Excess free energy of supercooled liquids at disordered walls

Ronald Benjamin and Jürgen Horbach
Institut für Theoretische Physik II, Universität Düsseldorf,
Universitätsstraße 1, 40225 Düsseldorf, Germany

Using a novel thermodynamic integration scheme, we compute the excess free energy, \( \gamma \), of a glass-forming, binary Lennard-Jones liquid in contact with a frozen amorphous wall, formed by particles frozen into a similar structure as the liquid. We find that \( \gamma \) is non-zero, becoming negative at low temperature. This indicates that the thermodynamics of the system is perturbed by the effect of the amorphous wall.

Recently, several studies have investigated the relaxation dynamics of glass-forming systems in contact with a wall, formed by particles that are frozen into a similar disordered structure \( [1,3] \). One of the objectives in these studies has been to identify a growing static length scale associated with the dramatic slowing down of glassy dynamics in the bulk \( [1] \). This is based on the assumption that the thermodynamics of the system is unaffected by the disordered wall, provided an average is performed over the thermal fluctuations as well as a sufficient number of wall realizations \( [3] \).

Since in such systems, the mobile particles are in contact with an amorphous wall, albeit whose structure is similar to that of the liquid, it involves the presence of an interface. A key question then is to ask what the free energy cost of the formation of such an interface is. The absolute free energy of a system is difficult to compute directly, as the free energy is not a simple function of the phase space variables. However, in an atomistic simulation the free-energy difference of a given state from a reference state of known free energy can be computed using thermodynamic integration (TI) \([11]\).

In this work, we compute the excess free energy, \( \gamma \), of a binary glass-forming Lennard-Jones (LJ) liquid \( [12] \) in contact with quenched disordered walls on either side over the bulk free energy, using a novel TI scheme in combination with molecular dynamics (MD) simulation \([13]\). We consider the distance between the walls to be large enough for the two interfaces to be independent of each other. The interfacial free energy \( \gamma \) is computed as a function of temperature. For low temperatures, we find that \( \gamma \) becomes negative and thus the amorphous wall imposes an attractive pinning field on the supercooled liquid. Furthermore, the non-zero value of \( \gamma \) indicates that the free energy of the liquid is affected by the amorphous walls, although these walls have a similar structure as that of the liquid. Therefore, one has to be careful with respect to the interpretation of the relaxation behavior of the supercooled liquid and following conclusions about the structural relaxation in the bulk liquid.

**Model Potential.** We consider a two-component (particles of type A and B) 80:20 Kob-Andersen (KA) binary Lennard-Jones mixture \( [12] \) with the interaction parameters chosen to yield a supercooled liquid at low temperatures. We denote the interaction potential by \( u(r) \), \( r \) being the distance between the particles. The \( N \) binary LJ particles are enclosed within a simulation cell of size \( L_x \times L_y \times L_z \), with periodic boundary conditions in the \( x \) and \( y \) directions. Along the \( z \) direction, the particles are confined by disordered walls such that there are two wall-supercooled liquid interfaces with each interface having an area \( A = L_x L_y \). In order to prevent the supercooled liquid from penetrating the disordered wall, a short-ranged flat wall, modelled by a shifted and scaled WCA potential is introduced, similar to the hard wall introduced by Scheidler et al. \( [3,4] \).

To integrate the equations of motion, the velocity form of the Verlet algorithm was used with a time step \( \Delta t = 0.002 \sqrt{m \sigma_{AA}^2 / \epsilon_{AA}} \), where the mass \( m \) of all particles is identical and \( \sigma_{AA} \) and \( \epsilon_{AA} \) are the size and interaction strength parameters corresponding to component A. To maintain constant temperature, the velocity of the particles was drawn from a Maxwell-Boltzmann distribution at the desired temperature, every 100 time steps.

