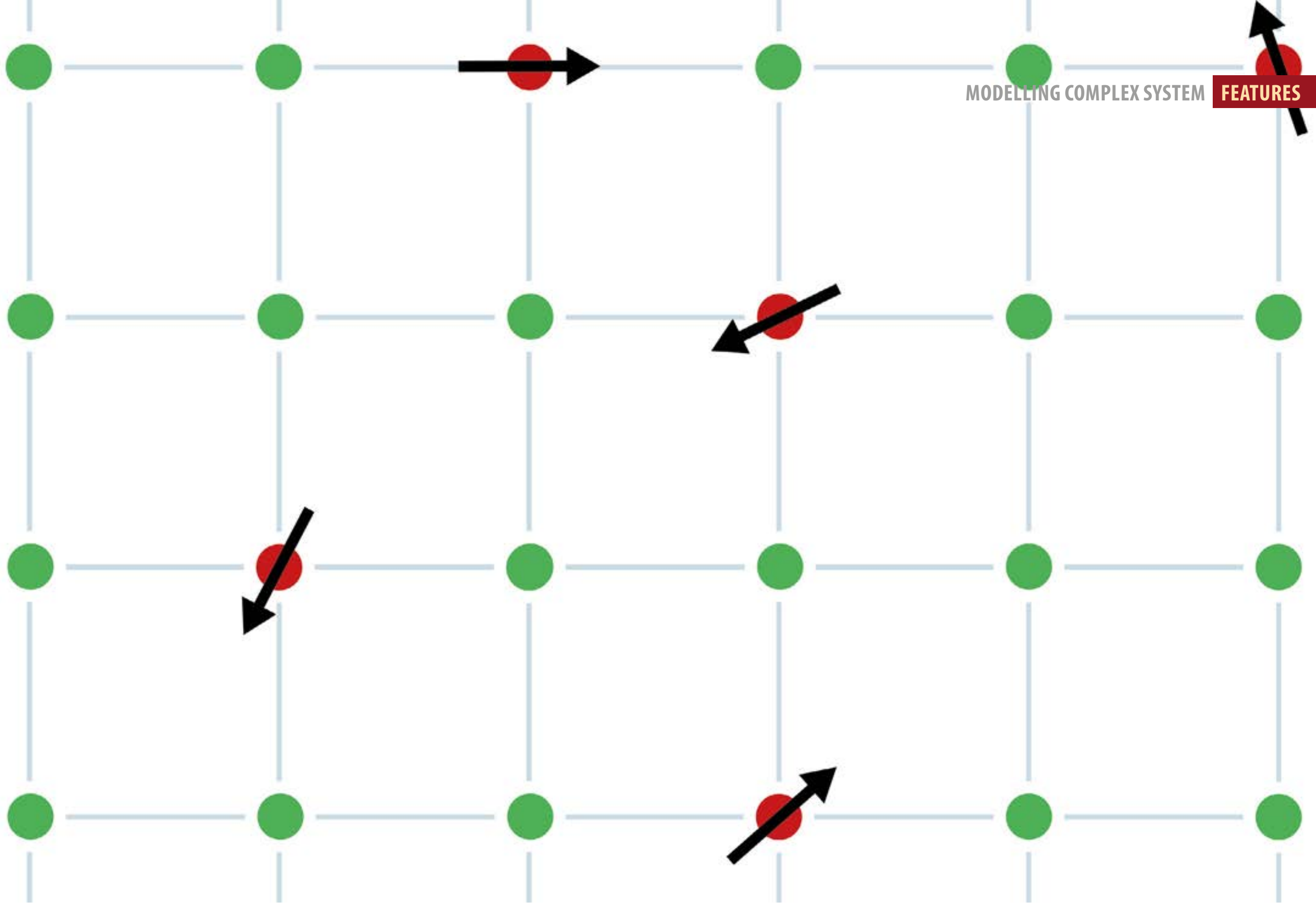

THE GLASS TRANSITION:
HOW DO COMPLEX CRAGGY FREE ENERGY LANDSCAPES EMERGE?

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Glass as a material was already known in ancient Egypt. Now its use for windows, bottles, *etc.* is very common; thus, it may sound surprising that the glassy state of matter and the transition from an undercooled melt to this state are grand challenge problems of physics. This article describes the basic concepts; then it points out how the discovery of "spin glasses" and the theory by Giorgio Parisi has given a new boost to the interest in these problems. The status of a theory of the glass transition will be critically discussed.

