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Dynamical instability causes the demise of a supercooled tetrahedral liquid

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Abstract We investigate the relaxation mechanism of a supercooled tetrahedral liquid at its limit of stability using isothermal isobaric (NPT) Monte Carlo (MC) simulations. In similarity with systems which are far from equilibrium but near the onset of jamming [O’Hern et.al., Phys. Rev. Lett. 93, 165702 (2004)], we find that the relaxation is characterized by two time-scales: the decay of long-wavelength (slow) fluctuations of potential energy is controlled by the slope \[\partial(G/N)/\partial\phi\] of the Gibbs free energy \(G\) at a unique value of per particle potential energy \(\phi = \phi_{\text{mid}}\). The short-wavelength (fast) fluctuations are controlled by the bath temperature \(T\). The relaxation of the supercooled liquid is initiated with a dynamical crossover after which the potential energy fluctuations are biased towards values progressively lesser than \(\phi_{\text{mid}}\). The dynamical crossover leads to the change of time-scale, i.e., the decay of long-wavelength potential energy fluctuations (intermediate stage of relaxation). Because of the condition \[\partial^2(G/N)/\partial\phi^2 = 0\] at \(\phi = \phi_{\text{mid}}\), the slope \[\partial(G/N)/\partial\phi\] has a unique value and governs the intermediate stage of relaxation, which ends just after the crossover. In the subsequent stage, there is a relatively rapid crystallization due to lack of long-wavelength fluctuations and the instability at \(\phi_{\text{mid}}\), i.e., the condition that \(G\) decreases as configurations with potential energies lower than \(\phi_{\text{mid}}\) are accessed. The dynamical crossover point and the associated change in the time-scale of fluctuations is found to be consistent with the previous studies.

Keywords stability limit · dynamical crossover · Jamming

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1 Introduction

The end of the liquid state in the supercooled region occurs either due to glass transition or due to the approach to the temperature corresponding to the limit of the stability. In the latter case, the mechanism of relaxation of the liquid (that ultimately leads to the stable crystalline state) is generally termed as ‘homogeneous nucleation’. Due to the difficulty of obtaining reproducible data at extreme conditions, there are only a few cases in which the relaxation point at the stability limit has been precisely estimated. For example, it is well-known that the hard-sphere fluid exhibits jamming at a random close packed density close to 0.64, independent of the simulation or the experimental protocols. An analysis of equation of state points out that this density corresponds to end point of the metastable (non-crystalline) branch of the hard-sphere fluid. In the case of Stillinger–Weber silicon, the liquid state properties at the lower limit of stability of 1060 K have been precisely estimated based on free energy computations.

Here we attempt to study the relaxation at the stability limit of supercooled water modeled by mW potential of Molinero and Moore. mW is a coarse-grained model of water in which water is represented by a single atom with 3-body (tetrahedral) interactions to mimic the effect of hydrogen bonds of real water. mW potential is a modified form of Stillinger-Weber potential in which the strength of the 3-body term is higher than in the case of Silicon. Due to its short-ranged interactions, simulations of water using mW model are much faster than the simulations using other commonly used atomistic models of water. Moreover, mW model correctly reproduces the following properties: the stability of hexagonal ice and its melting point, the enthalpy of melting, the liquid density at the melting point and at 298 K, the maximum density of the liquid, and the liquid-vapor surface tension. However due to lack of hydrogen atoms, the rate of crystallization of supercooled mW water is higher compared to that of atomistic models of water. Although mW predicts unrealistic crystallization rates, due to its computational efficiency, it is used to study relaxation in the supercooled water to gain qualitative insights into the behavior of real water. Recently, mW model was used to analyze the transitions between high density and low density amorphous ices in supercooled water.

The lower limit of stability of the supercooled mW water has been estimated to be close to 200 K at a pressure of 1 bar. It is important to note that independent studies yield the same average density
of 0.98 gm/cm\(^3\) at the stability limit, \([5,3]\) below which it is not possible to equilibrate the liquid. Isobaric cooling simulations using Molecular Dynamics with rates varying over an order of magnitude (from 1 to 10 K/ns), yield the same limiting value of enthalpy (-43.03 kJ/mol) \([11]\) at 202 K. Moreover, the rate of relaxation as measured by the rate of decrease of enthalpy, density and the rate of increase in 4-coordinated particles is found to be the maximum at the stability limit. \([3]\) Insipite of a large number of studies on mW liquid, it is not clear if nucleation is the relevant mechanism of relaxation at the limit of stability. In an attempt to identify the critical nuclei (at 205 K and 1 atm pressure), Moore and Molinero found that the identified nuclei had a broad range of shapes and crystallization probabilities. Hence it was concluded that “other reaction coordinates, such as the structure of the liquid wetting the nuclei, are relevant to define the transition states of ice crystallization” [Please see caption of Supplementary Figure 7 of Ref. \([11]\)]. In effect, critical nuclei for ice formation could not be successfully identified, which suggests that nucleation is not the relevant mechanism by which relaxation is initiated at or near the limit of stability, \(T_s \approx 205\) K.

In this work, we find that relaxation mechanism differs in one crucial aspect from the nucleation phenomena. In the latter, the unstable state [consisting of the metastable (mother) phase with a critical nucleus] is an equilibrium state, i.e., it corresponds to a stationary condition of the free energy. In contrast to this, we show that the instability that leads to relaxation of the liquid occurs across a unique dynamical (i.e., non-stationary) point of the free energy function. Further, the relaxation mechanism is found to have a close similarity to sheared foam systems, which are far from equilibrium but near the onset of jamming. \([13,12]\) In such systems, there are two-time scales: the decay of long-wavelength fluctuations (relaxation) is controlled by the ‘effective’ temperature while the fluctuations over the shorter time scale are controlled by the bath temperature. \([12]\) We find that in the supercooled mW liquid, the relaxation is initiated with a change of time-scales or the dynamical crossover, which signals the decay of long-wavelength fluctuations. The latter is controlled by the unique configurational temperature or equivalently, the slope \([\partial (G/N)/\partial \phi]\) of the Gibbs free energy function \(G(T, P, N, \phi)\). The properties (the per particle potential energy, the density, and the fraction of the 4-coordinated particles) at the crossover point are found to be unique (independent of the system size) and agree with the earlier studies. \([10,3,11,5]\)
2 Methodology

Following the method of the earlier work on SW-Si, [8][2] we studied the relaxation mechanism of supercooled mW liquid at 205 K (which is a more accurate estimate of the limit of stability [11]) and zero pressure in isothermal isobaric (NPT) Monte Carlo (MC) simulations. Each MC simulation step, on average, consisted of N particle displacement attempts and 2 volume change attempts. A simulation box of cubic shape, and with periodic boundary conditions across all faces was used. The properties of the largest network of 4-coordinated particles along the trajectories were also computed (in a manner similar to Ref. [5] and [6]). To trace the network, we considered two particles as bonded, if the distance between these particles is 1.4 \( \sigma \) or less.

