Heating and Cooling are Fundamentally Asymmetric and Evolve Along Distinct Pathways

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According to conventional wisdom, a system placed in an environment with a different temperature tends to relax to the temperature of the latter, mediated by the flows of heat and/or matter that are set solely by the temperature difference. It is becoming clear, however, that thermal relaxation is much more intricate when temperature changes push the system far from thermodynamic equilibrium. Interestingly, under such conditions heating was predicted to be faster than cooling, which we experimentally confirm using an optically trapped colloidal particle. More strikingly, we show with both experiments and theory that between any pair of temperatures, heating is not only faster than cooling but the respective processes in fact evolve along fundamentally distinct pathways, which we explain with a new theoretical framework we coin "thermal kinematics".

Introduction The basic laws of thermodynamics dictate that any system in contact with an environment eventually relaxes to the temperature of its surroundings as a result of irreversible flows that drive the system to thermodynamic equilibrium. If the difference between the initial temperature of the system and that of the surroundings is small, i.e. the system is initially "close to equilibrium" [1], the relaxation is typically assumed to evolve quasi-statically through local equilibrium states an assumption that is justifiable only a posteriori [1, 2]. However, if the temperature contrast is such that it pushes the system far from equilibrium, the assumption breaks down and the relaxation path is no longer unique, but depends strongly on the initial condition. This gives rise to counterintuitive phenomena, such as anomalous relaxation (also known as the Mpemba effect) [3–9] where, a system reaches equilibrium faster upon a stronger temperature quench, and the so-called Kovacs memory effect [10–14] which features a non-monotonic evolution towards equilibrium.

Intriguingly, thermal relaxation was recently predicted to depend also on the sign of the temperature change. Namely, considering two *thermodynamically equidistant* (TE) temperatures — one higher and the other lower than an intermediate one selected such that the initial free energy difference with the equilibrium state is the same — heating from the colder temperature was predicted to be faster than cooling from the hotter one [15, 16]. This prediction challenges our understanding of non-equilibrium thermodynamics as it compares reciprocal relaxation processes elusive to classical thermodynamics. The initially hotter system must dissipate into the environment an excess of both, energy and entropy, whereas in the colder system energy and entropy must increase [15, 17]. Moreover, the comparison of heating and cooling provokes an even more fundamental question, namely that of reciprocal relaxation processes between two *fixed* temperatures. According to the "local equilibrium" paradigm [1] the system relaxes quasi-statically and thus traces the same path along reciprocal processes. We show, however, that this is not the case: heating and cooling are inherently asymmetric and evolve along distinct pathways.

In this work, we use colloidal particles in temperature-modulated optical traps to interrogate relaxation kinetics upon temperature quenches (see Fig. 1), and unveil three fundamental asymmetries between heating and cooling. We experimentally confirm the prediction that heating is faster than cooling in three complementary situations, precisely (i) that heating from a



FIG. 1. Setup for probing the heating-cooling asymmetry. a. Schematic representation of the experiment. A charged dielectric microparticle dispersed in water is confined in a parabolic trap generated by a tightly focused infrared laser. Its effective temperature is controlled by an electric field that shakes the particle, mimicking a thermal bath at a higher temperature than the water. An arbitrary signal generator feeds a noisy signal with a Gaussian-white spectrum into a pair of gold microelectrodes immersed in the liquid, thus producing the required electric field. Therefore, the particle exhibits Brownian motion inside the trap, featuring a Gaussian distribution whose variance is determined by the effective temperature. b. In experiments, we track the evolution of the position distribution upon quenches of the effective thermal bath during heating (red arrows) and cooling (blue arrows). c. Schematic representation of the respective protocols: in the forward protocol, the system is initially prepared at equilibrium with the thermal bath with a temperature higher (T_h) or lower (T_c) than the target (T_w) temperature. T_h and T_c are chosen to be thermodyncamically equidistant from T_w with $T_h > T_w > T_c$. During the backward protocol the system relaxes at the respective thermodyncamically equidistant temperatures T_h and T_c , starting from a common initial condition that is the equilibrium at T_w . In a third situation, only two temperatures are compared, considering the evolution of the system upon heating and cooling between them. In **b** and **c** solid and dashed arrows stand for the forward and backward process, respectively, and thick lines indicate faster evolution than thin ones.

colder temperature towards an intermediate target temperature is faster than cooling from the corresponding TE hotter temperature [15]. Unexpectedly, we also show (ii) that the reverse process, i.e. heating from the intermediate temperature to a hotter temperature is faster than cooling to the corresponding TE colder temperature. Most surprisingly, we show (iii) that between a fixed pair of temperatures, heating is faster than the reciprocal cooling. In all cases, we provide mathematical proofs that establish these asymmetries as a general feature of systems with (at least locally) quadratic energy landscapes.

