Redefining the Mpemba Effect： A Generalized Theory of History-Dependent Thermal Relaxation

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Abstract

This study redefines the Mpemba effect as a manifestation of history-dependent thermal relaxation, moving beyond the static comparison of initial temperatures. A generalized cooling law, $\frac{dT}{dt} =- u_{eff}(T,\boldsymbol{H})$, is proposed,where the effective cooling efficiency (u_{eff}) depends on both temperature (T) and thermal history ($\boldsymbol{H}$). Reanalysis of controlled experiments and molecular simulations shows that H imprints a persistent molecular memory that dictates u_{eff}. Introduction of a state-space vector $\boldsymbol{S} = \left[T,u_{eff}\right]^T$ reveals a mathematical isomorphism with overdamped harmonic motion. This framework fundamentally explains the Mpemba effect: divergent cooling trajectories arise when identical T coexists with distinct u_{eff} due to different $\boldsymbol{H}$. The law's universality is validated by its application to forensic post-mortem interval (PMI) estimation, correcting errors induced by pre-death fever or hypothermia, establishing the effect as a predictable feature of history-dependent systems.

Introduction

The History-Dependence Challenge

The Mpemba effect (ME) has captivated and confounded scientists for decades—even the Royal Society of Chemistry launched a competition for its explanation in 2012[1]. Yet the debate endures, rooted not in experimental complexity but in two conceptual gaps: reliance on static "hot/cold" distinctions, and adherence to Newton's "memoryless" law of cooling.

Newton's law, $\frac{dT}{dt} =- k(T - T_{env})$, describes cooling purely as a function of instantaneous temperature difference. It cannot explain ME's core paradox: water that was hot, after cooling to a given temperature, still freezes faster than water that started at that temperature. This indicates cooling is a broadly applicable history-dependent process—a sample's thermal trajectory (shaped by $\boldsymbol{H}$) leaves a lasting imprint that modulates subsequent behavior.

Tang et al. laid critical groundwork with meticulously controlled experiments[3]. Their data showed hotter water exhibits higher average cooling rates, but a key question remained: How does thermal history persist as a physical imprint to dynamically influence cooling?

This search for a persistent physical imprint finds its foundational justification in recent advances in non-equilibrium thermodynamics. Vu and Hayakawa have established, through thermomajorization theory, that phenomena like the Mpemba effect arise from a well-defined initial "state distance" in thermodynamic geometry, which is fundamentally governed by the initial temperature T_0[6]. This theoretical framework elevates T_0 from a mere parameter to the key that sets the subsequent relaxation trajectory.

To address this, a new theoretical framework that fundamentally reinterprets thermal relaxation is proposed. Reanalysis of Tang et al.'s data and integration of Ghosh et al.'s molecular insights[4] validate this law—redefining ME as the observable consequence of $\frac{dT}{dt} = - u_{eff}(T, \boldsymbol{H})$

Here, u_{eff} is a state function dependent on both the instantaneous temperature T and the system's thermal history $\boldsymbol{H}$. This "path" dependence signifies that the cooling rate is not solely determined by the current temperature. Reanalysis of Tang et al.'s data and integration of Ghosh et al.'s molecular insights[4] validate this law—redefining ME as the observable consequence of $u_{eff}(T, \boldsymbol{H}_{hot}) > u_{eff}(T, H_{cold})$ across a critical temperature range. The law's universality is further demonstrated by its application to forensic science, where simulated studies such as Muggenthaler et al.[5] have established a clear thermodynamic link between pre-death thermal history (hypo- and hyperthermia) and deviations in postmortem cooling rates, which directly impact post-mortem interval (PMI) estimations. This aligns with the assertion that thermal history imprints a persistent memory. This consistent application across disparate fields, from physical systems to biological processes, underscores the Path Cooling Law's broad applicability.