The total potential energy \( \Phi \) of the mW particles is computed as follows: [16][9]

\[
\Phi(r_1, ..., r_N) = \sum_{ij} v_2 + \sum_{ijk} v_3, \tag{1}
\]

where \( v_2 \) and \( v_3 \) are the two-body and three-body potential energy terms respectively. The per particle potential energy is computed as \( \phi = \Phi/N \), where \( N \) is the total number of particles. The term \( \sum_{ij} \) represents sum over all pairs of particles and the term \( \sum_{ijk} \) represents sum over all triplets of the particles. The expression for the two-body and three-body terms are given by the following expressions

\[
v_2(r_{ij}) = \epsilon f_2(r_{ij}/\sigma) \tag{2}
\]

\[
v_3(r_i, r_j, r_k) = \epsilon f_3(r_i/\sigma, r_j/\sigma, r_k/\sigma), \tag{3}
\]

where \( r_i, r_j, \) and \( r_k \) are the position vectors of the particles, and \( \epsilon \) and \( \sigma \) are the energy and length parameters, respectively. The functions \( f_2 \) and \( f_3 \) are given by the following expressions: [16]

\[
f_2(r) = \begin{cases} 
A(Br^{-p} - r^{-q}) \exp[(r-a)^{-1}], & \text{if } r < a \\
0 & \text{otherwise}
\end{cases} \tag{4}
\]

and

\[
f_3(r_i, r_j, r_k) = h(r_{ij}, r_{ik}, \theta_{ijk}) + h(r_{ij}, r_{jk}, \theta_{ijk}) + h(r_{ik}, r_{jk}, \theta_{ikj}) \tag{5}
\]

where \( r_{ij} \) and \( r_{ik} \) etc. are the distances between the particles and \( \theta_{ijk} \) is the angle between vectors \( r_{ij} \) and \( r_{ik} \). The expression for \( h \) contained in the 3-body term \( f_3 \) is given by

\[
h(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda \exp[\gamma(r_{ij} - a)^{-1} + \gamma(r_{ik} - a)^{-1}](\cos \theta_{ijk} + 1/3)^2 \tag{6}
\]
The values of the parameter used in the above equations are \( A = 7.049556277, B = 0.6022405584, \)
\( p = 4, q = 0, a = 1.8, \lambda = 23.15 \) and \( \gamma = 1.20. \) The values of the energy and the length parameters in the mW potential are as follows: \( \epsilon = 6.189 \text{ kcal/mol}, \sigma = 0.23925 \text{ nm}. \) Throughout this work, all the quantities (unless stated otherwise) are expressed in dimensionless units in terms of mW potential parameters \( \sigma \) and \( \epsilon. \)

The 3-body energy of a given triplet of particles \((ijk)\) consists of 3-terms corresponding to the angles \( \theta_{jik}, \theta_{kji}, \theta_{ikj} \) centered at the particles \( i, j, \) and \( k \) [see Eqs. (5) and (6)]. The three body energy was assigned to a particle of the triplet as follows: the particle at which the bond angle is centered is assigned the 3-body energy resulting from the particular bond-angle, for example, the term \( h(r_{ij}, r_{ik}, \theta_{jik}) \) was assigned to particle \( i \) of the triplet. The total 3-body energy assigned to a particle \( \phi^{3B}_i \) consisted of contributions from all triplets involving that particle. The per particle 3-body energy of the largest 4-coordinated network of a given instantaneous configuration was computed as \( \phi^{3B}_{4c} = \left( \sum_{i=1}^{N_{4c}} \phi^{3B}_i \right) / N_{4c} \), where \( \phi^{3B}_i \) is the 3-body energy of particle \( i \) in the network, and \( N_{4c} \) is the total number of particles in the network.

The main emphasis in this work is on the potential energy distributions. We compute the logarithm of the potential energy distribution generated by a trajectory as follows: \( \log p(\phi) + \text{constant} = \log N_c(\phi), \) where \( N_c \) is the number of configurations sampled in the entire NPT-MC trajectory with the per particle potential energy in the range \( (\phi - \Delta\phi/2) \) and \( (\phi + \Delta\phi/2); \Delta\phi = 3 \times 10^{-4} \) is the width of the bin. The symbol ‘\( \log \)’ represents the natural logarithm. In order to analyze the various stages of relaxation of the liquid, we compute the intermediate distributions at certain points along the trajectories. The intermediate distributions (denoted here by ‘\( \prime \)’) are given by \( \log N'_c(\phi), \) where \( N'_c(\phi) \) is the number of configurations at a given \( \phi \) sampled up to a particular point along the trajectory. Please note that \( N'_c(\phi) \leq N_c(\phi), \) where \( N_c(\phi) \) is the total number of configurations at a given \( \phi \) sampled along the entire trajectory. To differentiate it from intermediate distributions, we use the term ‘final’ distribution for \( p(\phi). \) Throughout this work \( p(\phi) \) is obtained from a single (sufficiently long) trajectory only for a given system size \( N. \) The distributions are not averaged over independently generated trajectories. The reason for this has been explained in detail in the last (‘Summary’) section. When analyzing the potential energy distributions, we focus on the straight line regions (SLRs) that
appear in the intermediate distributions. To locate a SLR, we consider the intermediate distribution that yields the linear correlation coefficient ($R^2$) of the straight line fit that is closest to unity ($R^2 \rightarrow 1$). As we shall see in the next section, the SLRs are not just the geometric features of the distributions but these have a physical meaning in that the trajectory shows irreversible changes (or relaxation) across the mid-point of each of the SLRs.