A key result is that the production of entropy within the system during heating is more efficient than heat dissipation during cooling. Asymmetries (ii) and (iii) further imply that the microscopic relaxation paths during heating and cooling are distinct. Moreover, whereas a system prepared at TE temperatures is by construction equally far from equilibrium in terms of free energy, we show that the colder system is in fact statistically farther from equilibrium and yet heating from said colder temperature is faster. Developing a new framework we coin "thermal kinematics" we explain the asymmetry by means of the propagation in the space of probability distributions, which is intrinsically faster during heating.

Heating and cooling at thermodynamically equidistant conditions

Thermal relaxation kinetics beyond the "local equilibrium" regime can be quantified within the framework of Stochastic Thermodynamics [18–20] which requires the knowledge of statistics of all slow degrees of freedom. In the present work, where we use a colloidal particle with a diameter of 1 μ m in a tightly focused laser (see Fig. 1), the overdamped regime ensures that only the position has to be analyzed [21–23]. Due to the symmetry of the tweezers setup, it suffices to follow a single coordinate of the particle as a function of time which we denote by x_t . We consider two different initial conditions. By the nature of the setup (see Fig. 1) x_t is initially in equilibrium in the optical potential U(x) at either the "hot", T_h , or "cold", T_c , temperature, respectively, with a probability density $P_{eq}^j(x) = e^{(F_j - U(x))/k_B T_j}$ where $F_j \equiv -k_B T_j \ln \int_{-\infty}^{\infty} e^{-U(x)/k_B T_j} dx$ is the equilibrium free energy at temperature T_j . In the following, equilibrium probability densities are denoted by $P_{eq}^j(x)$, where j = h, w, c refers to the bath temperature T_j . Observables with both, subscript and superscript i, f = h, w, c, for example A_i^f , denote transient observables where the subscript refers to the initial and the superscript to the target state. The state of the system at any time is fully specified by, $P_i^f(x, t)$, the probability density of the particle's position at time t.

We first focus on the forward protocol where the relaxation occurs at the "warm" temperature T_w and i = h, c. The dynamics is ergodic and therefore $P_i^w(x, t)$ relaxes towards $P_{eq}^w(x)$. We use $\langle \ldots \rangle_i^w$ to denote averages over $P_i^w(x,t)$ and quantify the instantaneous displacement from the equilibrium distribution $P_{eq}^w(x)$ by means of the generalized excess free energy given by $[15, 24, 25] \mathcal{D}_{i}^{w}(t) = \langle U(x) \rangle_{i}^{w} - k_{\rm B} T_{w} \langle \ln P_{i}^{w}(x, t) \rangle_{i}^{w} - F_{w} =$ $k_{\rm B}T_w D[P_i^w(x,t)||P_{\rm eq}^w(x)]$ for i = h, c, where D[P||Q] = $\int P \ln(P/Q) dx$ is the relative entropy between the probability distributions P and Q. Temperatures T_h and T_c are said to be TE from T_w when the initial excess free energies are equal, i.e., $\mathcal{D}_h^w(0) = \mathcal{D}_c^w(0)$ [15]. The unexpected prediction was made in Ref. [15] that $\mathcal{D}_c^w(t) < \mathcal{D}_h^w(t)$ at all times t > 0. That is, the system heats up to the temperature of its surroundings faster than it cools down. Albeit an asymmetric relaxation is counter-intuitive, our experiments quantitatively corroborate this prediction to be true, see Fig. 2.

