The glass transition and liquid-gas spinodal boundaries of metastable liquids

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Abstract. – A liquid can exist under conditions of thermodynamic stability or metastability within boundaries defined by the liquid-gas spinodal and the glass transition line. The relationship between these boundaries has been investigated previously using computer simulations, the energy landscape formalism, and simplified model calculations. We calculate these stability boundaries semi-analytically for a model glass-forming liquid, employing accurate liquid-state theory and a first-principles approach to the glass transition. These boundaries intersect at a finite temperature, consistent with previous simulation-based studies.

When a substance is brought below its equilibrium freezing temperature and yet maintained in the liquid state, it is referred to as a supercooled liquid. Even if crystallization is avoided a liquid cannot be supercooled indefinitely; it transforms into an amorphous solid *via* the *glass transition*, at a temperature determined in experiments by the cooling rate. The *ideal glass transition* refers to the putative transformation to an amorphous solid which has been argued to occur in the limit of infinitesimally small cooling rates. Such a transition would define an ultimate limit beyond which a substance cannot exist in the supercooled liquid state.

If a liquid were instead to be heated beyond the boiling point —and the transformation into the gas phase averted— it is termed a superheated liquid. Such a liquid cannot be superheated to arbitrarily high temperatures since growing density fluctuations will trigger a catastrophic transformation into the gaseous state at rates which increase with the degree of superheating. Mean-field theory identifies a degree of superheating for which the compressibility diverges, at which point the liquid would spontaneously transform into a gas. The locus of such points defines another ultimate limit to the stability of the liquid state, the liquid-gas spinodal [1].

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Clarifying the relationship between these two limits is fundamental to a deeper understanding of the liquid state. In a previous investigation [2] of the model liquid studied in this letter, through computer simulations and the energy landscape approach, it was found that the glass transition line and the liquid-gas spinodal intersect at a finite temperature, thus predicting a glass-gas limit of mechanical stability at lower temperatures. More recently, similar results have been obtained from simulations of a model of ortho-terphenyl [3] as well as calculations based on model energy landscapes [4, 5].

In addition to conventional materials in the liquid state, much interest has recently focussed on such questions in the context of colloidal fluids. In these systems, a unified picture of arrested states (colloidal gels and glasses) has been the subject of considerable investigation [6]. Depending on the colloidal concentration, the strength and the nature of the interaction, structural arrest may arise in a variety of ways. These include the aggregation of clusters at low concentrations and strong interactions, gelation, a glass transition at high densities, a glass transition arising from attractive rather than repulsive interactions, and finally as a consequence of phase separation [7–13]. The understanding of the role of the unstable region in the phase diagram demarcated by the liquid-gas and gas-liquid spinodals is therefore a necessary component of a comprehensive picture of these arrested states [11]. Results presented in [2] and here, thus, have a direct bearing on the interplay of phase separation and structural arrest in colloidal fluids, in addition to corresponding phenomena in molecular glass formers.

In this letter, we describe an analysis of these limiting lines for a realistic glass former, which uses i) accurate liquid-state theoretical methods to calculate the equation of state [14] of the system, and thus the liquid-gas spinodal, coupled with ii) a first-principles approach to the glass transition proposed by Mezard and Parisi [15, 16] to evaluate the glass transition line. Our calculations are quantitatively in reasonable agreement with the previous study, and also predict that the glass transition line and the liquid-gas spinodal intersect at a finite temperature. Our results thus provide strong support for the proposal that such an intersection of these limiting lines is the generic behavior for liquids.

