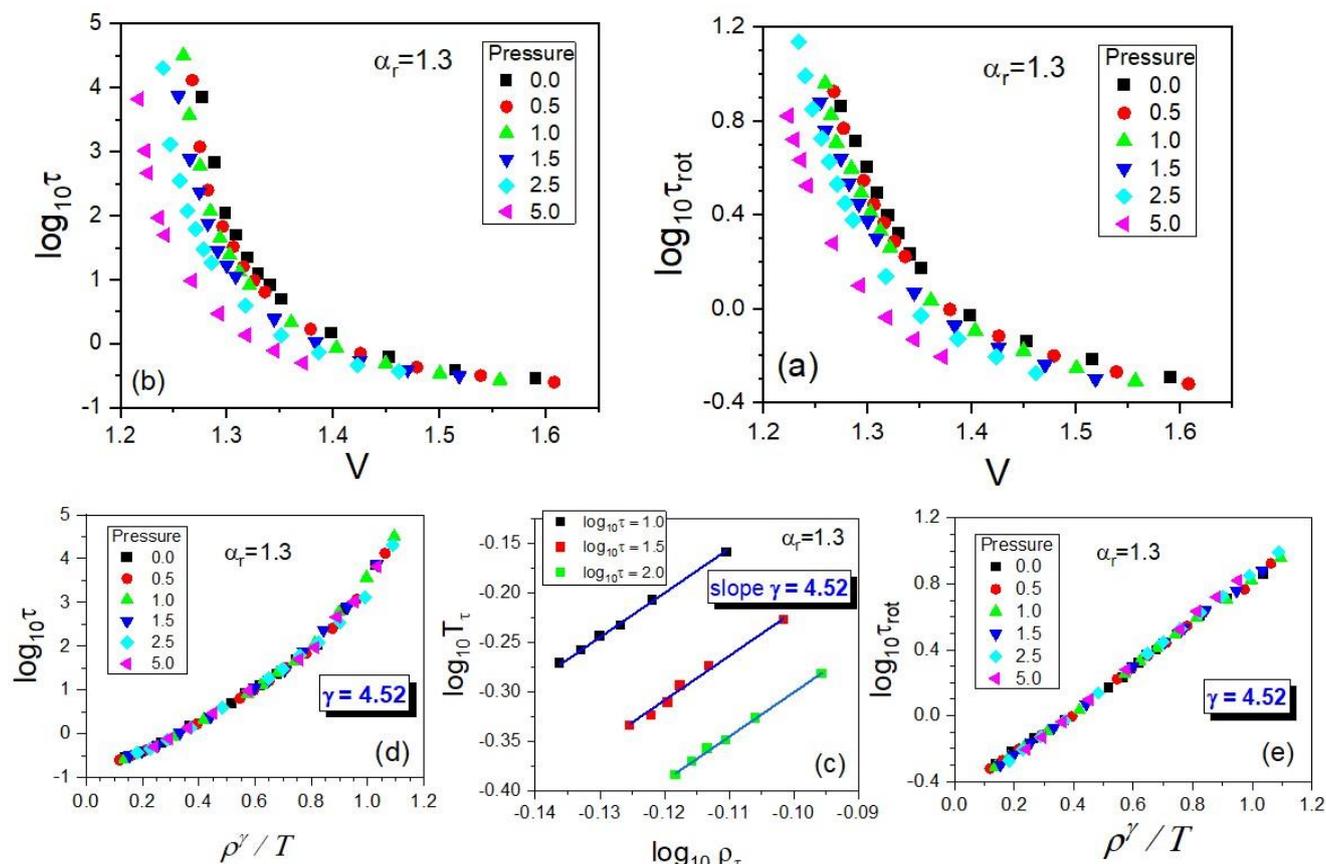
In the next step, we have focused on the thermodynamic aspect of the density scaling and its relation to the dynamic one [4]. First, in the supercooled liquid GB model, we have successfully verified the novel invariant earlier reported for molecular glass formers [5], which is the ratio of thermodynamic and dynamic moduli  $B_T/M_{V-T}$ , where  $B_T$  is the inverse of isothermal compressibility and  $M_{V-T}$  is the ratio of isochoric activation energy and activation volume. Consequently, we have discussed the recent suggestions about a state-point dependence of the density scaling exponent  $\gamma$ . Second, we have investigated the molecular anisotropy effect on the role of entropy in the thermodynamic evolution of the time scale of molecular dynamics near the glass transition by comparing our new results obtained from the molecular dynamics simulations in the GB model with our previous investigations of supercooled van der Waals and ionic liquids, and polymer melts [6,7]. Considering the total system entropy  $S$ , the configurational system entropy  $S_{\text{conf}}$ , and the excess system entropy  $S_{\text{ex}}$ , which is an excess of the ideal gas entropy in the same thermodynamic

conditions as the GB liquid is examined, we gain a new insight into the linkage between molecular dynamics and thermodynamics near the glass transition.

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## FIGURES



**Figure 1:** Illustration of the density scaling of translational and rotational relaxation times in the supercooled GB liquid of the anisotropy aspect ratio  $\alpha_r = 1.3$ . All quantities are in the LJ units. (a) Dependences of translational relaxation times  $\tau$  on volume  $V$ . (b) Dependences of rotational relaxation times  $\tau_{rot}$  on volume  $V$ . (c) Density scaling criterion (Eq. 1) implemented for  $\tau$ . (d) Density scaling of  $\tau$ . (e) Density scaling of  $\tau_{rot}$ .