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Supercooled superfluids in Monte Carlo simulations

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Abstract. We perform path integral Monte Carlo simulations to study the imaginary time dynamics of metastable supercooled superfluid states and nearly superglassy states of a one component fluid of spinless bosons square wells. Our study shows that the identity of the particles and the exchange symmetry is crucial for the frustration necessary to obtain metastable states in the quantum regime. Whereas the simulation time has to be chosen to determine whether we are in a metastable state or not, the imaginary time dynamics tells us if we are or not close to an arrested glassy state.

If a liquid can be cooled below its melting temperature T_m without the occurrence of crystallization, it is called a good glass former, and when the temperature is less than T_m the system is called supercooled. The static and dynamical properties of such systems can be studied over a large temperature range below T_m and it is found that their relaxation times increase very quickly by many decades if the temperature is lowered. At a certain temperature the relaxation time exceeds the timescale of the experiment and therefore the system will fall out of equilibrium. It is this falling out of equilibrium that is called the glass transition. At temperatures well below this glass transition temperature no relaxation seems to take place any longer, on any reasonable timescale, and it is customary to call this material a glass. This transition temperature will in general depend on the type of experiment, since its definition involves the timescale of the experiment. Understanding the transition from a supercooled liquid to a glass, or a disordered solid, is one of the major open problems in condensed matter.

In a liquid of number density ρ, made of mass m particles, moving in a d-dimensional space, the quantum effects will become important when the temperature T is comparable or smaller than the degeneracy temperature $T_D = 2\lambda\rho^{2/d}$, where $\lambda = \hbar^2/2m$ and $\hbar$ is the reduced Planck constant. A liquid such that $T_D > T_m$ is therefore likely to form a quantum glass.

At a temperature $T_{\rm MCT} < T_m$ a kinetic glass transition towards an arrested state is predicted by the mode coupling theory (MCT) [1,2]. Many of the qualitative predictions of this theory have been confirmed in experiments and computer simulations, and thus MCT can currently be regarded as the best available theory of the dynamics of supercooled liquids.

Our aim in this letter is to use path integral Monte Carlo (PIMC) simulations [3] to gain an understanding on the very general question of the search for an arrested state when the temperature approaches $T_{\rm MCT}$. Since we are interested in a universal property of glassy systems, our simulations are carried out with a very simple and unrealistic model liquid, namely the square-well bosons [4]. We will be working at very low temperatures $T \approx T_m < T_D$. We will find metastable supercooled superfluid states and evidence for development towards a superglass state [5–7] which should appear at even lower temperatures $T \approx T_{\rm MCT}$.

Using the terminology of reference [3] we are then looking for local minima of the *action* of the *primitive approximation*, up to thermal activation according to the Metropolis algorithm [8]. These may differ from the ones of the *inter-action* due to quantum tunneling. In particular we will be interested in how the identity of the particles and their exchange permutation cycles which forms in a PIMC simulation frustrates the development towards the global minimum of the action favoring the formation of the metastable supercooled states [9].

Consider a fluid (homogeneous and isotropic) of N bosons in a volume V and density $\rho = N/V$ at a given absolute temperature $T = 1/k_B\beta$, with k_B Boltzmann constant, with a Hamiltonian

$$\mathcal{H} = -\lambda \sum_{i=1}^{N} \boldsymbol{\nabla}_i^2 + \sum_{i<j\leq N} \phi(|\mathbf{r}_i - \mathbf{r}_j|)$$

symmetric under particle exchange, with $\lambda = \hbar^2/2m$, m the mass of the particles, and $\phi(|\mathbf{r}_i - \mathbf{r}_j|)$ the pair-potential of interaction between particle i at $\mathbf{r}_i$ and particle j at $\mathbf{r}_j$. The dynamic structure factor is defined as follows:

$$S(k,\omega) = \frac{1}{2\pi N} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \langle \rho_{-\mathbf{k}}(0)\rho_{\mathbf{k}}(t)\rangle$$
$$= \int_{-\infty}^{\infty} dt\, e^{-i\omega t} F(k,t),$$