The model system we study is the Kob-Andersen binary-mixture Lennard-Jones (KA BMLJ) liquid [17], consisting an $80 : 20$ mixture of A and B particles interacting via a Lennard-Jonnes potential with parameters $\epsilon_{AB}/\epsilon_{AA} = 1.5$, $\epsilon_{BB}/\epsilon_{AA} = 0.5$, $\sigma_{AB}/\sigma_{AA} = 0.8$, $\sigma_{BB}/\sigma_{AA} = 0.88$. We report energies in units of ϵ_{AA}, lengths in units of σ_{AA}, and temperatures in units of ϵ_{AA}/k_B. This system has been extensively studied as a model glass former. Our procedure for calculating the glass transition line, which we summarize below, is close to that employed in refs. [18, 19].

We compute the equation of state of the system we study, KA BMLJ, from evaluation of the A-A, A-B and B-B pair correlation functions. Liquid-state theoretical methods provide accurate analytic tools for the computation of such pair correlation functions and we exploit such methods here. Our calculations use the Zerah-Hansen (ZH) closure scheme [14] coupled to the Ornstein-Zernike (OZ) equation. The Zerah-Hansen closure interpolates between hypernetted chain (HNC) and the soft-core mean-spherical approximation (SMSA) closures [20]; as described in ref. [18], such an interpolation reproduces thermodynamic quantities (energy and pressure) accurately.

For the binary system, with indices a and b indicating particle types, the OZ equation is

$$h_{ab}(k) = c_{ab}(k) + \sum_{i=a,b} \rho_i c_{ai}(k) * h_{ib}(k), \tag{1}$$

where ρ_i are the partial number densities, h_{ab} is defined as $g_{ab}(r) - 1$ ($g_{ab}(r)$ being the ab pair correlation function) and $c_{ab}(r)$ is the direct correlation function. $h_{ab}(k)$, etc. indicate space

Fourier transforms. Defining $\gamma_{ab}(r) = h_{ab}(r) - c_{ab}(r)$,

$$\gamma_{ab}(k) = \sum_{i=a,b} \rho_i c_{ai}(k)(c_{ib}(k) + \gamma_{ib}(k)). \tag{2}$$

The ZH closure is of the form

$$
\begin{aligned}
c^a c^b \rho^2 g_{ab}(r) &= \exp[-\beta v_R^{ab}(r)] \times \\
&\times \left(1 + \frac{\exp[f^{ab}(r)[\gamma_{ab}(r) - \beta v_A^{ab}(r)] - 1}{f^{ab}(r)} \right),
\end{aligned} \tag{3}
$$

where $\beta \equiv 1/k_B T$, c^a and c^b are the concentrations of A-type and B-type particles, respectively, v_R and v_A are attractive and repulsive contributions of the pairwise potential v, and are given by $v_R v(r) - v_{min}$ $(r \leq r_{min})$ and $v_R = 0$ $(r \geq r_{min})$; $v_A = v_{min}$ $(r \leq r_{min})$ and $v_R = v(r)$ $(r \geq r_{min})$. The function f provides an interpolation between the SMSA and the HNC: $f^{ab} = 1 - \exp\left[-\frac{r}{\sigma_{ab}\alpha}\right]$, with α governing the switch between HNC and SMSA. The parameter α is typically chosen by demanding thermodynamic consistency between equations of states obtained by the virial and compressibility routes. Other choices, however, are possible [18], and here we choose the parameter α by comparison with the simulation data for the studied system in a range of temperature and density values. We find, as expected, that the value of α that yields the best match of energy and pressure values with those from simulations varies both with temperature T and density ρ. Based on the estimation of such α values for a small set of temperature and density values, we choose a linear functional form for the β- and ρ-dependence of α, $\alpha(\rho, T) = 11.17 - 11.7\rho + 6.65\beta$, which allows us to obtain quantitatively good results for thermodynamic quantities.