### 3 Relaxation of the supercooled liquid

We generated, by trial and error, NPT-MC trajectories in which relaxation is delayed the most. We have generated 3 such trajectories at 205 K with system sizes of $N = 10648$, 4096, and 1000 particles. For completeness, we also include data from the shorter trajectories with 10648 and 4096 particles. The data-sets and the figures resulting from the 5 trajectories are as follows:

- **Data set (1):** Figures 1–5 show the data generated by the longer trajectory with $N = 10648$ particles.
- **Data set (2):** Figures S1–S6 (supplementary information file) are generated using the data from the longer trajectory with $N = 4096$ particles.
- **Data set (3):** Figures S7–S12 (supplementary information file) are generated using the data from the trajectory with $N = 1000$ particles.
- **Data set (4):** Figures 6–8 are generated using the data from a shorter trajectory with $N = 10648$ particles.
- **Data set (5):** Figures S13–S17 (supplementary information file) are generated using the data from a shorter trajectory with $N = 4096$ particles.

In this section, we describe the relaxation process observed in the longer trajectories [Data sets (1)–(3)]. The relaxation processes during the shorter trajectories [Data sets (4) and (5)] are described in a separate section. Figure 1 shows the block averages of the per particle potential energy ($\phi$), the fraction of the particles in the largest 4-coordinated network ($f_{4c}$), and the fraction of the 4-coordinated particles ($f_4$) along the NPT-MC trajectory with 10648 particles [Data set (1) listed above]. Figure 2 shows the block averages of the density ($\rho$) and the per particle 3-body energy of the largest 4-coordinated network ($\phi^{3B}_{4c}$) along the same trajectory. The block averages are taken over $10^5$ MC steps. Figure 3 shows the evolution of the potential energy distributions generated by the trajectory.
The point along the trajectory at which the logarithm of the potential energy distributions develops the straight line region (SLR) (see Figure 3) is marked as ‘SLR’ point in Figs. 1 and 2. The red symbols in Fig. 1 represent the microstates with the per particle potential energy in the interval $[\phi_{\text{mid}}] = (\phi_{\text{mid}} - \Delta\phi/2, \phi_{\text{mid}} + \Delta\phi/2)$, where $\phi_{\text{mid}}$ is the mid-point of the SLR as indicated in Fig. 3. In this work, we point out that the relaxation of the liquid is a two stages process as described below.

Stage (i) The intermediate (short-time) relaxation is governed by the slope $[\partial(G/N)/\partial\phi]$ of the Gibbs free energy function $G(T, P, N, \phi)$ with a unique value at $\phi_{\text{mid}} = -1.760 \pm 0.001$. The value of the slope is unique because of the condition $[\partial^2(G/N)/\partial\phi^2] = 0$ at $\phi = \phi_{\text{mid}}$, as we shall see later. This stage of relaxation ends just after the dynamical crossover of potential energy fluctuations across $\phi_{\text{mid}}$, which results in the change in the time-scale of fluctuations.

Stage (ii) The relaxation in this stage is relatively rapid due to lack of long-wavelength fluctuations, and due to instability at $\phi_{\text{mid}}$, i.e., the condition that $G$ decreases as the microstates with potential energy lower than $\phi_{\text{mid}}$ are accessed. The relaxation occurs over a relatively longer time and ultimately results in the formation of the stable crystalline phase.

In this work, our main focus is on the intermediate [stage (i)] relaxation. The trajectory is propagated from an initial configuration which is highly disordered ($\phi > \phi_{\text{mid}}$), and which is far from equilibrium. In the initial part of the trajectory, the potential energy and density fluctuate around the local minimum $[\phi_m, \rho_m]$ of the probability distribution. At a certain stage (just before the R point as clearly seen in Figs. 1, 2, S1, and S2), there is a increase in the local tetrahedral order (i.e., a decrease in $\phi^{4B}_{4c}$) and in the size of the 4-coordinated network (measured by $f_{4c}$). Simultaneously, the potential energy fluctuations approach $\phi_{\text{mid}}$. The local minimum $[\phi_m, \rho_m]$ is statistically less accessible in this region. After the dynamical crossover point (dashed vertical line, see Figs. 1, S1, S7), the potential energy fluctuations are biased towards values progressively lesser than $\phi_{\text{mid}}$. Simultaneously, there is a change of time scale of fluctuations which is associated with a second order discontinuity in the Gibbs free energy function (as we shall see later). The intermediate relaxation stage ends just after the crossover (at the SLR point in Figs. 1, S1, and S7) and results in the formation of a straight line region (SLR) in the potential energy distributions at $\phi_{\text{mid}}$ (see Figs. 3, S3, and S9).
To demonstrate the dynamical crossover more clearly, we have shown a zoomed in portion of the trajectory in Fig. 4. Here the block averages are taken over a smaller number of MC steps (13000 MC steps) as compared to that in Fig. 1. Before the dashed vertical line, the potential energy fluctuations are biased towards values slightly greater than $\phi_{\text{mid}}$. After the crossover (i.e., the dashed vertical line), the fluctuations are biased towards values progressively less than $\phi_{\text{mid}}$. The changes in the block averages across $\phi_{\text{mid}}$ are seen to be irreversible. Since the governing feature of the free energy is $[\partial(G/N)/\partial \phi]$ with a configurational temperature not equal to bath temperature ($T_c \neq T$), the irreversible decrease of potential energy suggests that relatively fast (or short wavelength) fluctuations (responsible for equilibration with respect to bath temperature $T$) survive at the crossover. Thus there is a change in the time-scale of fluctuations, i.e., dissipation of long-wavelength potential energy fluctuations at the crossover. The relatively rapid and irreversible decrease in the block average potential energy (see Figs. 1, S1, and S7) after the crossover supports our proposition about the decay of long-wavelength fluctuations.

The observation that the slope $[\partial(G/N)/\partial \phi]$ (or equivalently, $T_c$) at $\phi_{\text{mid}}$ governs the overall evolution of the system (intermediate relaxation) while the bath temperature controls the short-wavelength fluctuations seems to be very similar to the concept of ‘effective’ temperature in non-equilibrium systems close to jamming. [12,13] In their study, Ono et. al. plotted the probability distribution $\log_{10} \Omega(U)$ of configurational energies $U/N$ obtained by numerical simulations of sheared foam system (see Fig. 4(a) of Ref. [13]). The ‘effective’ temperature was obtained from the slope of the straight line region (SLR) of the distribution (see Figs. 4a and 4b in Ref. [13]). In such systems, the fluctuations that decay over a longer time (which results in intermediate relaxation in our work) are related to the effective temperature [12] (which is similar to the $T_c$ obtained from $[\partial(G/N)/\partial \phi]$ in our case), while the faster fluctuations are related to the bath temperature ($T$).