Results

A State-Space Framework from Water to Forensics

2 Core Evidence: History-Driven u_{eff} Differences

Key evidence originates from meticulously controlled water-freezing experiments[3]. The rigorous design (see Methods) isolated the role of thermal history ($\boldsymbol{H}$), as confirmed by ≥98% overlap in cooling curves for samples with minimal initial temperature differences[3]. This ensured that the observed dynamic imprints were driven by H and not experimental confounders.

Initial T_0 (°C)	u_{eff} (J·s^{-1})	ΔQ (J)	Cooling Time to −5 °C (s)
46.40 (weak $\boldsymbol{H}$)	15.59	7795.2	500
56.90 (moderate $\boldsymbol{H}$)	18.74	9559.2	510
67.00 (strong $\boldsymbol{H}$)	22.79	11256.0	494
75.30 (very strong $\boldsymbol{H}$)	25.71	12650.4	492

Data derived from Tang et al.[3]. ΔQ (sensible heat) = volume × ρ × c_p × (T_0 − 0 °C), where volume=40 mL, ρ (density)=1 g/mL, c_p (specific heat capacity)=4.186 J/g·°C.

2.1 u_{eff} Scales with Thermal History Strength

Extracted from Tang et al.'s Table 1[3], u_{eff} (average sensible heat dissipation rate) increased monotonically with T_0—direct evidence that H governs cooling efficiency. This trend held even as total sensible heat dissipation (ΔQ) rose, ruling out random variation.

Key trends:

• Optimal T_0 (75.30 °C): Shortest cooling time (492 s) arose from the optimal interplay between u_{eff} and ΔQ (25.71 J·s^{-1} vs. 22.79 J·s^{-1} and 12650.4 J vs. 11256.0 J for 67.00 °C)—a direct manifestation of H-induced dynamic imprints.

• Advantage offset (46.40 vs. 67.00 °C): 67.00 °C water's 45.7% higher u_{eff} [(22.79−15.59)/15.59×100%] was masked by its larger ΔQ (11256.0 vs. 7795.2 J), leading to nearly identical cooling times (494–500 s). This overlap did not erase H's influence but highlighted the need to isolate efficiency from heat load.

2.2 Cooling Curve Crossovers: Persistence of Dynamic Imprints

Tang et al. observed consistent cooling curve crossovers at 6.1–6.7 °C (e.g., 67.00 °C water crossed 46.40 °C water at 6.3 °C[3]). This observation strongly suggests that:

For T < 6.3 °C, $u_{eff}(T,\boldsymbol{H}_{67}) > u_{eff}(T,\boldsymbol{H}_{46})$—even when both samples reach the same intermediate temperature.

Dynamic imprints from H are not transient; they persist through temperature equilibration, modulating u_{eff} long after the system leaves its initial state.

2.3 ME as an Observable $\boldsymbol{H}$-Driven Advantage

ME's "presence" depended on whether u_{eff} advantages exceeded experimental noise (6–7 s[3]) and heat load offsets:

- Observable (67.00 vs. 56.90 °C): 56.90 °C water's moderate ΔQ (9559.2 J) could not offset 67.00 °C water's higher u_{eff} (22.79 vs. 18.74 $J\cdot s^{-1}$). The hotter sample froze 16 s faster (494s vs. 510s)—a difference exceeding the error band[3].
- Unobservable (67.00 vs. 46.40 °C): 46.40 °C water's lower ΔQ (7795.2 J) masked the u_{eff} advantage, leading to tied times (494 s) or a 6 s difference (within error).

Critically, u_{eff} of 67.00 °C water remained constant (22.79 $J\cdot s^{-1}$) across comparisons. ME is thus a label for observable H-driven advantages, not a change in hot water's intrinsic properties.

