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## Comment on “An investigation of the liquid to glass transition using integral equations for the pair structure of coupled replicaes” [J. Chem. Phys. 141, 174505 (2014)]

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In a recent paper,<sup>1</sup> we determined the pair structure and free energy for a binary system of two weakly coupled replicaes of a soft-sphere fluid, using fluid integral equations, to locate the Kauzmann temperature<sup>2</sup>  $T_K$  and the “random first order transition” (RFOT) temperature  $T_{cr}$  to an “ideal glass.”<sup>3</sup> In this model, particles interact via the repulsive pair potential  $v(r) = \varepsilon(\sigma/r)^{12}$  (where  $\varepsilon$  and  $\sigma$  are the energy scale and particle diameter); its excess (non-ideal) equilibrium properties depend on a single dimensionless parameter  $\Gamma = \rho^*/(T^*)^{1/4}$  (where  $\rho^* = N\sigma^3/V$  and  $T^* = k_B T/\varepsilon$  are the reduced number density and temperature). Atoms of opposite replicaes (labeled 1 and 2) interact via an attractive potential, chosen to be  $v_{12}(r) = -\varepsilon_{12}[c^2/(r^2 + c^2)]^6$ , where  $\varepsilon_{12}$  sets the energy scale and  $c < \sigma$  is the range parameter chosen such that an atom of replica 1 interacts with at most one atom of replica 2. The pair structure of this symmetric binary system is characterized by two pair distribution functions (p.d.f.)  $g_{11}(r) \equiv g_{22}(r)$  and  $g_{12}(r)$ , related to two direct correlation functions by two coupled Ornstein-Zernike relations and a closure relation.<sup>4</sup> For the latter, we chose the hypernetted chain (HNC) closure<sup>4</sup> and a thermodynamically self-consistent closure due to Rogers and Young (RY).<sup>5</sup> The HNC approximation is thermodynamically inconsistent but allows the excess free energy  $F^{ex}$  to be expressed in terms of pair correlation functions alone, while the more accurate RY closure requires a tedious thermodynamic integration of the excess internal energy to calculate  $F^{ex}$  as a function of  $\Gamma$  (see Appendix C in Ref. 1).

The supercooled liquid phase is described upon setting  $\varepsilon_{12} \equiv 0$  (fully decoupled replicaes). The configurational part  $F_C$  of the free energy is calculated by subtracting the vibrational contribution  $F_V$  from the total free energy, using a standard estimate of the mean vibrational frequency in a dense fluid.<sup>1,4</sup> Upon increasing  $\Gamma$ ,  $F_C$  is found to go through a maximum at  $\Gamma_K$ , so that the configurational entropy  $S_C = -(\partial F_C/\partial T^*)_{\rho^*}$  vanishes at  $\Gamma_K$ , corresponding to the Kauzmann temperature  $T_K^* = 1/\Gamma_K^4$  ( $\rho^* = 1$  without loss of generality).

We used the two-replicaes system, with an initial  $\varepsilon_{12} > 0$ , to generate “ideal glass” states at sufficiently strong coupling  $\Gamma$ . The inter-replica p.d.f.  $g_{12}(r)$  allows the calculation of the mean overlap order parameter  $Q$ ;<sup>6</sup> the latter undergoes a discontinuous jump (d.j.) above its “random” value  $Q_r$  (characteristic of the supercooled liquid phase) beyond a coupling  $\Gamma_{dj}$ . When the inter-replica coupling is gradually switched off ( $\varepsilon_{12} \rightarrow 0$ ),  $Q$  remains much larger than  $Q_r$ , signalling the “ideal glass” phase, where the two replicaes remain trapped in the same free-energy minimum characterized by a set of frozen, disordered equilibrium positions  $\{\mathbf{R}_i\}$  ( $1 \leq i \leq N$ ).

The numerical solutions of both HNC and RY integral equations<sup>1</sup> reveal the existence of a supercooled liquid (L) branch (where  $Q = Q_r$ ) and of two glass branches  $G_1$  and  $G_2$  over an extended range of couplings  $\Gamma$ . States along the  $G_2$  branch have lower free energy than along  $G_1$  and exhibit a variation of  $Q(\Gamma)$  compatible with that expected for an “ideal glass.” The free energy curves of the L and  $G_2$  branches calculated within HNC intersect at  $\Gamma_{cr}^{HNC} = 1.65$ , corresponding to weakly first order RFOT from the L to the  $G_2$  phase;  $\Gamma_{cr}^{HNC} < \Gamma_K^{HNC} = 1.74$ , so that the Kauzmann “catastrophe” is preempted by the RFOT. The corresponding RY calculations predicted  $\Gamma_K^{RY} = 1.89$  while  $\Gamma_{cr}^{RY} = 2.01 > \Gamma_K^{RY}$ , which is unphysical. However, the free energy differences  $F_L^{RY} - F_{G_2}^{RY}$  are quite small and require a very careful choice of the thermodynamic integration path linking the L and  $G_2$  phases via an intermediate “molecular liquid” phase (where  $\varepsilon_{12} \neq 0$ );<sup>1</sup> the free energy estimates are also sensitive to the choice of a low enough  $\Gamma$  reference state. For this reason, we have repeated the numerical calculations of the free energies of the L and  $G_2$  phases, starting from the same initial reference state ( $\Gamma = 0.1$ ), and using a very small increment  $\Delta\Gamma = 0.01$  to improve the accuracy of the numerical integration of the excess internal energy. The RY results for  $U_{ex}(\Gamma)$  (with  $\varepsilon_{12}/\varepsilon = 0.5$ ) obtained using two spatial resolutions are shown in Fig. 1 over a restricted range of couplings  $\Gamma$ . They point to a marked but continuous change in slope of the excess energy curve, which may be the signature of a continuous transition from the initial liquid phase to the intermediate “molecular liquid” phase. This interpretation is supported by the faster increase of the