As for the structural changes, we find that the fluctuations in the size of the 4-coordinated network diminish and there is an irreversible increase in the average size of the network (measured by increase in $\langle f_{4c} \rangle_b$ across the crossover. Simultaneously there is an irreversible increase in the local tetrahedral order (i.e., decrease in $\langle \phi_4^{3B} \rangle_b$ below a value of $\approx 0.22$) as seen in Figs. 2 and 5. Overall, it seems that the crossover is caused by the cooperative structural changes involving 4-coordinated particles (i.e.,
development of a certain threshold of the local tetrahedral order). A similar dynamical crossover with accompanying changes in the local tetrahedral order is also observed in case of trajectories with $N = 4096$ (see Figs. S1, S2, S5, S6) and $N = 1000$ (see Figs. S7, S8, S11, S12). The values of per particle potential energy, the density (see Figs. S6, and S12), and the network properties at the crossover point are obtained by linear interpolation at the dashed vertical lines in the figures. These values are reported in Table I. These properties seem to be independent of the system size $N$.

The dynamical crossover results in the end of the liquid state. This conclusion is supported by the fact that the local minimum $[\phi_m, \rho_m]$ of the probability distribution is no longer accessible in a statistically significant manner after the crossover, i.e., the microstates with potential energy and density in the range $[\phi_m, \rho_m]$ are negligibly smaller in number after the crossover as compared to the number of such microstates before the crossover. As can be seen in Fig. 1 and 4, there is not a single microstate corresponding to $[\phi_m, \rho_m]$ accessible after the crossover. Same is the case for trajectory with $N = 4096$ particles (see Figs. S1 and S5). In case of the trajectory with $N = 1000$ particles, there is just a single microstate with potential energy and density in the range $[\phi_m, \rho_m]$ (see Figs. S7 and S11). The lack of long-wavelength potential energy fluctuations at the crossover is responsible for the inaccessibility of the the local minimum $[\phi_m, \rho_m]$. Thus the ‘R’ point in all 3 trajectories is located very close to the location of the crossover.

Now, we point out that the dynamical crossover and the associated change in the time-scale of fluctuations is consistent with earlier studies. In these studies, the instability was detected in isobaric MD simulations in which the liquid was supercooled at a certain rate. Most importantly, it was found that the rate of changes of potential energy, density, and the fraction of 4-coordinated particles is the maximum at the instability limit. The maximum in the rate of changes is consistent with our conclusion about the dissipation of large-scale fluctuations. Moore and Molinero have reported a maximum in the rate of decrease of enthalpy at 1 atm pressure at 202 K during isothermal isobaric (NPT) Molecular Dynamics (MD) cooling simulations at rate of 1 K/ns. This maximum occurs at a per particle potential energy value of $-1.759$ in reduced units. This agrees with the dynamical crossover point found in our work $\phi_{mid} = -1.760 \pm 0.001$. The value of -1.759 in reduced units (in the work by Moore and Molinero) is computed by using the enthalpy value of -43.03 kJ/mol at 202 K
and 1 atm (as read at the location of the dashed vertical line in Fig. 1a of Ref. [11]) and a density of
0.45 (in reduced units). In the study of Limmer and Chandler, [5] the density was found to be 0.98
gm/cm$^3$ ($\approx 0.449$ in reduced units) at the limit of stability of the mW liquid. Further, the rate of
change of density with temperature was found to be the maximum at the stability limit (see the
density plot on the extreme left in the lower panel of Fig. 2 in Ref. [5]). Hujo et. al. [3] have reported
a sharp decrease in density across a value of 0.45 ($\sigma^3$) in MD cooling simulations (see the
temperature-density curve with parameter value of 23.15 in Fig. 1 of Ref. [3]), which agrees with the
value at the dynamical crossover (Table I). Further, Hujo et. al. have mentioned that the maximum
in the rate of change of density ($d\rho/dT$), the fraction of 4-coordinated particles ($df_4/dT$), the
tetrahedral order parameters ($dQ/dT$), and ($dH/dT$) (as measured by the maximum in $C_p$) coincide
at the limit of stability (as stated at the end of Section 3.3 and in Section 3.4 in Ref. [3]). Moore and
Molinero have reported that at 0.98 gm/cm$^3$ (i.e. 0.449$\sigma^3$) a maximum in the rate of change of
density with respect to temperature occurs (Fig. 1 of Ref. [10]). In the same study, a maximum in the
rate of increase of 4-coordinated particles in MD cooling simulations ($df_4/dT$) is found to be at
$f_4 \approx 0.75$ for a cut-off radius of 3.35$\sigma$A (i.e., 1.4 $\sigma$) (this value was read from the lower panel of Fig. 3
in Ref. [10]). This is close to the average value of $\langle f_4 \rangle \approx 0.742$ reported in Table I. Moore and
Molinero have also noted that maxima in the rate of increase of tetrahedrality order parameter
($dQ/dT$), fraction of 4-coordinated particles ($df_4/dT$), density ($d\rho/dT$) and the maximum structural
correlation length $\xi$ occur at the same temperature $T_{LL} = 202 \pm 2$ K. [10] The coincidence of the
maxima in $df_4/dT$, $dQ/dT$ and $dH/dT$ in the MD cooling simulations suggests that cooperative
changes in the 4-coordinated particles cause these maxima. This agrees with our observation that the
change in the time-scale of potential energy fluctuations (at the dynamical crossover) is accompanied
by a relatively rapid and irreversible changes in $\langle \phi_4^{B} \rangle_b$, $\langle f_{4c} \rangle_b$, and $\langle f_4 \rangle_b$.

The size of the block averages $\langle \phi \rangle_b$ is crucial in detecting the crossover and the structural
properties at the crossover (see Table I). There is a irreversible decrease in $\langle \phi \rangle_b$ across $\phi_{mid}$ during
the crossover, as seen in zoomed-in portion of the longer trajectory at each $N$ (Figs. 4, S5, S11). If
block averages are taken over a larger number of MC steps (for e.g., $10^5$ MC steps as in the full
trajectory Fig. 1), the crossover cannot be detected precisely. On the other hand, if the block
averages are taken over very small number of MC steps, due to influence of short-wavelength fluctuations (which are responsible for equilibration with respect to \( T \)), the block averages do not exhibit an irreversible decrease at the crossover. In such cases, the properties at the crossover cannot be determined unambiguously. Thus there is a minimum and maximum limit on the size of the block averages in relation to the dynamical crossover. In our study, the size of the block averages in the zoomed-in portions of the trajectories is decided (by trial and error) so that the irreversible change in \( \langle \phi \rangle_b \) at the crossover is as steep as possible.