We carried out Molecular Dynamics simulations in the NVT ensemble at temperatures \( T = 0.53, 0.75, 1.0, 1.5 \) and 5.0, in reduced units. At \( T = 0.53 \), the temperature is low enough for the mixture to be in the supercooled regime and yet the equilibration to take place in a reasonable simulation time. At all temperatures, between 5–20 independent configuration of the system at that particular temperature were equilibrated, to pick reference configurations for the pinned disordered wall. To generate the reference configurations, the system was equilibrated for about 2–3 times the equilibration times reported in Ref. \( [12] \).

The disordered wall is constructed by choosing particle positions from a slab of width \( 5 \sigma_{AA} \), in the middle of the simulations box, from an equilibrium configuration. New particles fixed at these instantaneous equilibrated positions were then juxtaposed on the left and right sides of the simulation cell from the two halves of the slab each of width \( 2.5 \sigma_{AA} \) [equal to the cut-off range of the interaction potential \( u(r) \)], by shifting their \( z \)-positions by \( -L_z / 2 \) and \( L_z / 2 \), respectively.

**Method.** We adopt a thermodynamic integration scheme based on a similar approach developed by us earlier to compute the interfacial free energy of a LJ liquid/crystal in contact with structured walls \( [14] \) and a method to compute the crystal-liquid interfacial free energy \( [13] \). Our scheme consists of two steps. In the first step, the bulk supercooled liquid with periodic bound-
ary conditions, is transformed into a state where it is in contact with short-ranged flat walls on either side in the z direction, with the periodic boundary conditions still intact. The structureless flat wall (fw) is described by a shifted WCA potential and is denoted by, $u_{fw}(z')$, where $z' = z + 1.112\sigma_{AA}$. The two flat walls are located at the two ends of the simulation box along the z-direction, at 0 and $L_z$ respectively (for visualization see Fig. 1). Since the structureless flat wall has a very short-range of (0.01$\sigma_{AA}$), the contribution of this step to the total interfacial free energy is negligible and does not affect the structure of the supercooled liquid near the disordered walls.

In the second step, the interactions of the bulk system through the periodic boundaries are gradually switched off while interactions with the disordered wall are slowly switched on, such that at the end of the second step we have a supercooled liquid in contact with frozen amorphous walls on either side in the presence of short-ranged flat walls. From the free energy differences $\Delta F_1$ and $\Delta F_2$, corresponding to the two steps, the required interfacial free energy, $\gamma$, is obtained as, $\gamma = (\Delta F_1 + \Delta F_2)/A$.

In both steps of our TI scheme, the transformation from one equilibrium state to another is carried out by gradually changing a switching parameter $\lambda$, which couples directly to the interaction potential. The $\lambda$ dependent Hamiltonian for step one is given by: $H_1(\lambda) = \lambda^2\epsilon_w u_{fw}(z')$, where $\epsilon_w$ varies from 3800$\epsilon_{AA} - 40000\epsilon_{AA}$ from the lowest to the highest temperatures considered. For step two, the $\lambda$ dependent Hamiltonian takes the form: $H_2(\lambda) = (1-\lambda)^3u^*(r) + \lambda^3u_w(r + (1-\lambda)r_c)$, where $u^*(r)$ represents interaction between the mobile particles through the periodic boundaries, while $u_w$ represents interaction between a mobile and a wall particle and is of the same kind as the interaction between the free particles, viz. the 80:20 binary LJ mixture.

To study finite size effects in the supercooled regime ($T = 0.53$), we considered three system sizes with $N = 4000$, 6912, and 13500 particles having dimensions $10.0 \times 10.0 \times 33.22$, $11.5 \times 11.5 \times 43.41$, and $13.0 \times 13.0 \times 66.35$, respectively (in units of $\sigma_{AA}$). At $T = 0.53$, data was averaged over 20 independent wall configurations on either side of the liquid for $N = 4000$ particles, while for the larger system sizes, 10 realizations were considered. At the higher temperatures, only 5 independent wall and liquid configurations were considered and with a system size of $N = 4000$ particles.

