

Hysteresis-driven radiative Mpemba effect in phase-change nanostructures

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The Mpemba effect states that initially hotter systems cool faster than colder ones. While known in convective, conductive, and quantum systems, its radiative analog is unexplored. Here, this anomaly is realized via phase-change hysteresis of a VO₂ nanoparticle near a SiC substrate. After analytically deriving an onset condition, the phase space is mapped. Crucially, latent heat acts as a thermal buffer enabling both ordinary and inverse effects. Near-field coupling governs the relaxation time and enables a passive effect where memory is stored externally via substrate reflection.

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I. INTRODUCTION

The Mpemba effect describes the counterintuitive phenomenon where an initially hotter system cools down faster than an initially colder one, first documented for water [1]. In the last two decades, this anomalous relaxation has been translated to a variety of other systems, including Brownian particles trapped in optical tweezers [2]. This platform also enabled the observation of the inverse effect, where an initially colder system heats up faster [3], theoretically explained by the nonmonotonic temperature dependence of the maximum extractable work from a local-equilibrium state [4]. In granular fluids, numerical simulations revealed that nonequilibrium statistical velocity distributions can induce the effect [5]. More generally, in Markovian systems without a phase transition, the ruling factor is the second largest eigenvalue of the probability distribution trajectories, explaining why the Mpemba effect occurs in three-state models or antiferromagnetic Ising chains [6,7].

Very recently, the Mpemba effect was generalized to quantum systems. For instance, a qubit driven by a thermal photon source can undergo the inverse Mpemba effect due to interference [8]. In many-body quantum systems, configurations whose symmetry is initially more strongly broken can restore it faster [9], which was experimentally verified in a trapped-ion quantum simulator [10]. Additionally, in a single trapped-ion system prepared in a pure state, this anomalous relaxation was linked to Liouvillian exceptional points [11]. For both the classical and quantum Mpemba effect, recent reviews provide comprehensive overviews [12,13].

Inspired by these findings, this work translates the Mpemba effect to thermal radiative transport, moving beyond the

traditional realms of conduction, convection, or symmetry restoration. While previous work has demonstrated the Mpemba effect in radiative heat transfer for many-body systems via Markovian dynamics [7], the realization presented here exploits non-Markovian memory embedded in phase change hysteresis, enabling anomalous relaxation in a minimal two-body geometry. In non-Markovian quantum systems, the Mpemba effect occurs [14] due to memory effects, which are also a characteristic of macroscopic complex systems such as spin glasses [15]. In thermotronics, which design thermal analogs to electric components, materials undergoing a metal-insulator transition at a critical temperature T_c , such as VO₂, are widely used for thermal diodes [16,17], transistors [18,19], and logic gates [20,21]. In the transition regime, these phase-change materials exhibit a hysteresis separating the cooling and heating branches. This introduces an intrinsic memory effect and radiative bistability [22,23], which can drive thermal self-oscillations [23]. VO₂ is especially promising in the near field because the switch from the metallic ($T > T_c$) to the dielectric phase ($T < T_c$) triggers the excitation of strongly coupling surface phonon polaritons (SPhPs) in the dielectric phase, drastically enhancing the radiative heat transfer compared to the metallic phase [24].

The paper is organized as follows. In Sec. II, I introduce the theoretical framework coupling near-field radiative heat transfer with thermal hysteresis via the T-FORC model, and derive the general analytical onset criterion governing the radiative Mpemba effect. In Sec. III, I analyze the dynamic interplay between the caloric buffer of latent heat and near-field photon exchange for a phase-change nanoparticle above a metallic substrate. I then demonstrate the passive Mpemba effect, showing that anomalous relaxation can be driven purely by memory stored externally in the substrate reflection, which is a mechanism unique to the near-field regime. Finally, Sec. IV summarizes the key findings.