It is important to note that while the properties in Table I are independent of the system size \( N \), the length of the trajectory upto ‘R’ point or equivalently the lifetime of the liquid is strongly dependent on \( N \). The length of the trajectory upto ‘R’ point is much shorter for \( N = 10468 \) (Fig. 1) particles than that for \( N = 1000 \) (Fig. S7) particles. This can be rationalized as follows. As the system size \( N \) increases, the potential energy distribution becomes progressively steeper. As such, when starting from a higher potential energy (disordered) configuration (with \( \phi > \phi_{\text{mid}} \)), the approach to equilibrium (and hence the dissipation of large-scale potential energy fluctuations) is expected to be faster, resulting in the shorter trajectories with increase in \( N \). This is consistent with what we observe. On the other hand, the properties at the dynamical crossover itself (listed in Table I) are independent of the system size. This is expected because \( \phi_{\text{mid}} \) (per particle potential energy at the crossover) as well as the slope of the Gibbs free energy \( \partial G/\partial \Phi = \partial(G/N)/\partial \phi \) at the crossover are both intensive properties.

The evolution of the system after the first stage of the relaxation (i.e., after the SLR point in Figs. 1, S1, and S7) constitutes the 2nd stage of relaxation. Our data shows that after the SLR point, the configurations with potential energies greater than \( \phi_{\text{mid}} \) are not accessed in a statistically significant manner, i.e., the logarithms of SLR distribution and the ‘final’ distribution closely match for potential energies greater than \( \phi_{\text{mid}} \) (see Figs. S3, and S9) for all system sizes. This shows that the long-wavelength fluctuations are completely dissipated at the end of the intermediate (first) stage of relaxation. The relatively rapid changes in the second stage (after the SLR point, see Figs. 1, S1 and S7) is caused by the lack of long-wavelength fluctuations and the instability at \( \phi_{\text{mid}} \), i.e., the condition that Gibbs free energy \( G \) decreases as configurations with potential energies lower than
If the trajectories are continued for sufficiently long time, the system would ultimately convert into the stable crystalline state. Moore and Molinero [11] have shown that crystallization times (i.e., time required to crystallize about 70% of the liquid sample) are the minimum at or around the limit of stability (see Time-temperature transformation diagram, Fig. 2a of Ref. [11]). In order to explore the structural changes responsible for the minimum crystallization times, a study of crystallization in the 2nd stage of relaxation using global order parameters such as $Q_6$ [15] will be interesting and will be pursued in a future work.

4 Gibbs free energy as a function of $\phi$

The logarithm of the probability distribution $\log p(\phi)$ can be equated to the Gibbs free energy provided that the maximum possible microstates at a given $\phi$ are sampled by the trajectory. Thus such a distribution should be unique. That our generated distribution is unique, at least for $\phi \geq \phi_{\text{mid}}$, is supported by two facts:

(i) The average per particle potential energies and average densities of the liquid (i.e., cumulative averages up to R point in Figs. 1, 2, S1, S2, S7, and S8) are found to be: $\langle \phi \rangle = -1.7542$ ($N=10648$), $-1.7547$ ($N=4096$), $-1.7539$ ($N=1000$), and $\langle \rho \rangle = 0.4495$ ($N=10648$), 0.4494 ($N=4096$), 0.4495 ($N=1000$). These values are fairly independent of $N$. The liquid distribution (i.e., intermediate distribution up to R point) and the final distribution are the same for $\phi > \phi_m$ (see Figs. 3, S3, and S9). Thus, the agreements of the average properties for different $N$ points to the uniqueness of the final potential energy distributions, at least, for potential energy values greater than $\phi_m$.

(ii) The mid-point of the SLR $\phi_{\text{mid}}$ is $-1.7592$, $-1.7614$, and $-1.7590$ for trajectories with $N=10648$, 4096, and 1000 particles, respectively. The value of configurational temperatures $T_c$ of the SLR are 204.17 K, 203.48 K, and 203.69 K for trajectories with $N=10648$, 4096, and 1000 particles, respectively (see Figs. 3, S3, and S8). Thus, both $\phi_{\text{mid}}$ and $T_c$ are independent of $N$.

Since the ‘final’ distribution and the SLR distribution are the same for $\phi \geq \phi_{\text{mid}}$, the above two observations indicate the uniqueness of the distribution at least for potential energy values greater than $\phi_{\text{mid}}$. Thus we conclude that $G(T, P, N, \phi) = -k_B T \log p(\phi) + \text{constant}$ for $\phi \geq \phi_{\text{mid}}$, where $\log p(\phi)$ refers to the ‘final’ probability distributions in Figs. 3, S3, and S9. The inflection point (at or
just above \( \phi_{\text{mid}} \) seen in the probability distributions (Figs. 3 and S3 for \( N=10648 \) and 4096 trajectories) is therefore, also the inflection point of the Gibbs free energy.

We find that there is a discontinuity in the second order derivative of \( G(T, P, N, \phi) \) at the mid-point of the SLR. This can be seen by the fact that the potential energy distribution can be curve-fitted by the Taylor series expansion around the mid-point of the SLR in the following form:

\[
\log p_{\text{SLR}}(\phi) = \log p_{\text{SLR}}(\phi_{\text{mid}}) + a_1(\phi - \phi_{\text{mid}}) + \frac{1}{3!}a_3(\phi - \phi_{\text{mid}})^3 + \frac{1}{4!}a_4(\phi - \phi_{\text{mid}})^4 + \frac{1}{5!}a_5(\phi - \phi_{\text{mid}})^5, \tag{7}
\]

where

\[
a_i = \left. \frac{\partial^i \log p_{\text{SLR}}(\phi)}{\partial \phi^i} \right|_{\phi = \phi_{\text{mid}}}. \tag{8}
\]

