

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

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In a recent paper¹ we determined the pair structure and free energy for a binary system of two weakly coupled replica^e of a soft-sphere fluid, using fluid integral equations, to locate the Kauzmann temperature² T_K and the “random first order transition” (RFOT) temperature T_{cr} to an “ideal glass”³. In this model particles interact via the repulsive pair potential $v(r) = \varepsilon(\sigma/r)^{12}$ (where ε and σ 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 replica^e (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 ε_{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 relation⁴. For the latter we chose the hyper-netted chain (HNC) closure⁴, and a thermodynamically self-consistent closure due to Rogers and Young (RY)⁵. 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 Γ (see Appendix C in Ref. [1]).

The supercooled liquid phase is described upon setting $\varepsilon_{12} \equiv 0$ (fully decoupled replica^e). 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^{1,4}. Upon increasing Γ , F_C is found to go through a maximum at Γ_K , so that the configurational entropy $S_C = -(\partial F_C/\partial T^*)_{\rho^*}$ vanishes at Γ_K , corresponding to the Kauzmann temperature $T_K^* = 1/\Gamma_K^4$ ($\rho^* = 1$ without loss of generality).

We used the two-replica^e system, with an initial $\varepsilon_{12} > 0$, to generate “ideal glass” states at sufficiently strong coupling Γ . The inter-replica p.d.f. $g_{12}(r)$ allows the calculation of the mean overlap order parameter Q^6 ; the latter undergoes a discontinuous jump (d.j.) above its “random” value Q_r (characteristic of the supercooled liquid phase) beyond a coupling Γ_{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 replica^e 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 equations¹ 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 Γ . 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 $\varepsilon_{12} \neq 0$)¹; the free energy estimates are also sensitive to the choice of a low enough Γ 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

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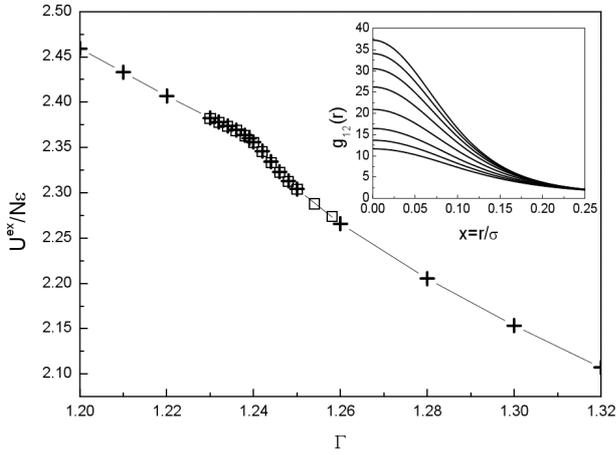


FIG. 1. Excess internal energy per particle $U^{ex}/(N\epsilon)$ vs Γ calculated within protocol **c** of Ref. [1] for $\epsilon_{12}/\epsilon = 0.5$ and $c = 0.5\sigma$. The RY equation was solved using two spatial grids: one with a spacing $\Delta r = 0.02\sigma$, and 4097 grid points (crosses) and the other with $\Delta r = 0.005\sigma$ and 16835 points (squares). The inset shows the behavior at short distances of $g_{12}(r)$ for eight equally spaced values of Γ . From bottom to the top: $1.230 \leq \Gamma \leq 1.258$ with $\Delta\Gamma = 0.04$.

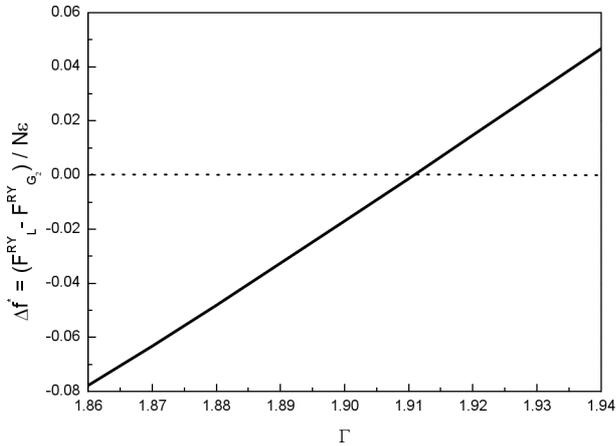


FIG. 2. RY results for the excess free energy difference $\Delta f^* = (F_L^{RY} - F_{G_2}^{RY})/(N\epsilon)$ along L and G_2 branches vs Γ .

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 $\epsilon_{12}/\epsilon = 0.5$) obtained using two spatial resolutions, are shown in Fig. 1 over a restricted range of couplings Γ . 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 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 Γ in Fig. 2; Δf^* 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 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 ($\Delta v = (v_L - v_{G_2})/v_L \simeq 0.01$ within RY theory) while earlier HNC-based theories predict that the transition is second order from a thermodynamic point of view⁷.

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