What may be even more surprising, heating also turns out to be faster along the reversed, backward protocol. That is, we prepare the system to be in equilibrium at the "warm" temperature T_w and track the relaxations at T_h and T_c , respectively. Likewise, we quantify the kinetics via the relative entropy $\mathcal{D}_w^i(t) \equiv k_{\rm B} T_w D[P_w^i(x,t) || P_{\rm eq}^w(x)]$, such that $\mathcal{D}_w^h(t)$ and $\mathcal{D}_w^c(t)$ evolve from zero and asymptotically converge to $\mathcal{D}_w^{h/c}(\infty) = \mathcal{D}_{h/c}^w(0)$. Although $\mathcal{D}_w^i(t)$ sensibly quantifies the departure from $P_{eq}^w(x)$, it is strictly speaking not an excess free energy, in contrast to $\mathcal{D}_i^w(t)$ defined above, because T_w and $P_{eq}^w(x)$ no longer refer to the target equilibrium. We observe in Fig. 2 that $\mathcal{D}_w^h(t) > \mathcal{D}_w^c(t)$ for all times t > 0, i.e. the system heats up to the new equilibrium at T_h faster than it cools back to T_c . This observation is remarkable as it shows that heating is inherently faster than cooling at TE conditions.

To confirm these observations theoretically, we assume that the particle's dynamics evolve in a parabolic potential with stiffness κ , $U(x) = \kappa x^2/2$, according to the overdamped Langevin equation $dx_t = -(\kappa/\gamma)x_t dt + d\xi_t^i$ with friction constant γ given by the Stokes' law $\gamma =$

 $6\pi r\eta$ where η is the viscosity of water. The thermal noise $d\xi_t^i$, where i = h, w, c denotes the temperature of the reservoir, vanishes on average and obeys the Fluctuation-Dissipation Theorem $\langle d\xi_t^i d\xi_{t'}^i \rangle = 2(k_{\rm B}T_i/\gamma)\delta(t-t')dtdt'$. Under these assumptions we determine TE temperatures T_h and $T_c(T_h)$, i.e., we calculate T_c after we arbitrarily set T_h , (see Eq. (S6) in the SM) and $\mathcal{D}_{i/w}^{w/i}(t)$ reads

$$\mathcal{D}_{i/w}^{w/i}(t) = \frac{k_{\rm B} T_w}{2} [\Lambda_{i/w}^{w/i}(t) - 1 - \ln \Lambda_{i/w}^{w/i}(t)], \qquad (1)$$

where $\Lambda_i^w(t) = 1 + (T_i/T_w - 1)e^{-2(\kappa/\gamma)t}$ and $\Lambda_w^i(t) = T_i/T_w + (1 - T_i/T_w)e^{-2(\kappa/\gamma)t}$. We consider $\mathcal{D}_i^w(t)$ during the forward and $\mathcal{D}_w^i(t)$ during the backward protocol. According to Eq. (1), by plotting $\mathcal{D}_{i/w}^{w/i}(t)/k_{\rm B}T_w$ as a function of $\rho = \Lambda_{i/w}^{w/i}(t)$ all data should collapse onto the master curve $f(\rho) = (\rho - 1 - \ln \rho)/2$, which is indeed what we observe in Fig. 2. Having established the validity of the model, we prove (see Theorem 1 in SM) that our observations hold for all TE temperatures and for any κ and γ , i.e.

$$\mathcal{D}_{c}^{w}(t) < \mathcal{D}_{h}^{w}(t) \quad \text{and} \quad \mathcal{D}_{w}^{h}(t) > \mathcal{D}_{w}^{c}(t), \quad \text{for all } 0 < t < \infty$$
(2)

Our observations in Fig. 2 and the inequalities (2) establish rigorously that at TE conditions heating is faster than cooling.

Notwithstanding, these results are still unsatisfactory for two reasons. First, $\mathcal{D}^i_w(t)$, unlike $\mathcal{D}_i^w(t)$, lacks a consistent thermodynamic interpretation and, in particular, is not an excess free en-Second, neither the relative entropy D[P||Q]ergy. nor $\sqrt{D[P||Q]}$ are a true metric; they are not symmetric, $D[P||Q] \neq D[Q||P]$, and do not satisfy triangle inequalities. The latter in particular implies that while a Pythagorean theorem holds (see [26]; see SM for an experimental validation), $D[P_{eq}^{i}(x)||P_{eq}^{w}(x)] \geq$ $D[P_{eq}^{i}(x)||P_{w}^{i}(x,t)] + D[P_{w}^{i}(x,t)||P_{eq}^{w}(x)]$, where we used $P_w^i(x,0) = P_{eq}^i(x)$, the triangle inequality does not, i.e., in general $\sqrt{D[P_{eq}^i(x)||P_{eq}^w(x)]} \leq \sqrt{D[P_{eq}^i(x)||P_w^i(x,t)]} +$ $\sqrt{D[P_w^i(x,t)||P_{eq}^w(x)]}$. As a result, $\mathcal{D}_{i/w}^{w/i}(t)$ does not measure "distance" from equilibrium and $\partial_t \mathcal{D}_{i/w}^{w/i}(t)$ is therefore not a "velocity", which seems to preclude a kinematic description of relaxation. In the following sections, we show that combining Stochastic Thermodynamics with Information Geometry [27] makes it possible to formulate a thermal kinematics.