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where

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$$

with $\langle \rho(\mathbf{r}) \rangle = \rho$, $\rho(\mathbf{r}, t) = e^{i\mathcal{H}t/\hbar} \rho(\mathbf{r}) e^{-i\mathcal{H}t/\hbar}$, $\rho_{\mathbf{k}}(t) = \int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} \rho(\mathbf{r}, t)$, and $\rho_{\mathbf{k}}(0) = \rho_{\mathbf{k}}$. Given an observable $\mathcal{O}$ we define the statistical average as $\langle \mathcal{O} \rangle = \mathrm{Tr}\left(\mathcal{O} e^{-\beta\mathcal{H}}\right)/Z$ with $Z = \mathrm{Tr}(e^{-\beta\mathcal{H}})$ the partition function.

We introduce the analytic continuation of $F(k,t) = \int_{-\infty}^{\infty} d\omega\, e^{-\hbar\omega t} S(k,\omega)$ in imaginary time as follows

$$F_k(t) = \frac{1}{NZ} \mathrm{Tr}\left(\rho_{-\mathbf{k}} e^{-t\mathcal{H}} \rho_{\mathbf{k}} e^{-(\beta - t)\mathcal{H}}\right). \tag{1}$$

So that $F_k(0) = 2\pi F(k,0) = \int_{-\infty}^{\infty} d\omega\, S(k,\omega) = S(k)$ is the static structure factor such that $\lim_{k\to\infty} S(k) = 1$.

Clearly we have that $F_k(t) = 2\pi F(k, i\hbar t)$ is defined for $t \in [0, \beta]$ being symmetric respect to $t = \beta/2$ since $S(k, -\omega) = e^{-\beta\omega} S(k, \omega)$.

The calculation of $F_k(t)$ of equation (1) becomes straightforward in path integral Monte Carlo (PIMC) [3] where it is sufficient to average the product of $\rho_{-\mathbf{k}}$ on the first time-slice with $\rho_{\mathbf{k}}$ at a time-slice a time t later.

The dynamic structure factor for the ideal Bose gas for particles of spin s at a temperature T below the critical temperature $k_B T_c = 4\pi\lambda\{\rho/[(2s+1)\zeta(3/2)]\}^{2/3}$, where ζ is the Riemann zeta function, is given by equation (18) in reference [10][1], where their λ is our $\sqrt{4\pi\lambda\beta}$, the de Broglie wavelength.

In particular one finds

$$\left.\frac{dF_k(t)}{dt}\right|_{t=0} = -\int_{-\infty}^{\infty} d\omega\, \hbar\omega S(k,\omega) = -\lambda k^2.$$

In Figure 1 we show how $F_k(t)$ is well-approximated by a pure exponential decay $S(k) e^{-\lambda k^2 t}$ for $t \in [0, \beta/2]$.

We performed grand canonical PIMC with the "worm" algorithm [11] for a system of spin zero square-well bosons in three spatial dimensions. As usual the path $\mathbf{R}(t)$ is discretized in imaginary time t extending from $t = 0$ to $t = \beta = n_\tau \tau$ with a time-step τ. It is made of $N n_\tau$ *beads* of coordinates $\mathbf{R}(t) = \{(x_i(t), y_i(t), z_i(t)) \quad \forall i = 1, \ldots, N\}$ at each time-slice $t = t_j = j\tau$. The particles pair-potential is as follows

$$\phi(r) = \begin{cases} +\infty & r < \sigma \\ -\varepsilon & \sigma \le r < \sigma(1+\Delta) \\ 0 & \sigma(1+\Delta) \le r. \end{cases} \tag{2}$$

We choose $\varepsilon > 0$ as the unit of energies and σ as the unit of lengths. We then introduce a reduced temperature $T^* = k_B T/\varepsilon$ (with $\beta^* = 1/T^*$), a reduced density $\rho^* = \rho\sigma^3$, and a reduced chemical potential $\mu^* = \mu/\varepsilon$. When the mass m of the bosons and/or the depth of their attractive well ε are sufficiently large, i.e. $\lambda^* = \lambda/(\varepsilon\sigma^2) \ll 1$ we are in the classical limit. The classical fluid has been studied originally by Vega et al. [12] who found that the critical point of the gas-liquid coexistence moves at lower temperatures and higher densities as Δ gets smaller. The quantum mechanical effects on the thermodynamic properties of nearly classical liquids can be estimated by the de Boer quantum delocalization parameter $\ell = \sqrt{2\lambda^*}$ [13]. The phase diagram of the system in the quantum regime, $T^* \lesssim T_D^* = 2\lambda^* (\rho^*)^{2/3}$, has recently been studied by us [4] with our quantum Gibbs ensemble MC algorithm [14].