We solve the OZ equation, along with the ZH closure, for γ_{ab} using the procedure outlined in ref. [21]. Pair correlation functions are obtained first for low density and high temperatures. The pair correlation functions so obtained are used as initial guesses for the iterative solution
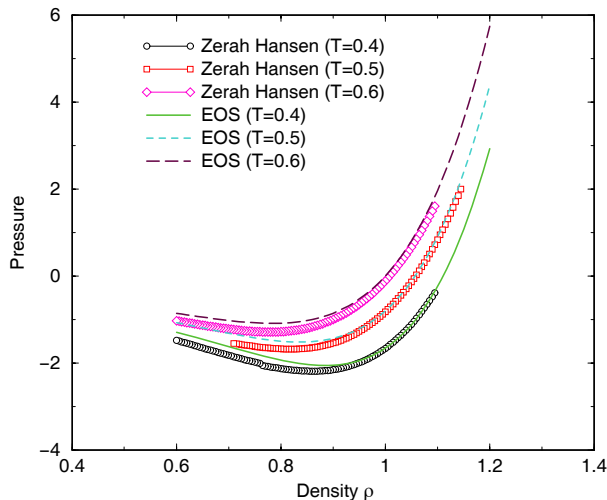

Fig. 1 – Pressure *vs.* density isotherms obtained using the Zerah-Hansen scheme (symbols), compared with the equation of state obtained from fits to the simulation data (lines) for temperatures $T = 0.4$, 0.5 and 0.6.
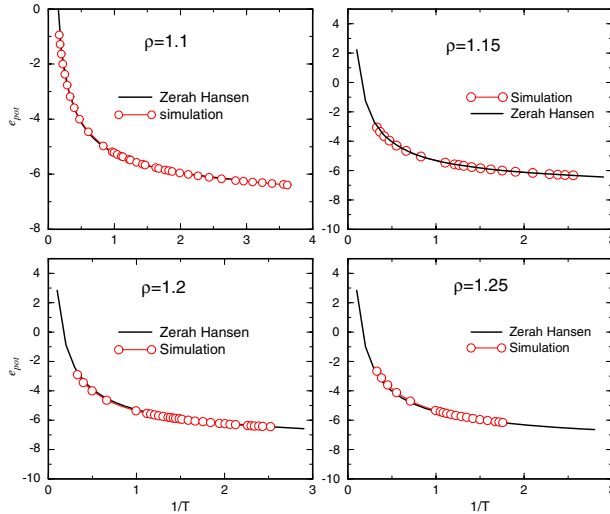
Fig. 2 – Comparison of potential energy obtained using the Zerah-Hansen scheme (lines) with data from molecular dynamics simulation, shown for densities $\rho = 1.1, 1.15, 1.2, 1.25$ as a function of the inverse temperature β.

of the OZ and ZH equations at lower temperatures and higher densities. We require iterative convergence at the level of 10^{-9} in $\sum_i (g_{n+1}(r_i) - g_n(r_i))^2$, with n being the iteration number and i the real-space mesh index.

In fig. 1, we compare isotherms obtained using this scheme for temperatures $T = 0.4, 0.5, 0.6$ with the isotherms derived, in [2], from an empirical equation of state based on simulation data. Data shown in fig. 1 demonstrate that the equation of state from the present calculations are in good quantitative agreement with the results in [2]. Figure 2 shows the potential energies (e_{pot}) obtained from the present calculations as a function of T and ρ, along with available values from computer simulations [2], demonstrating excellent agreement with the simulation results. The comparisons in figs. 1 and 2 indicate that the pressure and energy values obtained from the present calculations are quantitatively quite accurate.

In fig. 3, we show the isotherms obtained for temperatures in the range $T = 0.4$–0.9. We obtain the location of the spinodal at each temperature from the condition $\frac{\partial P}{\partial \rho} = 0$.