II. THEORY

To demonstrate the emergence of this radiative Mpemba effect, this work analyzes a VO₂ nanoparticle of radius R at

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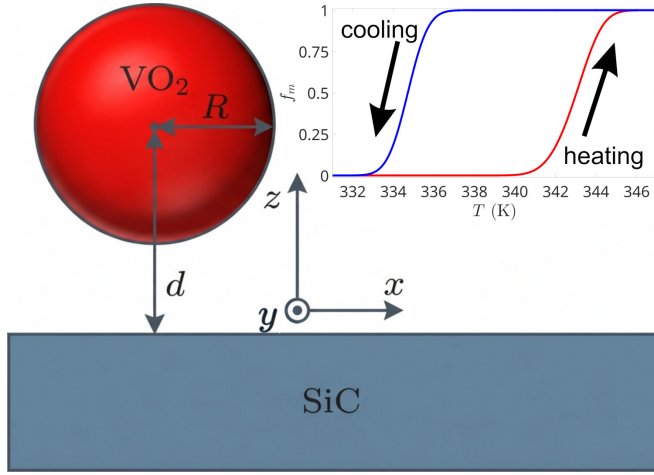


FIG. 1. Sketch of the considered system. A VO_2 nanoparticle of radius R is placed at center-to-surface distance d above a SiC substrate. The inset shows the hysteresis of the metallic volume fraction f_m in the transition regime $332 \text{ K} < T < 346 \text{ K}$.

a center-to-surface distance d above a SiC substrate, which also supports SPhPs, thereby enabling a detailed discussion of near-field radiative effects. This schematic setup is shown in Fig. 1. The substrate's temperature T_{sub} is held constant, while the temperature of the nanoparticle T_{dip} evolves.

If the temperature homogenization throughout the body is much faster than the thermal relaxation time, the time evolution of the temperature follows [25]

$$\frac{dT_{\text{dip}}}{dt} = -\frac{\mathcal{P}_{\text{sub} \leftrightarrow \text{dip}}}{\rho C_p V}, \quad (1)$$

where ρ is the mass density and V is the volume. The specific heat capacity C_p and the exchanged power $\mathcal{P}_{\text{sub} \leftrightarrow \text{dip}}$ are detailed in Sec. S1 of the Supplemental Material [26] (see also Refs. [27–48] therein). The calculations of the radiative heat transfer $\mathcal{P}_{\text{sub} \leftrightarrow \text{dip}}$ are based on the framework of fluctuating electrodynamics [49]. To have a Mpemba effect, the time evolution of two distinct trajectories have to cross at a certain time τ such that $T_1(\tau) = T_2(\tau)$ with $\frac{dT_1}{dt}|_{t=\tau} < \frac{dT_2}{dt}|_{t=\tau}$ assuming an initially hotter temperature compared to an initially colder one, i.e., $T_1(0) > T_2(0)$. Defining $T_1 = T + \Delta T$ and $T_2 = T$ with $\Delta T(\tau) = 0$, the following relation holds at $t = \tau$,

$$\frac{d\Delta T}{dt} = \zeta(T + \Delta T, f + \Delta f, \gamma + \Delta \gamma) - \zeta(T, f, \gamma) \quad (2)$$

with the definition

$$\zeta(T, f, \gamma) = -\frac{\mathcal{P}_{\text{sub} \leftrightarrow \text{dip}}(T, f)}{\rho C_p(T, \gamma)V}. \quad (3)$$

Here, f denotes the volume fraction, e.g. the metallic one, responsible for the hysteresis as shown in Fig. 1 and $\gamma = \partial f / \partial T$ denotes its time derivative. It stores the memory of whether the system was previously heated or cooled. Therefore, even though $\Delta T = 0$ at $t = \tau$ holds, a structural memory mismatch $\Delta f \neq 0$ and $\Delta \gamma \neq 0$ persists. For small deviations $\Delta T \ll T$, $\Delta f \ll f$, and $\Delta \gamma \ll \gamma$, ζ can be expanded around the state

of the colder trajectory yielding

$$\begin{aligned} \zeta(T + \Delta T, f + \Delta f, \gamma + \Delta \gamma) \\ \approx \zeta(T, f, \gamma) + \frac{\partial \zeta}{\partial T} \Delta T + \frac{\partial \zeta}{\partial f} \Delta f + \frac{\partial \zeta}{\partial \gamma} \Delta \gamma. \end{aligned} \quad (4)$$