**Results:** The simulation set-up for the supercooled liquid in contact with a wall made of frozen-in particles

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**FIG. 1:** (Color online) Simulation setup of supercooled liquid in contact with disordered walls along the z direction, showing the two components of the binary liquid mixture by different colors, with different (a) and same (b) color codes adopted for the mobile and pinned particles. The dashed vertical line, denotes the location of the flat walls. (c) Density profile averaged over 10 different wall configurations and those corresponding to two independent realizations. Data corresponds to $T = 0.53$ and $N = 6912$.

**FIG. 2:** (Color online) Thermodynamic integrand as a function of $\lambda$ for the first (in the inset) and second steps of the TI scheme at the temperature $T = 0.53$ and $N = 4000$.

**FIG. 3:** (Color online) Interfacial free energy as a function of the equilibration time corresponding to the first (a) and second (b) TI steps for $T = 0.53$ and $N = 4000$. 
and the thermal fluctuations. At the various independent realizations of the disordered wall, leads to a flat density profile near the wall as in the bulk. Hence the pinned particles do not affect the structural behavior of the free particles in the vicinity of the wall. We have also observed a similar behavior corresponding to the potential energy profile, in agreement with the findings by Scheidler et al. [3].

While this might lead to the conclusion that thermodynamics of the free particles is unperturbed in the presence of such a quenched disordered wall, in the following we show by our TI scheme that a non-zero excess free energy is associated with the interface between the wall and the liquid. The thermodynamic integrands corresponding to the two steps of the TI calculation are displayed in Fig. 4, corresponding to the temperature $T = 0.53$. As the two snapshots in Fig. 4 indicate, there is no change in the structure of the liquid near the walls and representing all regions by the same color scheme one is not able to distinguish any interface (Fig. 4b). This is also reflected in the density profile averaged over 20 independent wall configurations, with the profiles corresponding to two individual runs (Fig. 4b). Averaging over the thermal fluctuations and independent realizations of the disordered wall, leads to a flat density profile near the wall as in the bulk. Hence the pinned particles do not affect the structural behavior of the free particles in the vicinity of the wall. We have also observed a similar behavior corresponding to the potential energy profile, in agreement with the findings by Scheidler et al. [3].

In Fig. 4, we show the interfacial free energy $\gamma$ as a function of temperature, corresponding to the system size $N = 4000$. At all temperatures reported in this work, the potential energy per particle is always negative and the structure of the liquid is the same near the vicinity of the wall as in the bulk. The free energy difference $\Delta F = \Delta U - T\Delta S$, where $\Delta U$ is the change in the internal energy and $\Delta S$ is the change in the entropy of the system. Clearly, since $\Delta U = 0$, a non-zero free energy difference can only arise due to a change in the entropy of the system. Since the interfacial free energy at $T = 0.53$ turns out to be negative at this temperature, the entropy of the liquid in the supercooled regime increases in presence of such a disordered wall. With increasing temperature, however, $\gamma$ increases and eventually becomes positive. At higher temperatures, therefore the change in entropy is negative.

From these findings, one can infer that such a disordered wall exerts an effective pinning field on the particles, clearly perturbing the thermodynamics even though the structure of the liquid near the wall remains unchanged. At low temperatures, the negative value of $\gamma$ indicates that the disordered wall exerts an attractive potential on the confined supercooled particles acting as a trap, thus slowing down the dynamics. As temperature increases this potential field becomes positive. It is plau-
sible, therefore, that this behavior of $\gamma$ with respect to the temperature, is correlated to the relaxation time of the supercooled liquid near the wall, which as previous works have shown, decreases in the neighborhood of the wall as temperature increases [4]. It is to be noted that for glass-forming systems strongly confined by parallel flat walls, a Mode-coupling theory has been developed recently to explain the slowing down of the relaxation dynamics [16]. However, no such microscopic theories exist for supercooled liquids in contact with disordered walls.