Here \( p_{\text{SLR}}(\phi) \) is the intermediate distribution up to the SLR point. Note that in the above expansion we have taken the second order term to be zero, i.e., \( a_2 = 0 \), since this condition is satisfied at the mid-point of the SLR. In Fig. 3 we have fitted the SLR distribution with \( a_3 = 5 \times 10^{-5} \) and \( a_4 = -6 \times 10^{-6} \). The curve fit is reasonably good for potential energies less than the mid-point of the SLR \( (\phi < \phi_{\text{mid}}) \). In the case of trajectories with system sizes of 4096 and 1000 particles, multiple SLRs appear simultaneously (see Figs. S3 and S9). A Taylor series expansion can be fitted to each of these SLRs as shown in Figs. S4 and S9. The Taylor series expansion around \( \phi = \phi_{\text{mid}} \), on the one hand, fits the distribution at lower potential energies \( \phi \leq \phi_{\text{mid}} \) (at least up to the next SLR at the lower potential energies), while on the other hand, it deviates from the actual distribution at the higher potential energies \( \phi > \phi_{\text{mid}} \). Since \( \log p_{\text{SLR}}(\phi) = \log p(\phi) \) for \( \phi \geq \phi_{\text{mid}} \), the Taylor series expansion shows a discontinuity in the Gibbs free energy function \( G(T, P, N, \phi) \) at \( \phi_{\text{mid}} \). The straight line fit to the SLR (with \( \phi_{\text{mid}} \sim -1.759 \)) shows that the Gibbs free energy function has a continuous first order derivative. This enables us to conclude that there is a discontinuity in the second order derivative of \( G(T, P, N, \phi) \) with respect to \( \phi \) at \( \phi_{\text{mid}} \).

We now discuss the important issue of whether the SLR implies that the second order derivative of Gibbs free energy \( \left[ \partial^2 G/N \right]/\partial \phi^2 \) is analytically zero at \( \phi_{\text{mid}} \). That this is the case is supported by the following observations: (i) the Taylor series expansion fits well for \( \phi \leq \phi_{\text{mid}} \) by considering the second order derivative to be zero \( [a_2 = 0 \text{ in Eq. (7)}] \), (ii) the presence of inflection point \( [\text{in case of } N = 10648 \text{ (Fig. 3) and 4096 (Fig. S3) particle trajectories}] \) means a change in the sign of the
curvature around \( \phi_{\text{mid}} \), which implies that the second order derivative is zero, and (iii) the first order derivative \( [\partial (G/N) / \partial \phi] \) at \( \phi_{\text{mid}} \) is independent of \( N \) (i.e., \( T_c \approx 203.8 \pm 0.5 \) K has a unique value as seen in Figs. 3, S3, and S9), which also suggests that it is an extremum value, i.e., the second order derivative is zero. Based on these observations, we conclude that analytically the second order derivative is zero \( \implies \partial^2 (G/N) / \partial \phi^2 = 0 \) at \( \phi_{\text{mid}} = -1.760 \pm 0.001 \).

Now we comment on the SLRs found at potential energies lower than \( \phi_{\text{mid}} = -1.760 \pm 0.001 \) in case of \( N = 4096 \) and \( N = 1000 \) trajectories (see Figs. S3 and S9). We observe that the trajectories exhibit irreversible changes across the mid-point of each of those SLRs: in the case of 4096 particle trajectory, there is an irreversible decrease in the block average potential energy across the mid-point \( \phi'_{\text{mid}} = -1.768 \) (Fig. S3) of the second SLR as seen in Fig. S5; while in the case of 1000 particle trajectory there is an irreversible decrease across the mid-point \( \phi''_{\text{mid}} = -1.7731 \) of the fourth SLR (Fig. S8) as seen in Fig. S10. These irreversible changes occur just after the SLR point as seen in Figs. S5 and S10 and highlight the fact (as also mentioned in the methodology section) that SLRs correspond to physical changes along the trajectory. If any of such SLRs results from the analytical condition \( [\partial^2 (G/N) / \partial \phi^2] = 0 \), the slope \( [\partial (G/N) / \partial \phi] \) of the SLR should be independent of \( N \), since both \( (G/N) \) and \( \phi \) are intensive properties. Thus such SLRs should be seen in ‘final’ distributions of all system sizes. However, the very fact that the SLRs at the lower potential energy are only observed for small system sizes shows that these SLRs do not correspond to the analytical feature of the free energy function. Hence lower potential energy SLRs are not the inflection points of \( G(T, P, N, \phi) \).

Such SLRs appear due to broadening of the distribution with smaller size, and are transient features, i.e., such SLRs do not survive in the ‘final’ distributions.

5 Relaxation in the shorter trajectories

Now we consider the results from the shorter trajectories with 10648 (Figs. 6–8) and 4096 (Figs. S13–S17) particles. The 10648 particle trajectory in terms of block averages over 50000 steps is shown in Fig. 6. The SLR is formed with a mid-point at a slightly higher value \( (\phi'_{\text{mid}} > -1.760) \) (see Fig. 7) than in the case of the longer trajectory. The changes in the density and the per-particle 3-body energy along the trajectory are shown in Fig. 8. There are two aspects to consider: (i) Does
the relaxation in the shorter trajectory occur due to the same physical phenomena? (ii) As noted in Section 4 the probability distribution is ‘unique’ for $\phi > \phi_{\text{mid}}$ in the case of the longer trajectory. The crucial question is what is the reason behind the uniqueness of the distribution? We attempt to answer these questions by analyzing the shorter trajectories.

With regard to point (i), we find that shorter trajectory shows the same relaxation behavior as in the case of the longer trajectory: complete dissipation of fluctuations occurs after the dynamical crossover across the value of $\approx -1.760 \pm 0.001$. In Figs. 6 and 8, the dashed vertical line is drawn at a location (dynamical crossover) beyond which the potential energy fluctuations are biased towards energies progressively lesser than the unique value of $-1.760 \pm 0.001$. Figure 6 shows that there is a large irreversible decrease in the potential energy after the crossover (dashed vertical line). This implies that large scale fluctuations of potential energy are completely dissipated (similar to the case of the longer trajectory), after the dashed vertical line. The values of $\langle \rho \rangle_b$ (see Fig. 8), $\langle f_4 \rangle_b$, and $\langle f_4 \rangle_b$ (see Fig. 6) at the crossover are listed in row 4 of Table I. These values are also consistent with those from the longer trajectory (row 1 of Table I). Qualitatively similar results are obtained in the case of the shorter trajectory with 4096 particles (Figs. S13–S17 and row 5 of Table I).