Reinserting this expansion into Eq. (3) yields

$$\frac{d\Delta T}{dt}|_{t=\tau} = \frac{\partial \zeta}{\partial f} \Delta f + \frac{\partial \zeta}{\partial \gamma} \Delta \gamma, \quad (5)$$

confirming that $\Delta f \neq 0$ or $\Delta \gamma \neq 0$ are strictly necessary to observe a Mpemba effect. From Eq. (5) and the derivatives of ζ defined in Eq. (3), the final condition is obtained as

$$0 < \frac{\partial \mathcal{P}_{\text{sub} \leftrightarrow \text{dip}}}{\partial f} \Delta f - \frac{\mathcal{P}_{\text{sub} \leftrightarrow \text{dip}} L}{C_p} \Delta \gamma. \quad (6)$$

Note that the derivative $\partial C_p / \partial \gamma = L$ is taken from Eq. (S17) in the Supplemental Material [26]. Hence, the derivatives of the exchanged power and the specific heat capacity define whether an anomalous relaxation occurs. Note that this mathematical derivation holds for any internal variable f whose thermodynamic response introduces a rate-dependent or memory effect in the heat capacity, and is not restricted to hysteresis in phase-change materials. For example, it applies to materials whose optical and caloric properties depend on the heating or cooling rate itself via the fictive temperature ($f = T_f$, $\gamma = \partial T_f / \partial T$) due to structural aging [50,51] or under strain ($f = \sigma$, $\gamma = \partial \sigma / \partial T$) [52], provided that the parameter L is interpreted as the corresponding effective thermodynamic coefficient. An interesting limiting case is the exchange of the materials, placing a SiC particle above a VO_2 substrate. In this scenario, C_p only depends on T because the memory effect is stored externally in $\mathcal{P}_{\text{sub} \leftrightarrow \text{dip}}$ via the substrate's reflection. Then, Eq. (6) simplifies to

$$0 < \frac{\partial \mathcal{P}_{\text{sub} \leftrightarrow \text{dip}}}{\partial f} \Delta f. \quad (7)$$

Because the relaxing particle lacks an intrinsic memory, this scenario is referred to as the passive Mpemba effect and underscores a key theoretical insight of this work. The emergence of anomalous relaxation does not strictly require an internal state variable within the relaxing body itself. In this passive regime, the body acts as a memoryless probe, while the non-Markovian history is stored externally in the structural state of the substrate. As will be shown, this passive mechanism relies critically on evanescent wave coupling and vanishes in the far-field limit, proving that it is a unique feature of near-field radiative transport.

III. RESULTS AND DISCUSSION

For a VO_2 particle of radius $R = 100 \text{ nm}$ placed at $d = 500 \text{ nm}$ above a SiC substrate at $T_{\text{sub}} = 300 \text{ K}$, Fig. 2(a) maps the conditions for the Mpemba effect. The color represents the intersection time τ , where one particle is prepared on the cooling branch T_{cool} and another on the heating branch T_{heat} . Although the radiative contrast $\partial \mathcal{P} / \partial f_m$ is non-negligible, which is evidenced by the exchanged power discussed in Sec. S2 of the Supplemental Material [26], the characteristic features of the Mpemba effect are predominantly governed by