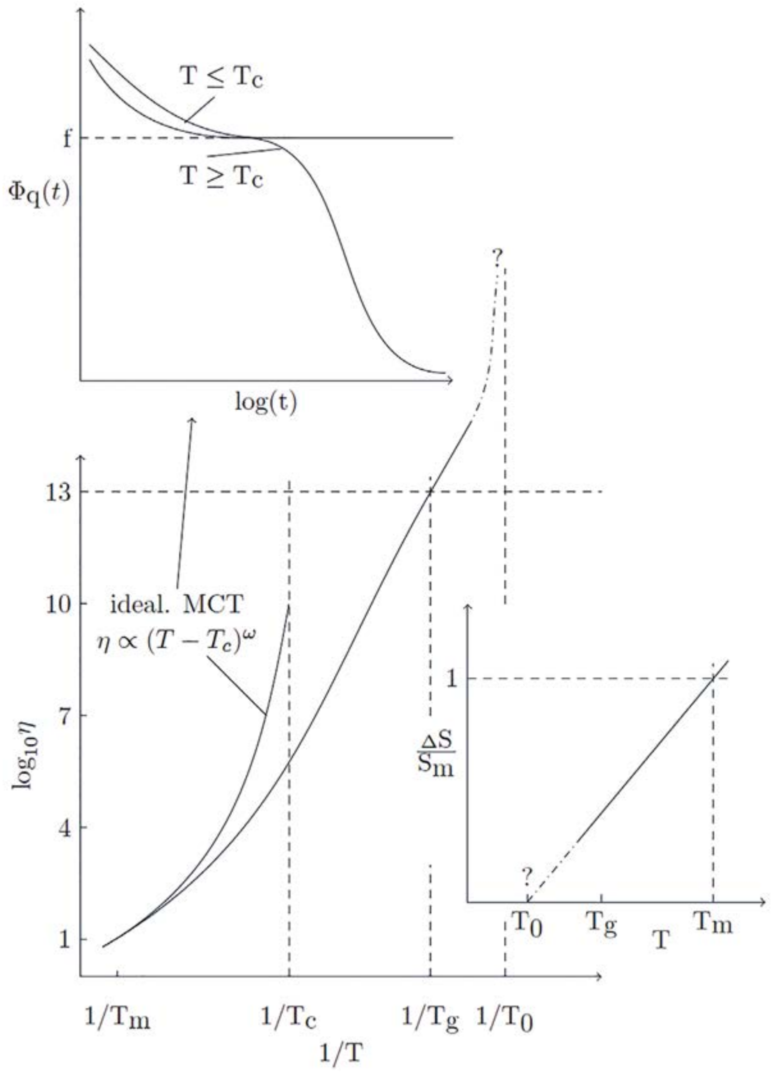
▲ A spin glass is a metal alloy where iron atoms, for example, are randomly mixed into a grid of copper atoms. Red dots: iron, green dots: copper. ©Johan Jarnestad/ The Royal Swedish Academy of Sciences

Experimental background

The state of solid materials in thermal equilibrium is crystalline. Thus, when a liquid is cooled down, crystallization occurs: Scattering experiments with X-rays or neutrons show Bragg peaks, reflecting the periodic arrangement of atoms on sites of a lattice.

However, the scattering pattern of a glass is different, it is strikingly similar to the liquid. But unlike the latter, diffusive motions and structural relaxation are "arrested" [1]. However, the mentioned techniques probe the pair correlation functions between the particles. So more subtle forms of "order" that do not show up in pair correlations are not ruled out! Also, one must understand which mechanisms slow down the particles that during the time to cool down the fluid no crystallization could occur.

In addition, all physical properties of glasses depend both on the thermodynamic state (temperature T, pressure p) that is considered, and on the "preparation history". Interestingly, NOT ONLY HUMANS AGE: GLASSES AGE AS WELL!



▲ **FIG 1:** Properties of glassforming fluids. Schematic plot of the viscosity η(T) of a fluid as a function of inverse temperature 1/T. The inverse melting temperature $1/T_m$, glass transition temperature $1/T_g$ and critical temperature $1/T_c$ of MCT are indicated. The temperature T_0, where η(T) would diverge, often is associated with the temperature where the extrapolated entropy difference ΔS(T) between fluid and crystal vanishes ("Kauzmann temperature" (1)); see insert ($S_m = \Delta S(T_m)$). The idealized MCT predicts the time-dependent density correlation function $\phi_q(t \to \infty) = f$. This is not the case in reality; the further decay requires thermally activated processes, not described within idealized MCT. From Ref. (1) (Fig. 1.18).