Towards thermal kinematics Immense progress has been made in recent years in understanding nonequilibrium systems. The discovery of thermodynamic uncertainty relations [28–31], and "speed limits" [26, 27, 32, 33] revealed that the entropy production rate, which

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FIG. 2. Experimental evolution of the generalized excess free energy during heating and cooling at thermodynamically equidistant conditions. Panels a and c correspond to the forward protocol and b and d to the backward counterpart. Thick, red arrows stand for heating while blue, thin arrows represent cooling. a., b. Time evolution of the generalized excess free energy for a characteristic time $\tau_c = \gamma/\kappa = 0.1844(3) \text{ ms}, T_c/T_w = 0.11(1), T_h/T_w = 3.56(1)$. Red circles stand for heating and blue squares stand for cooling. Solid lines correspond to the theoretical predictions without fitting parameters. Insets represent the initial value of the relative entropy $\mathcal{D}_i^w(0)/k_BT_w$ (y-axis) as a function of the temperature (x-axis) on the logarithmic scale. The arrows represent the evolution direction along the master curve $f(\rho) = (\rho - 1 - \ln \rho)/2$. The confidence regions have been estimated by quadratic uncertainty propagation from the standard deviation of the experimental histograms. c., d. Generalized excess free energy $\mathcal{D}_{i/w}^{w/i}(t)/k_BT_w$ as a function of $\Lambda_{i/w}^{w/i}(t)$, along the master curve $f(\rho)$, for several different TE conditions. The corresponding time series are included in the Supplemental Material (Fig. S5).

quantifies irreversible local flows in the system, universally bounds fluctuations and the rate of change, respectively, in a non-equilibrium system. Closely related is the so-called Fisher Information known from Information Geometry, which quantifies how local flows change in time and allows for defining a *statistical distance* [27, 34, 35].

In our context of thermal relaxation, an infinitesimal statistical line element may be defined as follows. Since $D[P_i^f(x, t + dt)||P_i^f(x, t)] = I_i^f(t)dt^2 + \mathcal{O}(dt^3)$ (see SM, Eq. (S16)), where we introduced the Fisher information $I_i^f(t) \equiv \langle (\partial_t \ln P_i^f(x, t))^2 \rangle_i^f$, we can define the line element as $dl \equiv \sqrt{D[P_i^f(x, t + dt)||P_i^f(x, t)]} = \sqrt{I_i^f(t)}dt$ and thus $v_i^f(t) \equiv \sqrt{I_i^f(t)}$ is the instantaneous statistical velocity of the system [27] relaxing from $P_{eq}^i(x)$ at

temperature T_f towards $P_{eq}^f(x)$. The statistical length traced by $P_i^f(x,\tau)$ until time t is $\mathcal{L}_i^f(t) = \int_0^t v_i^f(\tau) d\tau$ and the distance between initial and final states is thus given by $\mathcal{L}_i^f(\infty)$ and does *not* depend on the direction, i.e. $\mathcal{L}_a^b(\infty) = \mathcal{L}_b^a(\infty)$, for two different temperatures T_a and T_b . To establish a kinematic basis for quantifying thermal relaxation kinetics we define the *degree of completion* $\varphi_{i/w}^{w/i}(t) \equiv \mathcal{L}_{i/w}^{w/i}(t)/\mathcal{L}_i^w(\infty)$, which increases monotonically between 0 and 1.