The glass transition temperatures at each density are calculated using the approach proposed by Mezard and Parisi [15, 16, 22, 23], which has been employed to calculate the glass transition line for the KA BMLJ in [18]. In this calculation, assuming the existence of an exponentially large number of free-energy minima whose degeneracy determines the configurational entropy or complexity, the thermodynamics of a system of m copies of the system which are restricted to be in the same free-energy minimum is considered. With the replicas remaining confined close to each other, the free-energy can be written in terms of their center-of-mass coordinates and the excursions of individual replicas from the center of mass. Evaluation of the contribution from the latter is done within approximation schemes pertaining to the Hessian or potential-energy second-derivative matrix. The configurational entropy is obtained by differentiating the resulting free energy per replica with respect to their number, in the limit of $m \to 1$. The resulting expression for the configurational entropy is
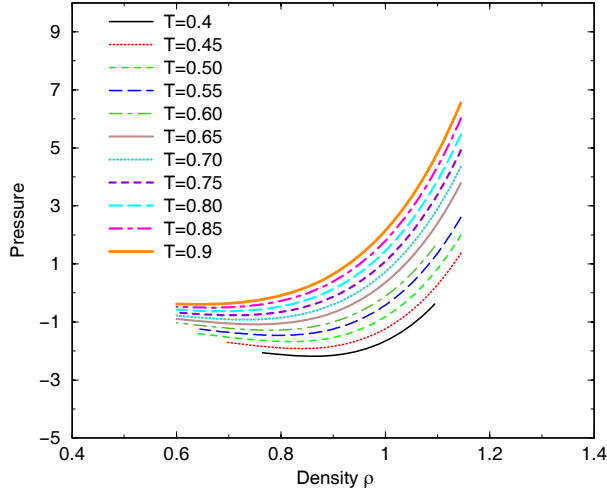
$$S_{conf} = S_{liq} - S_{glass}, \tag{4}$$

Fig. 3 – Pressure *vs.* density isotherms obtained using the Zerah-Hansen scheme for temperatures varying from $T = 0.4$ to $T = 0.9$. The spinodal lines are obtained from the location of the minima along these isotherms.

where S_{liq} is the entropy of the liquid, and

$$S_{glass}(\beta) = \frac{3N}{2}(1 + \log(2\pi)) - \frac{1}{2}\langle \mathrm{Tr}(\log(\beta M)) \rangle, \tag{5}$$

where M is the Hessian matrix of the form $M_{(i\mu),(j\nu)} = \delta_{ij} \sum_k v_{\mu\nu}(r_i - r_k) - v_{\mu\nu}(r_i - r_j)$ with $v_{\mu\nu} = \frac{\partial^2 v}{\partial r_\mu \partial r_\nu}$. The indices μ and ν run over the coordinates and i, j and k run over particle indices. The trace is calculated using the harmonic resummation scheme, details of which (and of the discussion above) can be found in [15, 16, 18]. As in [2, 24], the ideal glass transition T_K is located with the condition $S_{conf}(T_K) = 0$.

The entropy of the liquid is obtained from the internal energy ($e(\beta) = \frac{3k_B T}{2} + e_{pot}$) *via*

$$S_{liq}(\beta) = S_{liq}^o + \beta e_{liq} - \int_0^\beta \mathrm{d}\beta' e(\beta'). \tag{6}$$

Here S_{liq}^o is the entropy of the perfect gas in the infinite-temperature limit and is given by $S_{liq}^o = 1 - log(\rho) - c^a log(c^a) - c^b log(c^b)$, where c^a is the concentration of A particles and c^b is the concentration of B-type particles.

Both S_{liq} and S_{glass} require knowledge of the liquid-state pair correlation functions. However, at low temperatures the liquid integral equations do not converge, and hence extrapolations (of the form $aT^{-2/5} + b$ for S_{liq} and $a' + b' \log(T)$ for S_{glass}, based, respectively, on theoretical predictions for dense liquids [25] and the harmonic approximation to the glass free energy) are used to obtain S_{conf} at low temperatures. Figure 4 shows the configurational entropy *vs.* T for $\rho = 1.0, 1.05, 1.1, 1.15, 1.20$.