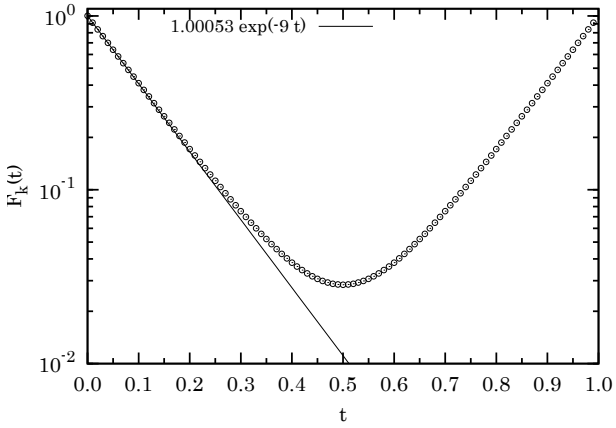

Fig. 1. Behavior of $F_k(t)$, as a function of the imaginary time $t \in [0, \beta]$, for an ideal Bose gas below its critical temperature at $k = 3$, $\lambda = 1$, $k_B T = 1$, $\rho = 0.4$, and $s = 0$. The critical temperature is $k_B T_c = 3.597$. The points are the numerical results from equations (1) and equation (18) of reference [10]. On the ordinates axis we use a logarithmic scale.

Unlike the work of Biroli et al. [6] we will work far away from the sticky limit [15] obtained by setting the stickiness parameter $\mathcal{T}^{-1} = 12 e^{\beta\varepsilon}\Delta$ and taking the double limit $\varepsilon \to \infty$ and $\Delta \to 0$ at fixed $\mathcal{T}$. We could reach numerically such limit by taking Δ small enough [16–18]. Instead we will fix $\Delta = 0.5$ in all cases as was done in the previous analysis of reference [4].

In the present letter we want to study the relaxation to zero of the $F_k(t)$ in the quantum regime, so we must choose $\lambda^* \gg 0$ and $T^* \lesssim T_D^*$. Choosing $\lambda^* = 1$ we must choose a sufficiently small temperature and a sufficiently high density. For $T^* = 1$ we need a reduced density $\rho^* \gtrsim (1/2)^{3/2} = 0.35$. The maximum reduced density allowed for our system is $\sqrt{2} = 1.41$ for the close packed configuration of the hard cores. The small attraction between the particles will be responsible for a shift at lower packing fractions, $\eta = \pi\rho\sigma^3/6$, of the melting value for pure hard-sphere (which in the classical limit is approximately 0.54).

In our PIMC we had to choose a discretization time-step, $\tau^* = \beta^*/n_\tau$, for the imaginary time extending from $t\varepsilon = 0$ to $t\varepsilon = \beta^*$. We then chose $n_\tau = 100$ time-slices [3]. The "worm" algorithm uses a menu of 9 different moves: advance, recede, insert, remove, open, close, swap, wiggle, and displace. Labeling each of these moves with $q = 1, 2, \ldots, 9$ respectively, a single random attempt of any one of them with probability $G_q = g_q / \sum_{q=1}^{9} g_q$ constitutes a MC step. In our simulations we always chose

[1] There is a misprint in equation (18) where the denominator of the term containing the Dirac delta functions should read $1 - e^{-\omega/\omega_T}$.

Table 1. Reduced properties of the simulated system with $\Delta = 0.5$ at $\lambda^* = 1, V = 100\sigma^3$ and different μ^*. For the simulation at $T^* = 0.5, \mu^* = 80$ (stable) we considered the first 20 000 blocks as equilibration time and they were therefore discarded from the averaging. In all the other cases the equilibration time was taken equal to 1000 blocks, i.e. the ones necessary to bring the system from the empty box to the equilibrium number of particles.