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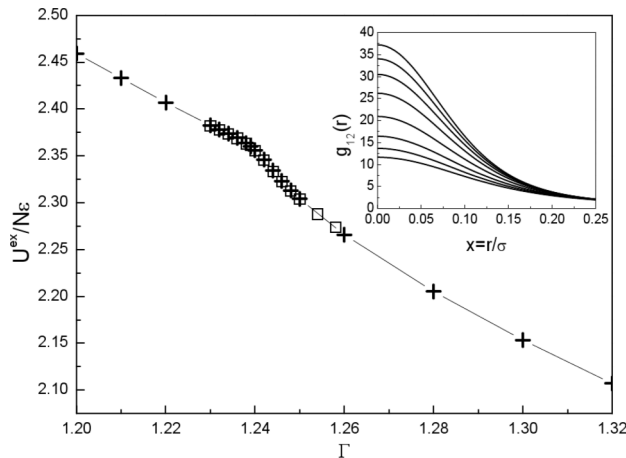


FIG. 1. Excess internal energy per particle  $U^{ex}/(N\epsilon)$  vs  $\Gamma$  calculated within protocol **c** of Ref. 1 for  $\epsilon_{12}/\epsilon = 0.5$  and  $c = 0.5\sigma$ . The RY equation was solved using two spatial grids: one with a spacing  $\Delta r = 0.02\sigma$  and 4097 grid points (crosses) and the other with  $\Delta r = 0.005\sigma$  and 16 835 points (squares). The inset shows the behavior at short distances of  $g_{12}(r)$  for eight equally spaced values of  $\Gamma$ . From bottom to the top:  $1.230 \leq \Gamma \leq 1.258$  with  $\Delta\Gamma = 0.04$ .

amplitude of the central peak of  $g_{12}(r)$  in the immediate vicinity of  $\Gamma = 1.24$  (see inset of Fig. 1), suggestive of enhanced pairing of atoms of opposite replica. The new estimate of the free energy difference  $\Delta f^* = (F_L^{RY} - F_{G_2}^{RY})/N\epsilon$  is plotted as a function of  $\Gamma$  in Fig. 2;  $\Delta f^*$  changes sign at  $\Gamma_{cr}^{RY} = 1.91$ . The intuitively satisfactory result is that  $\Gamma_{cr}^{RY} = \Gamma_K^{RY}$  (within numerical accuracy), suggesting that the RFOT to an “ideal glass” coincides with the Kauzmann crisis of vanishing configurational entropy, whereas the HNC closure predicts these two events to occur at significantly different couplings. Our finding that  $T_{cr} = T_K$  may be partly serendipitous, since RY is not an exact closure, even if it is thermodynamically self-consistent. In order to check that the coincidence of the

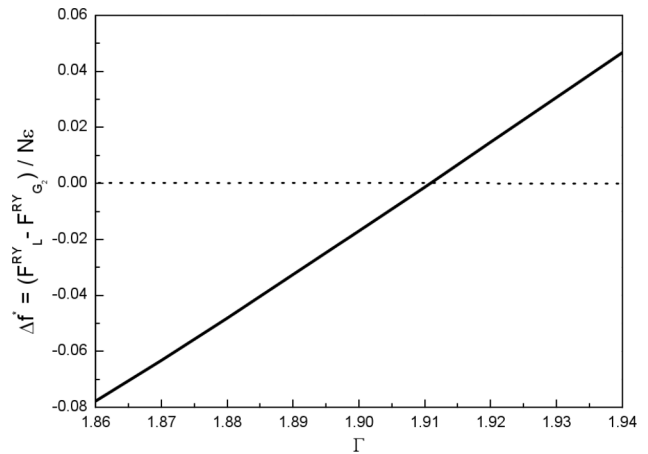


FIG. 2. RY results for the excess free energy difference  $\Delta f^* = (F_L^{RY} - F_{G_2}^{RY})/N\epsilon$  along L and  $G_2$  branches vs  $\Gamma$ .

two temperatures is not restricted to the particular soft-sphere system, we are currently investigating the case of the Lennard-Jones system. We stress once more that both HNC and RY integral equations predict that the RFOT is a weakly first order transition, characterized by a small relative volume change ( $\Delta v = (v_L - v_{G_2})/v_L \approx 0.01$  within RY theory), while earlier HNC-based theories predict that the transition is second order from a thermodynamic point of view.<sup>7</sup>

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