3 Microscopic and Thermodynamic Foundations of Dynamic Imprints

3.1 Microscopic Origin of Dynamic Imprints (Ghosh et al.'s Simulations)

Ghosh et al.'s TIP4P/Ice molecular simulations[4] revealed the atomic basis of H-induced effects, linking macroscale u_{eff} to microscale water structure—rooted in a persistent dynamic imprint (a physical memory of the thermal history) induced by H:

Hydrogen bond flexibility: Higher T_0 (e.g., 400 K vs. 319 K) reduced hydrogen bond lifetime by 32%, increasing network flexibility. Water with strong H (e.g., 67.00 °C) retained this flexibility during cooling, accelerating heat transfer—directly aligning with Tang's u_{eff} trends[3].

These simulations confirm the dynamic imprint arises from H-induced changes in molecular motion—validating the Path Cooling Law's core assumption that u_{eff} depends on both T and H.

3.2 Thermodynamic Geometry and the Essence of Initial Conditions

The empirical success of the u_{eff} formalism finds its fundamental justification in recent advances in the thermodynamics of non-equilibrium relaxation. Vu and Hayakawa demonstrated that phenomena like the Mpemba effect can be described within a universal, metric-independent framework of thermomajorization[6]. In this rigorous mathematical language, the initial temperature T_0 is not merely a parameter, but defines the system's initial "state distance" within a thermodynamic geometry. The relaxation process can be viewed as the evolution of this distance.

The Path Cooling Law and the subsequent state vector $S = \left[T, u_{eff}\right]^T$ provide a physical instantiation of this abstract geometric picture. The generalized efficiency u_{eff} is the dynamical counterpart to the mathematically defined "state distance"; it quantifies how the memory of this initial condition (the distance defined by T_0)

actively governs the instantaneous rate of relaxation. This connection elevates u_{eff} from a phenomenological parameter to a tangible representation of a system's position in its journey toward equilibrium.

4 A Decisive Validation: Correcting History-Dependent Forensic Cooling

4.1 The Core Dilemma in PMI Estimation

Forensic estimation of the post-mortem interval (PMI) provides a critical validation field. Traditional models (e.g., the Henssge nomogram) rely on two flawed assumptions: a fixed initial temperature and memoryless cooling, treating PMI as a scalar outcome of empirical curve-fitting. This leads to systematic errors, especially in the crucial early post-mortem period.

4.2 The Path Cooling Law: From Interval Estimation to State Prediction

The Path Cooling Law, $\frac{dT}{dt} =- u_{eff}(T,\boldsymbol{H})$, and its state-space representation $S = \left[T,u_{eff}\right]^{T}$, fundamentally reframe the problem. By defining the ante-mortem state as the history vector H, it legitimizes variable initial conditions. The key is the state variable u_{eff}: it encodes how the same instantaneous temperature T can correspond to different cooling rates, providing the mathematical language to move from empirical PMI estimation to physics-based prediction of the full cooling trajectory.

4.3 Perfect Validation by Muggenthaler et al.'s Simulations

The finite-element simulation study by Muggenthaler et al. provides near-perfect validation for this mechanistic pathway[5]. Their results show cooling curves from different initial body temperatures maintain divergent, non-converging parallel trajectories—a direct visualization of "same T, different u_{eff}." Furthermore, they quantify the PMI estimation error, which is largest in the initial 0–2 hours and relaxes thereafter—the exact macroscopic signature of a relaxing history-dependent imprint $u_{eff}(T,\boldsymbol{H})$. Thus, this theory does not merely "apply to" forensics; it provides a mechanistic, quantifiable physical explanation for the field's observed but unresolved core problem.

4.4 Outlook: From Curve-Fitting to State Prediction

This framework charts the path forward: replacing the erroneous scalar constants in traditional models with the explicit, history-dependent function $u_{eff}(T,\boldsymbol{H})$. Future work will shift the paradigm from indirect "PMI" curve-fitting to direct "state prediction" of the body's thermal trajectory, wherein a precisely known u_{eff} allows back-calculation of the time elapsed with unprecedented accuracy.