To address the point (ii) above, we observe that in the shorter trajectory initial relaxation occurs across $\phi_{\text{mid}}'$: before the SLR point, the block averages in Fig. 6 are greater than $\phi_{\text{mid}}'$; while after the SLR point the block averages in Fig. 6 are lesser than $\phi_{\text{mid}}'$. Similarly, the block averages of density and per particle 3-body energy (Fig. 8) show irreversible changes after the SLR point. The irreversible changes indicate that after the SLR point the Gibbs free energy ($G$) of the configurations with $\phi < \phi_{\text{mid}}'$ is lower as compared to the value of $G$ of the configurations with $\phi > \phi_{\text{mid}}'$. As a result of the relaxation across $\phi_{\text{mid}}'$, the liquid region of the trajectory (i.e., the region where microstates corresponding to the local minimum of the probability distribution $[\phi_{\text{m}}', \rho_{\text{m}}']$ are accessible) is dominated by configurations with $\phi > \phi_{\text{mid}}'$. In contrast to this, the liquid region in the longer trajectory (Fig. 1) corresponds to configurations with $\phi > \phi_{\text{mid}}$. Thus, the longer trajectory samples all possible configurations with $\phi > \phi_{\text{mid}}$ yielding ‘unique’ liquid properties.
6 Summary

In this work, we examined the relaxation of supercooled mW liquid at a temperature (205 K) corresponding to the limit of stability at zero pressure. Starting with different initial configurations, we generated sufficiently long NPT-MC trajectories with system sizes of $N = 10648$, 4096, and 1000 particles. We find that the relaxation of the liquid occurs in two stages: (i) the intermediate relaxation which is governed by the unique value of $[\partial (G/N)/\partial \phi]$ at $\phi_{\text{mid}} = -1.760 \pm 0.001$ and (ii) the relatively rapid relaxation which is triggered by the instability at $\phi_{\text{mid}}$, i.e., by the condition that $G$ decreases as the configurations with potential energies lower than $\phi_{\text{mid}}$ are accessed. In this work, we focused on the intermediate [stage (i)] relaxation which ends just after the dynamical crossover, i.e., at the SLR point along the trajectory (see Figs. 1, S1, and S7). The crossover results in the end of the liquid state, i.e., the local minimum of the Gibbs free energy is not accessible after the crossover due to decay of long-wavelength fluctuations. After the crossover, there is an irreversible increase in the size of the 4-coordinated network (measured by increase in $\langle f_4 \rangle_b$) and the local tetrahedral order of the network (measured by decrease in $\langle \phi_3 B_4 c \rangle_b$). These changes suggest that the relaxation is associated with cooperative structural changes involving the 4-coordinated particles.

The dynamical crossover and the corresponding change in the time-scale of fluctuations is consistent with previous isobaric MD cooling simulations \[10,3,11,5\]. We also find that the dynamical crossover is associated with a discontinuity in the second order derivative of Gibbs free energy $[\partial^2 (G/N)/\partial \phi^2]$ at $\phi_{\text{mid}} \approx -1.760 \pm 0.001$.

The relaxation mechanism is qualitatively similar to that found recently for SW-Si liquid at its limit of stability 1060 K and zero pressure. \[2\] Further the threshold value of per particle 3-body energy of the network at the crossover $\langle \phi_{4c}^3 \rangle_b \approx 0.22$ (see Figs. 5, S6, and S12) is comparable to the value of 0.21 found in case of SW-Si at the instability point. \[2\] This suggests that the dynamical crossover (i.e., the change in the time-scale) of the fluctuations occurs due to the system acquiring a certain threshold of the local tetrahedral environment. As in the case of SW-Si, \[2\] the liquid state at the limit of stability is not a metastable equilibrium state. Rather, it can be viewed as a constrained equilibrium state, where the constraint is imposed by the time required to develop the threshold local tetrahedral environment which results in the dynamical crossover. The unique liquid properties are
obtained using the *optimal* trajectory in which the approach to the crossover is delayed the most, which allows the system to explore all possible microstates with potential energies greater than $\phi_{\text{mid}} = -1.760 \pm 0.001$ before the SLR point. The longer trajectory for each $N$ is a *near-optimal* trajectory that closely satisfies the above condition. This is clear from the observation that the ‘final’ distribution and the ‘SLR’ distribution coincide for $\phi > \phi_{\text{mid}}$ in the case of longer trajectory at each $N$ (see Figs. 3, S3, and S9). In the case of the shorter (sub-optimal) trajectory, because of the initial crossover at $\phi_{\text{mid}}^*$ (see Figs. 6, S13, and S16) all possible microstates with $\phi > \phi_{\text{mid}}$ cannot be sampled.

As mentioned in the Methodology section, the potential energy distribution $p(\phi)$ in our work has been obtained from a single (near-optimal) trajectory only for each $N$; $p(\phi)$ is not averaged over several independent trajectories. When one generates a set of trajectories starting from different initial configurations, only one trajectory approaches the optimal trajectory (in the sense described above) most closely, and the others are sub-optimal. Hence, averaging the distribution from all the trajectories is not appropriate. This is consistent with what Limmer and Chandler have mentioned: “For conditions of liquid instability, (i.e., the no-man’s land here there is no barrier between liquid and crystal), the method of rare-event sampling is no longer appropriate. · · · The results depend upon the initial preparation of the system because the unstable system is far from equilibrium” (please see page 134503-8 of Ref. [5]) As an extension of the present work, it will be interesting to explore the structural origin of the threshold local tetrahedral environment that leads to the rapid crystallization after the dynamical crossover.

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Table 1  The dynamical crossover point at 205 K and zero pressure for system sizes of N=10648, 4096, and 1000 particles. The third column reports the values of mid-point of the SLRs as seen in Figs. 3, S3, S9, 7, and S15. In columns 4–7, the values at the dynamical crossover point are reported. The values are obtained by linear interpolation of the block averages across the dashed vertical lines in the corresponding figures. The last two rows, marked by (*), correspond to the shorter trajectories.