The liquid-gas spinodal and the glass transition lines obtained are shown in fig. 5, along with results from earlier work [2]. Our results reproduce the features observed in earlier work both qualitatively and, to a good extent, quantitatively, thus providing support for the general applicability of this approach. The calculated spinodal temperatures are in reasonable
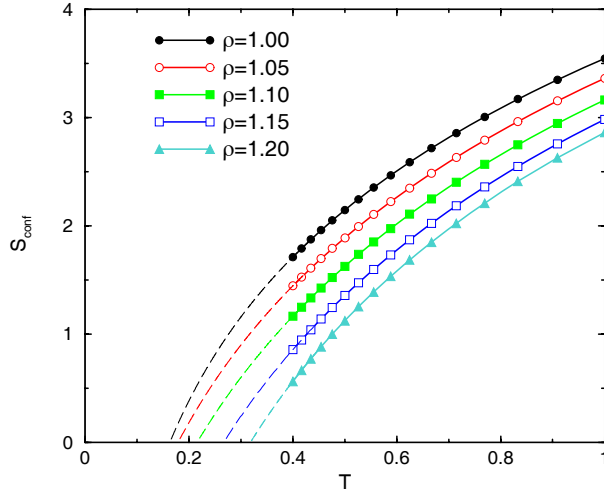
Fig. 4 – Configurational entropy S_{conf} for densities $\rho = 1.0$, 1.05, 1.10, 1.15, 1.20 are shown. For low temperatures the S_{conf} is obtained via an extrapolation shown by the dashed lines. The Kauzmann temperature is identified with the temperature at which the configurational entropy vanishes.
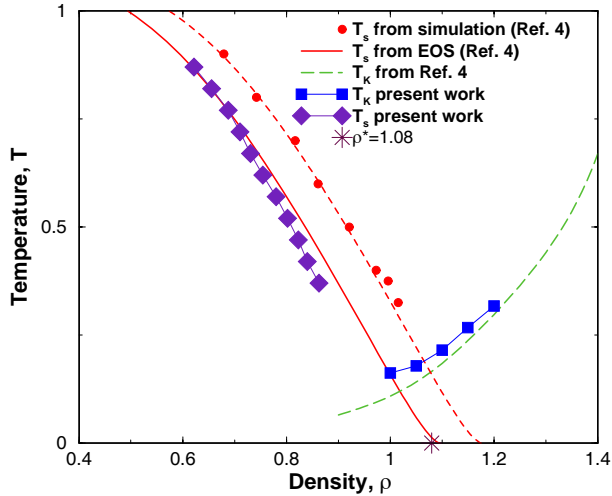

Fig. 5 – Limits of stability of the liquid phase from present work —spinodal labeled T_s and glass transition labeled T_K— compared with previous work [2]: (circles) spinodal estimated from inverse compressibility (the dashed line is a guide to the eye), (solid line) from the empirical equation of state, and (long-dashed line) glass transition line from energy landscape approach. The present calculation of the spinodal agrees quite well with that from the empirical equation of state, while the glass transition temperatures are seen to be slightly overestimated. The two limiting lines intersect at $\rho \sim 0.95$, as compared to $\rho \sim 1.08$ from earlier work. (The intersection density in [2] is 1.02 if the spinodal estimate from the empirical equation of state is used instead of the simulation estimates, a number closer to the one obtained from our present calculations.)

agreement with the ones estimated earlier from the empirical free energy. The glass transition temperatures obtained here are slightly higher than those estimated in previous work; this may be a consequence of the approximations involved in evaluating the glass entropies in the present case.

Together with previous work [2–5], these results lend strong support to the scenario that the liquid-gas spinodal and the glass transition line should typically intersect at a finite low temperature. Unlike previous work, where the results were based either on simulations, or on assumed model energy landscapes, our calculations describe a realistic-model glass former, whose properties are evaluated within a self-contained and accurate framework. We believe that the approach used here and its extensions may be useful in understanding arrested states in contexts similar to the one we study.

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