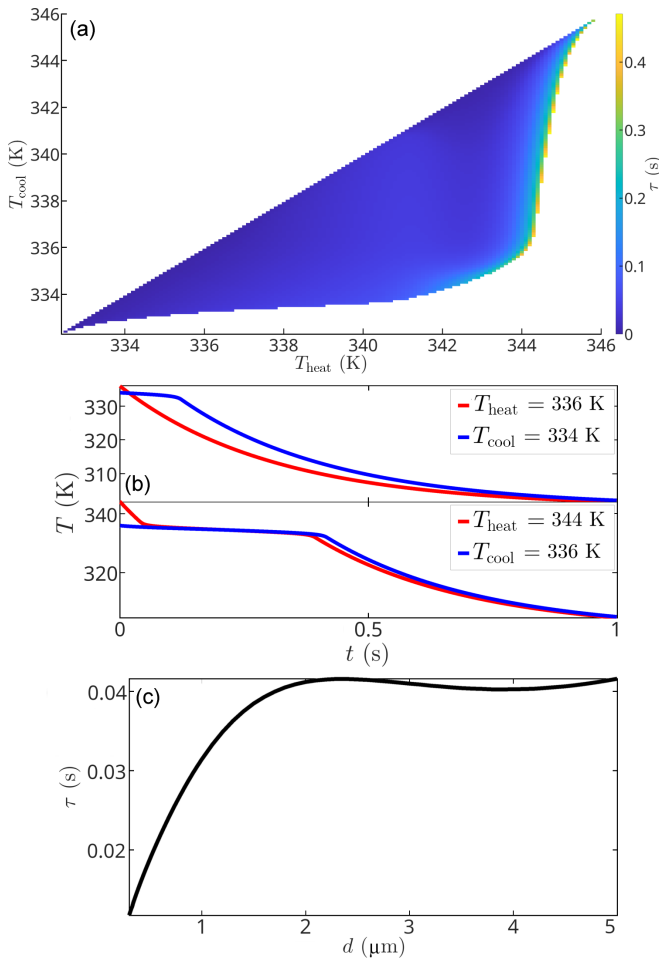


FIG. 2. Mpemba effect. (a) Heat map of the time τ at which two temperature curves intersect, which were initially prepared on the heating branch T_{heat} and the cooling branch T_{cool} of the hysteresis. The VO_2 particle's radius is $R = 100$ nm, the distance to the substrate $d = 500$ nm, and the substrate's temperature $T_{\text{sub}} = 300$ K. (b) Two exemplary temperature combinations for which the Mpemba effect occurs. (c) Distance dependence of τ for $T_{\text{heat}} = 336$ K and $T_{\text{cool}} = 334$ K.

the caloric channel. This dominance arises from the transient behavior of C_p within the phase-change regime. While the radiative power $\mathcal{P}_{\text{sub} \leftrightarrow \text{dip}}$ varies gradually over the transition width, the latent heat contribution introduces a massive, localized peak in C_p via the derivative $\partial f / \partial T$. This caloric peak acts as a strong thermal buffer that dynamically alters the cooling trajectories. Consequently, the distinct features of the observed Mpemba effect can be almost exclusively attributed to this latent-heat-induced modulation of the heat capacity.

Figure 2(b) shows two exemplary temperature curves exhibiting early and later intersection times τ . In both cases, the latent heat delays the temperature decay, generating a visible plateau. This plateau emerges in the regime of rapid change in f_m/d after entering the hysteresis slopes illustrated in Fig. 1. The case for $T_{\text{heat}} = 344$ K and $T_{\text{cool}} = 336$ K shows that for certain temperatures within the transition regime (e.g., $T_{\text{heat}} = 345$ K), two curves can miss each other if the intersection does not coincide with the phase of latent heat release. If

T_{heat} has not yet reached the steep slope of the heating branch, there is no delay due to latent heat because $\partial f / \partial T \approx 0$. This enables the initially hotter curve to overtake the T_{cool} curve while the latter experiences the latent heat delay, as illustrated for $T_{\text{heat}} = 336$ K and $T_{\text{cool}} = 334$ K in Fig. 2(b). Note that the here implemented temperature first-order reversal curve (T-FORC) model (see Sec. S1 in the Supplemental Material [26]) prevents a steep slope of f_m/d at early times, physically accounting for the kinetic delay in domain reorganization upon thermal reversal. This explains why the region $T_{\text{heat}} < T_{\text{cool}}$ does not yield a Mpemba effect when preparing T_{heat} directly on the heating slope. Conversely, near $T_{\text{heat/cool}} \approx 332$ K, the curves can miss each other if the cooling branch is not yet steep enough at T_{cool} . If $T_{\text{heat}} < T_{\text{cool}}$ is prepared at those lower temperatures, latent heat will always delay the decay of T_{cool} , generally preventing an intersection.

Additionally, Fig. 2(c) depicts the distance dependence of τ for $T_{\text{heat}} = 336$ K and $T_{\text{cool}} = 334$ K, highlighting the role of near-field coupling. Shorter distances accelerate the temperature decay. For $d > 2$ μm , the near-field coupling becomes negligible, and τ oscillates around a far-field asymptote of $\tau_{\infty} \approx 0.04$ s. These oscillations stem from the propagating waves embedded in the local density of states (LDOS), which dominates once the evanescent contributions can be neglected. Similar oscillatory relaxation behaviors in the far field have been reported in Ref. [27] for SiC and gold configurations, where they were analytically evaluated using the stationary phase method. Note that changing the distance primarily shifts the intersection time τ but leaves the boundaries of the Mpemba phase space in Fig. 2(a) almost unchanged.