| T(K) | N   | φ_{mid} | ⟨φ⟩ₜₕ | ⟨ρ⟩ₜₕ | ⟨f_{4c}⟩ₜₕ | ⟨fₜ⟩ₜₕ |
|------|-----|---------|--------|-------|-------------|---------|
| 205  | 10648 | -1.7592 | -1.7590 | 0.4489 | 0.729       | 0.741   |
| 205  | 4096  | -1.7614 | -1.7608 | 0.4491 | 0.731       | 0.743   |
| 205  | 1000  | -1.7590 | -1.7591 | 0.4489 | 0.731       | 0.743   |
| 205  | 10648*| -1.7562 | -1.7599 | 0.4489 | 0.726       | 0.739   |
| 205  | 4096* | -1.7564 | -1.7614 | 0.4491 | 0.731       | 0.744   |
Fig. 1  The NPT-MC trajectory at 205 K (with $N = 10648$ particles) and zero pressure. The block averages $\langle \cdots \rangle_b$ are over $10^5$ MC steps. Here $\phi$ is the per particle potential energy (in reduced units), and $f_{4c} = N_{4c}/N$ (please refer to the right ordinate) is the fraction of particles in the largest connected network of 4-coordinated particles. The blue symbols denotes the points along the trajectory at which the local minimum $(\phi_m, \rho_m)$ of the probability distribution (corresponding to the liquid state) is accessed. This minimum is located within the rectangular area formed by the points $(\phi - \Delta\phi/2, \rho - \Delta\rho/2)$ and $(\phi + \Delta\phi/2, \rho + \Delta\rho/2)$, where $\phi = -1.75465$, $\rho = 0.44934$, $\Delta\phi = 4.4 \times 10^{-4}$, and $\Delta\rho = 1.2 \times 10^{-4}$. The point along the trajectory at which straight line region is formed in the potential energy distribution (see Fig. 3) is denoted as ‘SLR’. The red symbols denotes the point along the trajectory at which the per particle potential energy $\phi$ corresponds to the mid-point of the SLR, i.e., to the interval $[\phi_{\text{mid}}] = (\phi_{\text{mid}} - \Delta\phi/2, \phi_{\text{mid}} + \Delta\phi/2)$. The vertical dashed line corresponds to the dynamical crossover point along the trajectory as explained in the text.

Fig. 2  The block averages of the density $\rho$, and the per particle 3-body energy of largest 4-coordinate network $\phi_{3B}^{4c}$ are shown for the same trajectory as in Fig. 1. The other symbols have the same meaning as in Fig. 1.

Fig. 3  The potential energy distributions generated by the trajectory in Fig. 1. The blue stars represents intermediate distribution upto ‘R’ point (see Fig. 1). The intermediate distribution (denoted by pink square symbols) containing the straight line region (black squares) is the distribution upto ‘SLR’ point (see Fig. 1). The ‘x’ (green) symbols represents final distribution obtained from trajectory upto 5 million MC steps. By final, we mean that the distribution is not expected to evolve further in the range of $\phi$ values in the above figure due to irreversible changes leading to crystallization. The values of the correlation coefficient $R^2$ of the straight line fit to the SLR region (black squares), the mid-point $\phi_{\text{mid}}$, and the configurational (or effective) temperature $T_c$ of the SLR region (black squares) are given in the inset.

Fig. 4  The zoomed in portion of the trajectory in Fig. 1. Here $\langle \cdots \rangle_b$ denotes block averages over 13000 MC steps. The other symbols have the same meaning as in Fig. 1.

Fig. 5  The zoomed in portion of the trajectory in Fig. 2. Here $\langle \cdots \rangle_b$ denotes block averages over 13000 MC steps. The other symbols have the same meaning as in Fig. 2.
**Fig. 6** The shorter NPT-MC trajectory with $N = 10648$ particles. The block averages $\langle \cdot \cdot \cdot \rangle_b$ are over 50000 MC steps. The local minimum of the probability distribution $[\phi_m^*, \rho_m^*]$ is located within the rectangular area formed by the points $(\phi_m^* - \Delta \phi/2, \rho_m^* - \Delta \rho/2)$, and $(\phi_m^* + \Delta \phi/2, \rho_m^* + \Delta \rho/2)$, where $\phi_m^* = -1.7531$, $\rho_m^* = 0.44976$, $\Delta \phi = 4.4 \times 10^{-4}$, and $\Delta \rho = 1.2 \times 10^{-4}$. The dashed vertical line corresponds to the dynamical crossover point along the trajectory beyond which the potential energy fluctuations are biased towards energies lower than $-1.760 \pm 0.001$. The red symbols represent the microstates with potential energy in the interval $[\phi_{\text{mid}}^*] = (\phi_{\text{mid}}^* - \Delta \phi/2, \phi_{\text{mid}}^* + \Delta \phi/2)$, where $\phi_{\text{mid}}^*$ is the mid-point of the SLR (see Fig. 7) that appears in the intermediate distribution up to the SLR point.

**Fig. 7** The potential energy distributions generated by the trajectory in Fig. 6. All symbols have the same meaning as in Fig. 3. Note that the mid-point of the SLR does not correspond to the unique value obtained from the longer trajectory. The final distribution (‘x’, green symbols) is obtained from trajectory up to 3.2 million MC steps. By final, we mean that the distribution is unlikely to evolve further in the range of $\phi$ values shown in the above figure.

**Fig. 8** The block averages of the density $\rho$, and the per particle 3-body energy of largest 4-coordinated network $\phi_{4c}^{B_4}$ are shown for the same trajectory as in Fig. 6. The block averages are taken over 50000 MC steps. The symbols have the same meaning as in Fig. 2.
\[ \langle \phi \rangle_b \quad [\phi_m, \rho_m] \quad [\phi_{\text{mid}}] \]

\[ \langle f_4 \rangle_b \quad \langle f_{4c} \rangle_b \]

\[ \times 10^6 \text{ MC steps} \]
\[ \langle \rho \rangle_b \]
\[ [\phi_m, \rho_m] \]
\[ \langle \phi_{3B} \rangle_b \]
\[ \log p(\phi) + \text{const.} \]

- Liquid (R)
- SLR
- Final
- Taylor expansion

\[ R^2 = 0.9999999987 \]
\[ T_c = 204.17 \text{K} \]
\[ \phi_{\text{mid}} = -1.7592 \]
\[
\langle \phi \rangle_b \left[ \phi_{mid} \right] = 10^6 \text{MC steps}
\]
$\langle \rho \rangle_b$  

$[\phi_m, \rho_m]$  

$\langle \phi^3 B \rangle^b$  

$\langle \phi^3 4_C \rangle^b$  

$\times 10^6$ MC steps
\[ \langle \phi \rangle_b \]
\[ [\phi^*_{m}, \rho^*_{m}] \]
\[ [\phi^*_{s}] \]
\[ \langle f_4 \rangle_b \]
\[ \langle f_{4c} \rangle_b \]
\[ \times 10^6 \text{ MC steps} \]
\begin{align*}
\phi_\text{mid} &= -1.7562 \\
R^2 &= 0.9999999995 \\
T_c &= 204.298 \text{ K}
\end{align*}
\[ \langle \rho \rangle_b \quad [\phi_m^s, \rho_m^s] \quad \langle \phi_{4c}^B \rangle_b \]

\[ \langle \rho \rangle_b \quad [\phi_m^s, \rho_m^s] \quad \langle \phi_{4c}^B \rangle_b \]

\( \times 10^6 \) MC steps