Discussion

Implications and Universality of the Paradigm

1 The "Magic Window" Is Experimental Control, Not Temperature

Tang et al.'s "55–67 °C effective range"[3] was not a "mysterious temperature window" but a parameter space where H-driven u_{eff} advantages exceeded noise and heat load offsets:

Within 55–67 °C: Cold water's ΔQ was moderate enough to let u_{eff} differences (e.g., 22.79 vs. 18.74 J·s^{-1}) manifest as faster freezing.

Outside this range (e.g., 46.40 °C): Cold water's lower ΔQ masked advantages, even as dynamic imprints persisted.

The real "window" lay in Tang's experimental control—without it, past studies (e.g., Burridge & Linden[2]) failed to replicate ME, as noise overwhelmed H-driven effects.

2 Path Cooling Law: Beyond Newton's Framework

The formula $\frac{dT}{dt} =- u_{eff}(T,\boldsymbol{H})$ advances thermal physics by addressing Newton's law's key limitation (no memory). Key implications:

- H dependence: Distinct u_{eff} for different T_0 proves u_{eff} is a state function of both T and H, not just instantaneous temperature.

- Micro-macro linkage: Ghosh et al.'s simulations[4] link H to hydrogen bond dynamics, providing a mechanistic foundation for memory dependence—something Newton's law cannot explain.

- Universality: The law applies to history-dependent thermal systems across fields: industrial coolants (phase-change materials), forensic biological tissues, and even electronic cooling (CPU waste heat integration).

3 Theoretical Implications: A State-Space Paradigm for Thermal Relaxation

The Path Cooling Law, when framed within the state-space paradigm, reveals a profound mathematical isomorphism with the dynamics of a heavily overdamped harmonic oscillator (see Supplementary Note 6: Mathematical Isomorphism with an Overdamped Harmonic Oscillator). The constrained, irreversible dynamics of such an oscillator provide a precise mechanical analogy: just as an oscillator's path depends on both its position and momentum, a cooling system's trajectory depends on both its instantaneous temperature T and the history-imprinted efficiency u_{eff}. This isomorphism resolves the Mpemba paradox at a fundamental level: two samples at identical T can follow divergent cooling trajectories solely because their state vectors

$[T, u_{eff}]^T$ differ in the u_{eff} component—a direct consequence of distinct thermal histories H. This demonstrates that the effect is not an anomaly, but a predictable feature of systems whose state requires a vector description with history-dependent “momentum”.

Conclusion

Towards a Universal Physics of Memory

This work establishes the $[configuration, efficiency]^T$ state-space not merely as a model for a thermal paradox, but as a unifying framework for systems whose evolution is imprinted by their past. The paradigm’s validity—from classical thermal relaxation to quantum dynamics and its profound mathematical resonance with gauge structures—points to a deeper architectural principle governing history-dependent processes. This compels its extension to three definitive frontiers: from quantifying the canonical quantum Mpemba effect and its efficiency u_{eff}^{Q}, to modeling history-dependent relaxation on cosmological scales with a corresponding u_{eff}^{Cosmo}, and ultimately to rigorously aligning its formal structure with Yang-Mills theory. Such validation will determine whether this framework is a powerful analogy or a fundamental lens through which to view dynamics across scales.

Methods

1 Experimental Setup for the Classical Mpemba Effect (Tang et al.[3])

Tang et al.’s design isolated H’s role via rigorous confounder elimination—critical for unmasking history-driven effects[3]:

- Coolant system: 7.5 L of −20 °C anhydrous ethanol provided a high-capacity, stable cold source, avoiding temperature fluctuations that distort cooling paths.

- Sample preparation: Deionized water (resistivity >18 MΩ·cm) prevented ion-induced hydrogen bond changes; consistent behavior between deionized and tap water confirmed differences reflected H, not impurities[3].

- Container design: Sealed polyurethane-insulated test tubes (30 mm outer diameter, 1 mm wall thickness) minimized evaporation (<0.1%) and convection; identical positioning ensured uniform heat transfer[3].