While here we have studied the effect of pinned particles on a supercooled liquid, similar behavior of the interfacial free energy is also observed in other systems. In a previous work, as part of a TI scheme to compute the crystal-liquid interfacial free energy, we computed the free energy difference between a bulk crystal and the crystal in contact with a structured wall made of crystalline particles frozen into their equilibrium positions [13]. A negative value for the interfacial free energy was obtained (see Fig. 4 of Ref. [15], where the area in the negative region under the thermodynamic integrand curve is much greater than the positive part) even though the structure and potential energy of the crystal in contact with such a wall is the same as in the bulk. We also observed that the free energy difference became less negative at higher temperatures. This shows that even for the simpler case of a crystal evolving under the effect of pinned crystalline particles, the thermodynamics of the moving particles is definitely perturbed by the presence of the pinned particles and is not the same as in the bulk.

Conclusion.- In this work, we have obtained the interfacial free energy of a supercooled liquid in contact with frozen amorphous walls having the same structure as the liquid. We obtain a negative value for the interfacial free energy at low temperatures which becomes less and less negative at higher temperatures and then reaches a positive value. This indicates that thermodynamics of the supercooled liquid is not the same as in the bulk but is perturbed by the presence of such a disordered wall. Since the structure of the liquid in the vicinity of the wall is the same as in the bulk, the non-zero interfacial free energy is a purely entropic effect.

Our results have implications for studies which interpret the relaxation dynamics of supercooled liquids in the neighborhood of an amorphous wall to be correlated to the bulk behavior since such studies are based on the assumption that the pinned particles do not affect the thermodynamics of the confined liquid. However, one has to be careful when drawing conclusions about the bulk behavior of a supercooled liquid from the dynamics of the liquid near an amorphous wall, since the thermodynamics of the system is affected by the pinned particles.

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[1] V. Krakoviack, J. Chem. Phys. 141, 104504 (2014).
[2] A. Cavagna, Phys. Rep. 476, 51 (2009).
[3] P. Scheidler, W. Kob, and K. Binder, J. Phys. Chem. B 108, 6673 (2004).
[4] P. Scheidler, W. Kob and K. Binder, Europhys. Lett. 59, 701 (2002).
[5] L. Berthier and W. Kob, Phys. Rev. E 85, 011102 (2012).
[6] A. Cavagna, T. S. Grigera, and P. Verrocchio, Phys. Rev. Lett. 98, 187801 (2007).
[7] G. Gradenigo et al., J. Chem. Phys. 138, 12A509 (2013).
[8] W. Kob, S. Roldán-Vargas, and L. Berthier, Nature Phys. 8, 164 (2011).
[9] C. Cammarota and G. Biroli, Proc. Nat. Acad. Sci. 109, 8850 (2011).
[10] T. R. Kirkpatrick, D. Thirumalai, and P. G. Wolynes, Phys. Rev. A 40, 1045 (1989).
[11] D. Frenkel and B. Smit, Understanding Molecular Simulation (Academic, San Diego, 2002); T. P. Straatsma, M. Zacharias, and J. A. MacCammon, Computer Simulations of Biomolecular Systems (Escom, Keiden, 1993).
[12] W. Kob and H. C. Andersen, Phys. Rev. E 51, 4626 (1995).
[13] M. P. Allen and D. J. Tildesley, Computer Simulations of Liquids (Clarendon, Oxford, 1987).
[14] R. Benjamin and J. Horbach, J. Chem. Phys. 137, 044707 (2012); 139, 039901 (2013); 139, 084705 (2013).
[15] R. Benjamin and J. Horbach, J. Chem. Phys. 141, 084715 (2014).
[16] S. Lang, R. Schilling, V. Krakoviack, and T. Franosch, Phys. Rev. E 86, 021912 (2012).