T^*	μ^*	$e_{\rm tot}/\varepsilon$	$e_{\rm kin}/\varepsilon$	$e_{\rm pot}/\varepsilon$	$p\sigma^3/\varepsilon$	$\langle N\rangle$	$\rho\sigma^3$	ρ_s/ρ
1.0	50 (stable)	12.81(6)	17.70(7)	–1.889(6)	3.33(2)	33.92(7)	0.3392(7)	1.05(8)
1.0	80 (stable)	19.20(7)	21.94(8)	–2.734(8)	6.20(3)	42.41(8)	0.4241(8)	1.1(1)
1.0	100 (stable)	24.12(6)	27.46(7)	–3.335(7)	8.75(3)	47.79(6)	0.4779(6)	0.03(1)
0.5	80 (stable)	17.029(8)	20.325(8)	–3.297(3)	6.504(3)	48	0.48	0.013(4)
0.4	80 (metastable)	13.64(4)	17.09(5)	–3.446(5)	5.72(2)	50.19(5)	0.5019(5)	1.2(1)
0.4	90 (metastable)	15.23(4)	18.98(5)	–3.744(6)	6.73(2)	53.16(5)	0.5316(5)	1.05(8)

$g_q = 1$ for $q = 1, 2, \ldots, 7, 9$, and $g_8 = 10$. For each move, except the displace one, a maximum number of time-slices involved, $\overline{m}$, is also defined [11] to control their acceptance ratios. We always chose $\overline{m}_q = 5$ for all q. For the displace move we chose a displacement of the path of the order of $V^{1/3}/1000$. We always chose the C parameter defined in reference [11] equal to 0.1. This value ensured an acceptance ratio for the Z-sector [11] lower but close to 1/2 even if in the simulations converging towards the solid state this increased passed 1/2.

Our simulations were 5×10^4 blocks long with one block made by 100 steps where we did not accumulate the averages and by 100 steps where we did. This sets the simulation (experiment) time.

We studied the model with $\Delta = 0.5$ and $\lambda^* = 1$ at $T^* = 1$, $V = 100\sigma^3$, and $\mu^* = 50, 80, 100$. Starting from the empty box we reached a stable superfluid for $\mu^* =$ 50 (stable), 80 (stable) and a stable normal solid for $\mu^* =$ 100 (stable). Then we lowered the temperature at $T^* = 0.5$ and we studied the model with $\mu^* = 80$. Now *quenching* from the empty box we reached a metastable superfluid at $\mu^* = 80$ (metastable) for the first 20 000 blocks which later converged towards its stable normal solid state: $\mu^* =$ 80 (stable). We then quenched from the empty box at a slightly lower temperature $T^* = 0.4$ keeping the chemical potential at $\mu^* = 80$ (metastable) (which resulted in a slightly higher density respect to the case at the higher temperature $T^* = 0.5$) and we observed that the system, instead of entering the stable solid phase, stayed, for the whole length of our numerical experiment, in a metastable supercooled superfluid state.

In Table 1 we report some properties of the simulated system such as: the total energy per particle $e_{\rm tot}$, the kinetic energy per particle $e_{\rm kin}$, the potential energy per particle $e_{\rm pot}$, the pressure p, the average number of particles $\langle N\rangle$, the density $\rho = \langle N\rangle/V$, and the superfluid fraction ρ_s/ρ, as calculated according to reference [3]. All the presented simulation were *well converged* and the correlation simulation time $k_{\mathcal{O}}$ was never bigger than 500 blocks in any simulation for any property $\mathcal{O}$. The statistical error was as usual calculated as $\sqrt{\sigma^2(\mathcal{O})k_{\mathcal{O}}/N_s}$, where $\sigma^2(\mathcal{O})$ is the estimator of the variance of the random walk and N_s the number of MC steps.