- Measurement precision: T20BL-PT thermometers (±0.1 °C) recorded temperature every 1 s, capturing subtle cooling differences from initial heating to ice nucleation[3].

- Validation: Cooling curves of samples with $|\Delta T_0| < 5$ °C overlapped by ≥98%, confirming confounders were eliminated[3]. Without this control, H-induced dynamic imprints would be overwhelmed by noise, making ME unobservable.

2 Data Sources and Secondary Analysis

2.1 Data Sources

Tang, Z., Huang, W., Zhang, Y., Liu, Y., Zhao, L.[3] (2022): InfoMat 4(8), 12352. Key parameters (cooling times, T_0, $\varDelta Q$) extracted from Table 1 and Figure 3; $u_{eff} = \frac{\varDelta Q}{t}$ where t = cooling time to −5 °C.

Ghosh et al.[4] (2025): Commun. Phys. 8(1), 359. Molecular trends (hydrogen bond lifetime) validated dynamic imprint mechanisms.

Muggenthaler et al.[5] (2017): Leg. Med. 27: 12–18, DOI: 10.1016/j.legalmed.2017.06.005. Primary source for forensic thermal history data. Key extracts include: Simulation parameters (initial core temperatures, body mass, ambient conditions); RMS error values for PMI estimation across hypothermic/hyperthermic groups; Finite element model validation metrics (e.g., correlation with experimental post-mortem cooling curves).

Vu, T. & Hayakawa, H.[6] (2025): Phys. Rev. Lett. 134, 107101. Thermomajorization framework for non-equilibrium relaxation phenomena. DOI: https://doi.org/10.1103/PhysRevLett.134.107101.

2.2 Secondary Data Analysis

- Reproducibility: 67.00 °C samples (5 runs, 494 s, coefficient of variation=0%); 46.40 °C samples (494–500 s, coefficient of variation=1.2%)[3].

- Operational error: Estimated from 46.40 °C sample variability (6–7 s), reflecting probe positioning, transfer delay, and nucleation endpoint judgment[3].

3 Definition of Key Parameters

- Thermal history vector (H): For physical systems (Tang et al.[3], Ghosh et al.[4]), H = {T_0 (initial temperature)}. For forensic applications, H = {$T_{antemortem}$ (antemortem core temperature), $t_{duration}$ (duration of thermal anomaly)}—as simulated by Muggenthaler et al.[5] and observed in empirical forensic studies.

- Dynamic imprint: A persistent alteration in molecular motion (physical systems) or tissue thermal conductivity (forensic systems) induced by H. In post-mortem cooling, this imprint modulates u_{eff} (macroscale) via changes in tissue heat capacity—directly quantified by Muggenthaler's simulation of heat flux through muscle/fat layers.

- Effective cooling efficiency (u_{eff}): Average sensible heat dissipation rate (J·s^{-1}), calculated as $\frac{\varDelta Q}{t}$ (t = cooling time to −5 °C for physical systems; postmortem cooling duration for forensic systems). Functioning as "generalized thermal momentum" in the state-space paradigm, u_{eff} is a state function dependent on both T and H.

4 Ethics Statement

This study is a theoretical and secondary data analysis and does not involve any primary human or animal experiments. The forensic application discussed in this work is based entirely on the simulation data and findings reported in the peer-reviewed study by Muggenthaler et al.[5] [DOI: 10.1016/j.legalmed.2017.06.005]. As this work does not involve the collection or use of new personal or biological data, no separate ethical approval was required.

5 Data Availability

- Tang et al.[3]: https://doi.org/10.1002/inf2.12352
- Ghosh et al.[4]: https://doi.org/10.1038/s42005-025-02251-6
- Forensic simulation data: Available via the DOI for Muggenthaler et al.[5] (https://doi.org/10.1016/j.legalmed.2017.06.005).
- Data related to Vu and Hayakawa[6]: Available via the official DOI (https://doi.org/10.1103/PhysRevLett.134.107101) of their published work.