An important issue is the fact that not every fluid forms a glass. There are no glassy states for fluids of noble gas atoms. Also, simple metals do not freeze into glasses. Also, simple molecular fluids do not exist in glassy states.

In order that a glass forms when a fluid is cooled, there must be some energetic "frustration effect" in the local arrangement of atoms in the dense fluid. A prototype example is SiO_2. There is always a Si atom in the centre of a regular tetrahedron, with O atoms at the four corners, each O atom is shared by two neighbouring tetrahedra. These tetrahedra form perfect networks in the crystal structures, with 6-membered rings in various arrangements. In the glassy structure of SiO_2, these tetrahedra are not regular but distorted, and also 5-membered and 7-membered rings are frozen in. In the deeply cooled SiO_2 melt the covalent Si-O bonds break up and reform to allow structural relaxation. This picture is not only due to imagination, but emerges also from simulations [1], which also show that physical properties depend on the cooling rate. As a caveat, we mention that the cooling rate in simulations is orders of magnitude larger than in experiments; but when one locates a glass transition in real glasses, from a kink in the curve of volume versus temperature, there is a cooling rate dependence of the glass transition temperature T_g as well! Alternatively, a heuristic definition of T_g is that the shear viscosity has reached 10^{12} Pa.s (which corresponds to relaxation times of about one minute). Of course, this choice is arbitrary – it is broadly accepted, since larger viscosities can hardly be measured.

When one plots the logarithm of the viscosity η versus T_g/T to compare different glass formers ("Angell plot") one finds a straight line for SiO_2, i. e. an Arrhenius behaviour, $\eta \propto \exp(E_{act}/k_BT)$, where E_{act} is an activation energy and k_B Boltzmann's constant. Many other glassformers, *e.g.* molecular fluids such as glycerol, show pronounced curvature on this plot, consistent with the Vogel-Fulcher-Tammann (VFT) (1) relation,

$$\eta(T) \propto \exp[B/(T-T_0)], \qquad (1)$$

Where B is a constant and T_0, where η(T) would diverge, is about 30K below T_g.

Glassforming fluids exhibit many more interesting properties; some are shown schematically in Fig. 1, where also mode coupling theory (MCT) [2] is mentioned. Particularly interesting is the strong decrease of the entropy. When the fluid falls out of equilibrium, its entropy is frozen in, and thus the glass does not comply with the 3rd law of thermodynamics. If the entropy of small amplitude, vibration-like, motions in the fluid and crystal are similar, the extrapolation of ΔS in Fig. 1 might imply that a transition at T_0 is needed to avoid the "entropy catastrophe" (a negative entropy); but this conclusion is a speculation. The MCT predictions, are only useful for understanding the initial stages of structural relaxation of the moderately supercooled fluid. The density correlator $\phi_q(t)$ are often well described by a stretched exponential decay: $\phi_q(t) \propto \exp(-(t/\tau_q)^\beta)$ where τ_q is the structural relaxation time, and the exponent β is often close to 3/5. Another important property of glassforming fluids is their "dynamical heterogeneity" [3]: near the glass transition the Stokes-Einstein relation between selfdiffusion and viscosity and the Stokes-Einstein-Debye relation between translational and rotational diffusion of molecules fail.