In Figure 2 we show the static structure factor of the first five systems. This clearly shows how the $T^* = 0.5, \mu^* = 80$ (stable) case is a solid state (the structure factor peak is between 6 and 7) whereas the $T^* = 0.4, \mu^* = 80$ (metastable) one is a fluid state (the structure factor peak is here between 1.6 and 1.8). Note that in all cases the simulation was 5×10^4 blocks long and the acceptance ratio of the Z-sector comparable. The difference between the two cases immediately also appears by looking at the evolution of the superfluid fraction during the progress of the simulations, as shown in Figure 4. We clearly see how the $T^* = 0.5, \mu^* = 80$ (stable) case has a transition from a superfluid state, before block 20 000, to a normal solid, after. The behavior of $F_k(t)$ as a function of the imaginary time for some chosen reciprocal wave-numbers around the first peak of the correspondent static structure factor for the system with $T^* = 0.4$ and $\mu^* = 80$, which is a precursor of a superfluid glass, a superglass [5,6,19], is such that we observe exponential decays going below 10^{-2} for $t\varepsilon > 0.6$. Whereas for the systems in the solid state at $T^* = 1, \mu^* = 100$ (stable) and $T^* = 0.5, \mu^* = 80$ (stable) we observe an almost constant value for $F_k(t)$ at the wave-number of the first peak of the correspondent static structure factor and exponentially decaying the other wave-numbers.

In Figure 3 we show the $(x_i(t), y_i(t))$ particles positions at all time-slices at the end of the simulation for the cases $T^* = 0.5, \mu^* = 80$ (stable) and $T^* = 0.4, \mu^* = 80$ (metastable), respectively.

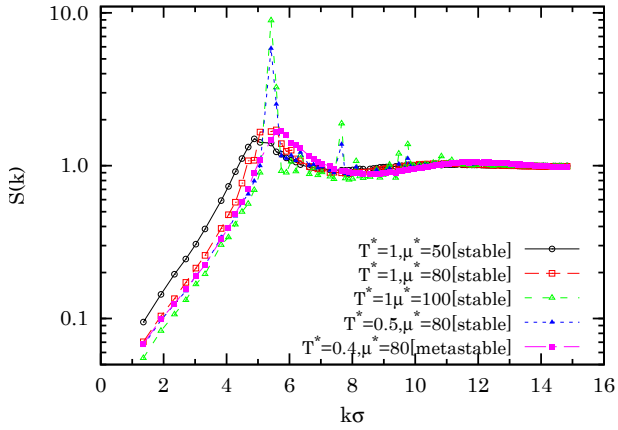

Fig. 2. Static structure factor $F_k(0) = S(k)$ at $\lambda^* = 1$ and $T^* = 1, \mu^* = 50$ (stable), 80 (stable), 100 (stable) and $T^* = 1/2, \mu^* = 80$ (stable), 80 (metastable). On the ordinates axis we use a logarithmic scale.

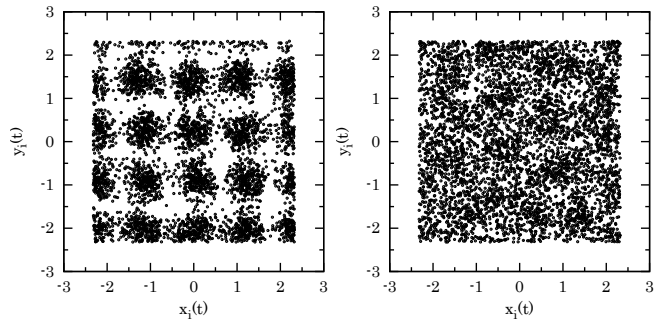

Fig. 3. The $(x_i(t), y_i(t))$ particles positions at all time-slices at the end of the simulation with: $\lambda^* = 1, T^* = 0.5, \mu^* = 80$ (stable) (left panel) and $\lambda^* = 1, T^* = 0.4, \mu^* = 80$ (metastable) (right panel).

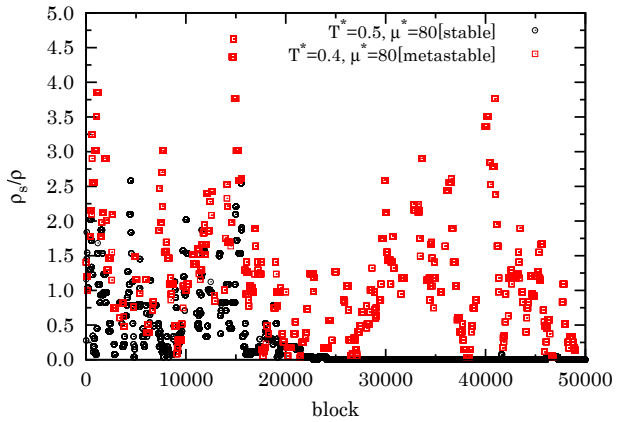

Fig. 4. Superfluid fraction at each PIMC block during the simulation at $\lambda^* = 1$ and $T^* = 0.5, \mu^* = 80$ (stable) and $T^* = 0.4, \mu^* = 80$ (metastable).