It is important to emphasize that this radiative Mpemba effect is not a simple thermal delay. Rather, it represents a selective trajectory crossing induced by the strong, localized peak in the specific heat capacity C_p due to latent heat release during path-dependent domain reorganization. While the near-field radiative channel dictates the global relaxation time scale τ , the caloric peak acts as a dynamic buffer that allows initially hotter trajectories to overtake cooler ones.

Figure 3(a) illustrates the conditions for the inverse Mpemba effect, obtained by setting the substrate temperature to $T_{\text{sub}} = 378$ K to induce heating. While the overall topology of the heat map resembles that of the ordinary Mpemba effect, the maximum intersection times τ shift toward lower initial temperatures. This shift reflects the fundamental inversion of the hysteresis pathways. During heating, the structural evolution along the primary heating branch remains unaltered, acting as a fixed reference where latent heat absorption occurs at higher temperatures. In contrast, a particle prepared on the cooling branch at T_{cool} is now forced onto an ascending T-FORC pathway upon reversal. Because this T-FORC trajectory starts flat, the cooler particle is temporarily shielded from latent heat suppression due to $\partial f / \partial T \approx 0$. Consequently, an intersection either occurs when T_{heat} is delayed by latent heat at an early stage, or while both curves are simultaneously delayed by latent heat, which yields the maximum τ values. Both regimes are exemplified in Fig. 3(b).

To discuss the possibility of a passive Mpemba effect when exchanging the materials of the particle and the substrate, the

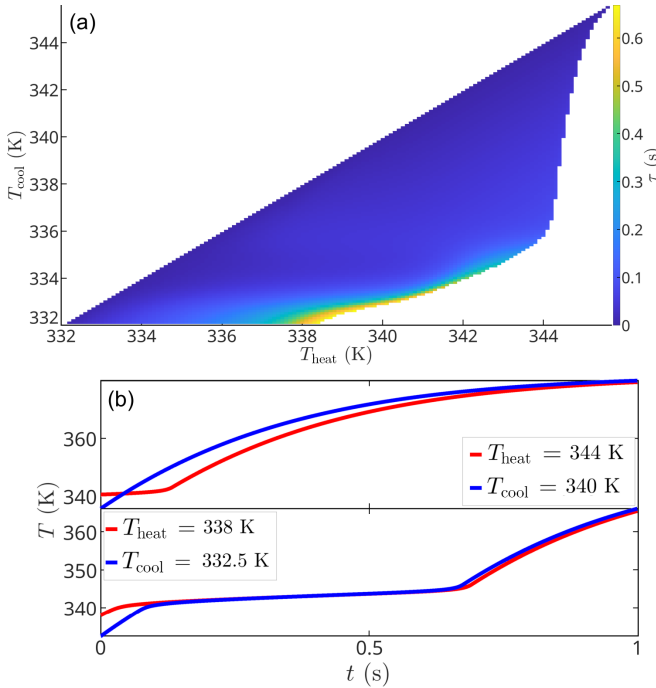


FIG. 3. Inverse Mpemba effect. (a) Heat map identical to Fig. 2 but with the substrate temperature $T_{\text{sub}} = 378$ K causing an inverse Mpemba effect. (b) Two exemplary temperature combinations for which the inverse Mpemba effect occurs.

semi-infinite substrate is replaced by a thin film of thickness $t_{\text{sub}} = 100$ nm. This prevents the necessity of accounting for the anisotropy of bulk VO_2 , which otherwise manifests for large thicknesses [24,53]. Therefore, the Fresnel amplitude reflection coefficients $r_{s/p}$ of a semi-infinite half-space described in Sec. S1 of the Supplemental Material [26] are replaced by the Airy-type expressions [54]

$$r_{s/p,\text{slab}} = \frac{r_{s/p}(1 - e^{2ik_z \text{sub} t_{\text{sub}}})}{1 - r_{s/p}^2 e^{2ik_z \text{sub} t_{\text{sub}}}}. \quad (8)$$