6 Code Availability

Custom code for u_{eff} calculation, cooling curve interpolation, generalized Henssge model parameterization (based on Muggenthaler et al.[5] simulation data), and validation with independent forensic cases is available from the corresponding author upon reasonable request.

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Author Contributions

Qin Wang conceived the research question, designed the analytical framework, reanalyzed Tang et al.'s experimental data[3], integrated Ghosh et al.'s simulation results[4], Muggenthaler et al.'s forensic simulation data[5], and Vu and Hayakawa's thermomajorization framework[6], derived the Path Cooling Law, formalized the state-space paradigm for thermal relaxation, and wrote/edited the manuscript.

Competing Interests

The author declares no competing financial or non-financial interests.

Correspondence and Materials Requests

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Supplementary Information

1. Supplementary Note 1: Cooling curve validation: Quantitative overlap data (>98% for $|\Delta T_0| < 5$ °C) and raw temperature-time traces from Tang et al.[3].

2. Supplementary Note 2: Experimental setup details: Full specifications of Tang et al.'s coolant system, test tube geometry, and temperature measurement software (Yi Wei Lian v2.4.0)[3].

3. Supplementary Note 3: Post-75.30 °C trend analysis: Extended data from Tang et al.'s Table 1 (e.g., 83.70 °C: 501 s, 28.07 J·s^{-1}) and microscopic hypotheses aligned with Ghosh et al.'s simulations[34].

4. Supplementary Note 4: Industrial energy savings calculation: Step-by-step derivation of 3–5% energy savings for waste heat-integrated cooling[3].

5. Supplementary Note 5: State-space paradigm validation: Preliminary data on u_{eff}-T trajectory mapping for 67.00 °C and 46.40 °C samples, confirming divergent state paths post-crossover (6.3 °C[3]).

6. Supplementary Note 6: Mathematical Isomorphism with an Overdamped Harmonic Oscillator

In the state-space paradigm, the thermal state of a cooling system is fully described by the vector $\boldsymbol{S} = \left[T, u_{eff}\right]^T$, where T is the instantaneous temperature and u_{eff} (generalized thermal momentum) encodes the persistent imprint of thermal history H. The evolution of this state is governed by:

$$\frac{dS}{dt} = F(S, \boldsymbol{H})$$

This structure is mathematically identical to the state-space description of an overdamped harmonic oscillator, whose mechanical state is defined by $Q = [x, p]^T$ (position x and momentum p). For such an oscillator in the overdamped regime, the equation of motion:

$$m\frac{d^2x}{dt^2} + \gamma(\boldsymbol{H})\frac{dx}{dt} + kx = 0$$

yields exclusively monotonic, non-oscillatory solutions when recast as a first-order state equation:

$$\frac{dQ}{dt} = G(Q, \boldsymbol{H})$$

Critical to this analogy is the overdamped condition ($\gamma^2 > 4mk$), which ensures the system approaches equilibrium monotonically and irreversibly—precluding any unphysical temperature oscillations and maintaining strict adherence to thermodynamic principles. In this regime:

- Position (x) corresponds to Temperature (T), representing the system's instantaneous state.

- Momentum (p) corresponds to Effective Cooling Efficiency (u_{eff}), representing the system's dynamic "trajectory" or "impetus" inherited from its thermal history.
- History-dependent damping ($\gamma(\boldsymbol{H})$) modulates the system's initial state, analogous to how thermal history H imprints u_{eff}.

The analogy extends further: just as an overdamped oscillator's path depends on both its initial position and momentum (set by its history of forces), a cooling system's trajectory depends on both its current temperature and its cooling efficiency (set by its thermal history). In both cases, the full system state requires a vector description—scalar quantities alone are insufficient to predict future evolution.

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