Early theoretical concepts

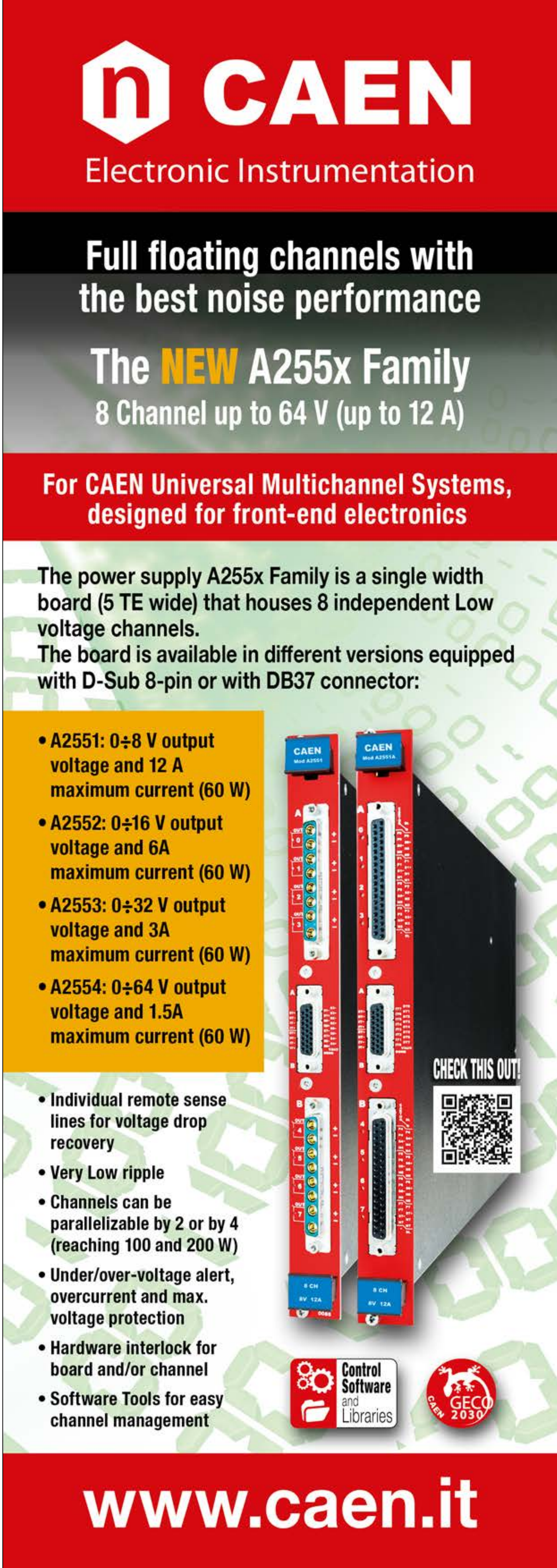
There has never been a consensus how to understand the glass transition; very different ideas were developed, which are sketched here only very roughly.

A theory related to the decrease of entropy (Fig. 1) is the idea to introduce subsystems of dimensions ξ, in which cooperative rearrangements of the particles take place, independent of other subsystems. Each subsystem has a few energetically preferred states, and a configurational entropy of order unity. The total configurational entropy S_{conf} is proportional to the number of those regions, *i.e.* inversely proportional to their volume. Some assumptions on the kinetics of the rearrangement process yield for the relaxation time $\tau(T) \propto \exp[C/(TS_{conf})]$, where C is a constant. Assuming then that S_{conf} is proportional to $\Delta S(T) \propto T\text{-}T_0$, Eq. (1) results since $\eta(T) \propto \tau(T)$. Unfortunately, it is not clear how to define these cooperatively rearranging regions; experiments attempting to extract estimates for ξ independently were not encouraging (typically $\xi = 2\text{-}3$ nm), and the assumptions on the kinetics are doubtful either [1]. Simulations [1] find a gradual increase of ξ with decreasing T but cannot reach temperatures near T_g.

Contrary to emphasizing collective rearrangements, the free volume theory focuses on single particle motions. Each particle needs to find "free volume" in its neighbourhood that it can move into. Diffusion over large distances is possible if the regions identified as free volume percolate. Also, this theory can lead to Eq. (1); but the concept of free volume is somewhat vague, and the treatment requires many assumptions that cannot easily be tested.

The MCT [2] has a sound starting point in the theory of liquids. It starts out from an exact equation for the time-dependence of $\phi_q(t)$, and invokes a useful factorization of the so-called "memory functions". MCT predicts onset of slow relaxation, compatible with a stretched exponential relaxation, as seen experimentally. For $T \to T_c$ a plateau (describing the "cage effect") develops in $\phi_q(t)$. The "lifetime" of this plateau diverges as a power law in this limit (Fig. 1). While the two-step relaxation is compatible with experiments and simulations, the critical power-law is not: the predicted T_c clearly is higher than T_g. It is argued that going beyond this "idealized" version of MCT the critical divergence at T_c is rounded off: instead, a crossover to thermally activated behaviour in the region $T_g < T < T_c$ occurs [2]. However, a convincing description of this thermally activated relaxation in the framework of MCT remains to be developed.