Now, Fig. 4 shows the time evolution for two initial temperatures $T_{\text{dip}} = 360$ K and $T_{\text{dip}} = 370$ K while keeping the VO_2 film at $T_{\text{sub}} = 342$ K, once prepared in the dielectric phase and once in the metallic phase. The distance is varied between $d = 500$ nm and $d = 1$ μm . For $d = 500$ nm, the initially hotter SiC particle cools down faster than the initially colder one, intersecting it at $\tau \approx 0.08$ s. The reason for this is shown in the insets, which depict the exchanged power for both phases. In the metallic phase of the VO_2 film, the SiC particle cannot couple as effectively to the substrate as in the dielectric phase due to higher reflection. Therefore, the heat exchange takes much longer in the metallic phase than in the dielectric one, giving rise to the passive Mpemba effect. When, however, increasing the distance to $d = 1$ μm , this coupling becomes weaker in the dielectric phase so that the passive Mpemba effect effectively vanishes and cannot be distinguished from numerical noise anymore. This directly proves that the passive Mpemba effect only occurs in the near field.

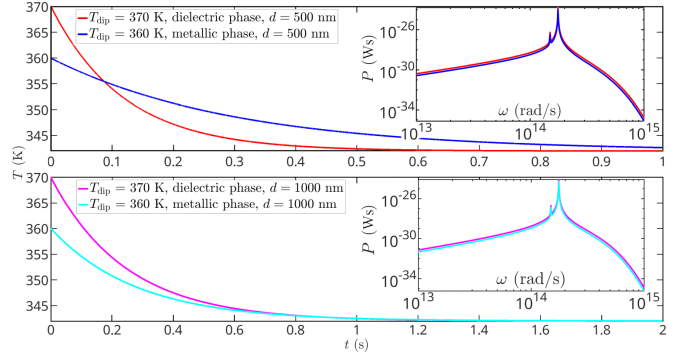


FIG. 4. Passive Mpemba effect. Temperature evolution of a $R = 100$ nm SiC particle at $d = 500$ nm (red and blue) and $d = 1$ μm (magenta and cyan) above a VO_2 substrate of thickness $t = 100$ nm. The initial temperature of the particle above the substrate prepared in the dielectric phase is $T_{\text{dip}} = 370$ K (red and magenta), whereas $T_{\text{dip}} = 360$ K (blue and cyan) corresponds to the case where the substrate is prepared in the metallic phase. Insets: Corresponding spectral power for each initial temperature.

IV. CONCLUSION

In conclusion, this work has translated the anomalous relaxation of the Mpemba effect to thermal radiative transport. By exploiting the coupling between near-field radiation and the hysteresis pathways of phase-change materials, it is demonstrated that an initially hotter system can cool down faster than an initially colder one. Beyond establishing this baseline phenomenon, this study reveals that the radiative Mpemba effect is not a simple thermal delay, but rather a dynamic interplay where latent heat acts as a caloric buffer, controlling trajectory crossings while near-field photon exchange dictates the overall relaxation time scale. A generalized analytical condition for this radiative Mpemba effect has been derived, showing that its emergence is dictated by the interplay between radiative power and specific heat capacity derivatives. Through numerical simulations of a VO_2 nanoparticle interacting with a SiC substrate, the Mpemba phase space has been mapped, verifying the three distinct manifestations of the ordinary, inverse, and passive Mpemba effects. Crucially, the passive variant highlights that the anomaly can be triggered solely via external memory storage in the substrate reflection, proving that the relaxing system itself does not require intrinsic hysteresis. Furthermore, the breakdown of this passive variant at larger separation distances confirms its strictly near-field nature, demonstrating geometric tunability as the system transitions from the near-field to the far-field regime.

The chosen setup matches readily accessible experimental configurations, facilitating laboratory verification via pump-probe microscopy [55,56]. The magnitude of the effect could potentially be enhanced by using symmetric VO_2 - VO_2 configurations instead, maximizing the phase-change radiative contrast due to ideal resonant frequency matching of the SPhPs in the dielectric phase [24]. Additionally, the underlying hysteresis loop can be precisely tailored to specific operating temperatures, for instance, by doping with tungsten [57,58]. Consequently, these findings open up novel avenues

for exploiting material history and structural memory in radiative heat transfer, establishing a versatile cornerstone for advanced dynamic thermal management on the nanoscale.

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DATA AVAILABILITY

There are no publicly available research data or software supporting this paper. Requests for further information or data should be sent to the author.

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