Regarding the size effects we can say that the solid state we observed has a triclinic lattice structure with a unit cell with base vectors $\boldsymbol{a} = (0, 0, a), \boldsymbol{b} = (a, 0, a/2), \boldsymbol{c} = (0, a, a/2)$ accommodating approximately 48 particles. At $T^* = 0.4$, a chemical potential of $\mu^* = 80$ is sufficient to reach approximately 50 particles which could be adjusted in a different unit cell with the same crystal structure. Thus we think that the size effects should not be considered as responsible for the observed metastability.

In order to get closer to an arrested metastable state we restarted from the the equilibrated supercooled superfluid configuration of $T^* = 0.4, \mu^* = 80$ (metastable) and increased μ^* by 10. This allowed us to reach another metastable supercooled superfluid state closer to an arrested state where the $F_k(t)$, for the k around the first peak of the static structure factor at 2, shows an initial exponential decay followed by a plateau. This is clearly shown in Figure 5 taken at the end of the simulation and is in accord with the MCT predictions. In order to observe the plateau it is essential the restarting or *aging* procedure.

In conclusion, we proved, for the idealized model of spinless square well bosons, that superfluidity is able to sustain metastability at low temperature and high density. In order to define whether we are on a metastable state

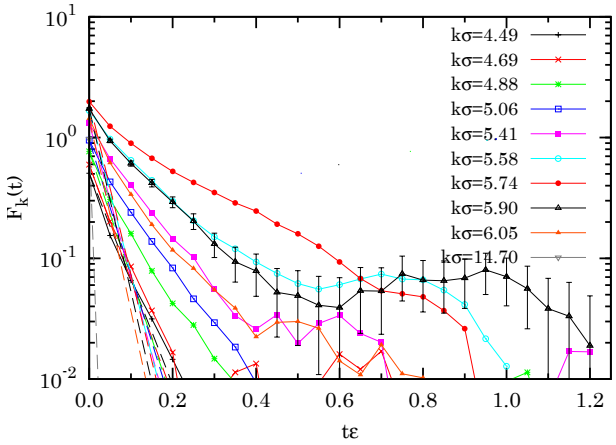

Fig. 5. The behavior of $F_k(t)$ as a function of the imaginary time for various values of k around the first peak of the structure factor. We used $\lambda^* = 1, T^* = 0.4$, and $\mu^* = 90$ (metastable). The dashed lines are the approximate ideal gas results. On the ordinates axis we use a logarithmic scale. For $k\sigma = 5.90$ also the statistical errors are shown.

we need to fix a simulation time interval much longer than the correlation simulation time. We were able to maintain the system in a metastable supercooled superfluid state for a rather long simulation time. The metastable state may not be unique and there may be many of those for a given set of thermodynamic conditions (e.g. μ, V, T in the grand canonical ensemble) all different from one another depending from the kind of quench. The real (diffusive) dynamical (imaginary) time of the physical system can be used to define the insurgence of an arrested glassy state through the aging procedure, even if it is limited to the interval $[0, \beta/2]$.

We should mention here that the simulation time for a classical molecular dynamic and for a MC numerical experiment have profoundly different meanings. The first one can be mapped into the real dynamical time of the classical physical system whereas the second one has nothing to do with it but is merely the number of stochastic moves made to sample the configuration space of the system within the Metropolis algorithm. In the quantum regime one has at his disposal only simulations of the MC type but, as we showed, the simulation time can give an indication of metastability. Whereas the imaginary time real dynamics of the system tells us if we are close to an arrested glassy state.

We are presently implementing a better hard-core propagator [20] to substitute to the primitive approximation which would allow us to use fewer time-slices.

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