Thus, some theories of glassy relaxation use as an input thermodynamic properties. However, there is also the view that all what matters are kinetic constraints. This view is exemplified by kinetic Ising models, without any static correlation. Constraints on the flipping rates of the Ising spins, give rise to slow relaxation resembling glassy behaviour. These models also lend support to describing the glass transition as a symmetry breaking in the space of system trajectories: rather than ensembles of states in phase space, one deals with "ensembles of histories", and dynamical transitions then can be identified. However, the precise connection between this approach and the traditional approaches remains unclear.



Spin glasses: do they provide a solution to the puzzle?

Fifty years ago, it was discovered that metals like Cu containing a few percent randomly distributed magnetic ions undergo a new type of phase transition: the magnetic susceptibility χ exhibits a cusp at a temperature T_f, but one cannot detect any ferro- or antiferromagnetic order for $T < T_f$. Dynamic spin correlations, reveal a dramatic slowing down as T approaches T_f from above: relaxation times gradually increase from picoseconds to macroscopic times! Since the sign of the interaction between the magnetic moments oscillates as function of distance, and the distances are random, for $T < T_f$ spins are frozen in random directions: hence, one has a magnetic analog of a structural glass, a SPIN GLASS!

This discovery spurred great interest: the hope was to gain insight for glass transitions in general. Soon there was consensus to simplify the model, take spins with a Gaussian distributed interaction J between any pairs of neighbours in the mean-field version; for a short-range version, the simplest model takes Ising spins on the sites of a lattice.

While these models look simple, dealing with them is still difficult; the averaging over the quenched random disorder is a real obstacle for statistical mechanics. The ingenious approach of Giorgio Parisi [4] clarified the nature of "order": there is no simple order parameter, like the magnetization for a ferromagnet, but rather an order parameter function. This function reflects the fact that for $T < T_f$ the free energy "landscape" is split into many "valleys", separated by barriers (infinitely high in the meanfield limit). The valleys correspond to the possible states of the spin glass (*i.e.*, "ergodic components").

This theory has been extremely fruitful for many other problems, in rather different fields (*e.g.* neural network models, optimization, *etc.*). It has also provided guidance to interpret numerical simulations on the ± J spin-glass, believed to correspond reasonably well to real systems.

HOWEVER, GLASSES LACK THE SPIN REVERSAL SYMMETRY OF SPIN GLASSES. Approaching T_f from above, the spin glass exhibits standard critical phenomena. So if spin-glass theory can be useful for structural glasses at all, clearly a generalization without this special symmetry is needed.

Such generalizations exist, *e.g.* the p-state Potts glass with $p > 4$: Each site can take one out of p states. The energy J between the "Potts spins" occurs if they are in the same state; else the energy is zero. Such models exhibit a 1st order transition at T_0 where glass order appears discontinuously. Interestingly, dynamic versions of this model (in the meanfield limit) experience a divergence of the relaxation time at a temperature $T_D > T_0$, and for $T < T_D$ the system is nonergodic. Denoting the probability that a state ℓ occurs by P_ℓ, we can define a configurational entropy (also called "complexity") of this nonergodic system as $I = - k_B \Sigma_\ell P_\ell \ell n P_\ell$. For the disordered phase at $T > T_D$ there is a single "valley" in the free energy landscape; but for $T_0 < T < T_D$ then are infinitely many such "valleys" when I is extensive. No order then is possible, but I vanishes at T_0 where the glass order appears discontinuously.

To describe real systems, one would need to generalize this model with infinite range of the interactions to finite range. The many valleys at $T_0 < T < T_D$ then are separated by barriers of finite height only, so the transition at T_D is rounded, the state for $T < T_D$ can be viewed as patchwork of subregions of characteristic size ξ, each in one of the possible metastable states (different from neighbouring regions). Due to thermally activated fluctuations transitions in this "mosaic state" of subregions between different states occur. With some assumptions in this "random first order theory" one can obtain the VFT relation for the divergence of the relaxation time at T_0.

Unfortunately, this description still does not make many testable predictions, and numerical simulations [1] have not (yet?) provided clear evidence in favour or against this description, SO THE GLASS TRANSITION CONTINUES TO STAY A CHALLENGE… ■

> **"Numerical simulations have not (yet?) provided clear evidence in favour or against this description, so the glass transition continues to stay a challenge… "**

About the Author

Kurt Binder made his Ph.D. in 1969 at the Technical University of Vienna and then moved to the Physics Department of the Technical University of Munich where he received his Habilitation in 1973. he held positions as a professor at the universities of Saarbrücken , Köln and (since 1983) Mainz, where he retired in 2012. He received many distinctions, such as the Max-Planck and Boltzmann Medals.

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