Assuming that the system evolves according to overdamped Langevin dynamics in a parabolic potential, we find (see Sec. A.5 in SM) $\mathcal{L}_{i}^{w}(\infty) = |\ln(T_{i}/T_{w})|/\sqrt{2}$ and

$$\varphi_{i/w}^{w/i}(t) = 1 - \frac{\ln(1 + (T_{i/w}/T_{w/i} - 1)e^{-2(\kappa/\gamma)t})}{\ln(T_{i/w}/T_{w/i})}.$$
 (3)



FIG. 3. Thermal kinematics of heating and cooling processes at thermodynamically equidistant conditions. All data corresponds to the series shown in Fig. 2. As in previous figures, red arrows stand for heating while blue ones represent cooling, solid and dashed arrows refer to forward and backward protocol, respectively, and thicker lines indicate a faster evolution than thin ones. **a.** Initial value of the relative entropy $\mathcal{D}_i^w(0)/k_B T_w$ as a function of the temperature. **b.** Total traversed statistical distance $\mathcal{L}_i^w(\infty) = \mathcal{L}_w^i(\infty) = \mathcal{L}(\infty)$ as a function of the temperature. **c-f** Temporal evolution of the instantaneous statistical velocity $v_i^w(t)$ (**c** and **e**) and the degree of completion $\varphi_i^w(t)$ (**d** and **f**) during the forward (**c** and **d**) and backward (**e** and **f**) protocol. Red circles stand for heating while blue squares correspond to cooling. Solid lines are theoretical predictions without fitting parameters. Confidence regions have been estimated by quadratic uncertainty propagation from the standard deviation of the experimental histograms.

Moreover, we prove (see Theorem 2 in SM) for any pair of TE temperatures T_h, T_c that $\mathcal{L}_c^w(\infty) > \mathcal{L}_h^w(\infty)$ and yet

$$\varphi_c^w(t) > \varphi_h^w(t) \quad \text{and} \quad \varphi_w^h(t) > \varphi_w^c(t) \quad \text{for all } 0 < t < \infty.$$
(4)

That is, the colder system is statistically farther from equilibrium than the hotter system, but nevertheless, heating is faster than cooling. On the one hand, Eq. (4) confirms the asymmetry (2) from a kinematic point of view. On the other hand, it reveals something more striking; during heating, the system traces a longer path in the space of probability distributions but it does so faster. The reason lies in the propagation speed $v_{w/i}^{i/w}(t)$ at short times that is intrinsically larger during heating than during cooling. This speed-up is due to the entropy production in the system during heating being more efficient than heat flow from the system to the environment during cooling (see also [15]). These predictions are fully confirmed by experiments (see Fig. 3). The results show that an initial overshoot in $v_c^w(t)$ and $v_w^h(t)$ ensures that under TE conditions heating is, in both protocols, at all

times faster than cooling according to the inequalities (4). Since both processes relax to the same equilibrium, $v_c^w(t)$ and $v_w^h(t)$ eventually must cross.

Heating between any pair of temperatures is faster than cooling We now take our thermal kinematics approach one step further and consider two arbitrary fixed temperatures $T_1 < T_2$ and observe heating, i.e relaxation at T_2 in a temperature quench from an equilibrium prepared at T_1 , and the reverse cooling, i.e. relaxation at T_1 in a temperature quench from the equilibrium at T_2 . By construction, the distance between initial and final states along the reciprocal processes is the *same*, $\mathcal{L}_2^1(\infty) = \mathcal{L}_1^2(\infty)$. Nevertheless, according to our model, in particular Eqs. (3), we have for any $T_1 < T_2$ (see Theorem 3 in SM) that

$$\varphi_1^2(t) > \varphi_2^1(t) \quad \text{for all} \quad 0 < t < \infty.$$
(5)

That is, between any pair of temperatures heating is faster than cooling, which is a much stronger statement. Notice that it was not possible to make such a statement based on the generalized excess free energy, since in



FIG. 4. Thermal kinematics of heating and cooling between any pair of temperatures. The data shown corresponds to $T_1 = 302(3)$ K and $T_2 = 2753(7)$ K, and a characteristic time $\tau_c = \gamma/\kappa = 0.1844(3)$ ms. a. Instantaneous statistical velocity v(t) as a function of time. b. Degree of completion $\varphi(t)$ as a function of time. Red circles stand for heating, while blue squares correspond to cooling. Solid lines are theoretical predictions without fitting parameters. The confidence regions have been estimated by quadratic uncertainty propagation from the standard deviation of the experimental histograms.

this case, the description of the backward process lacked physical consistency. This result highlights that heating and cooling are inherently asymmetric processes and that this is neither limited to the TE setting nor to strong quenches. The asymmetry (5) is fully corroborated by experiments (see Fig. 4). As before, it emerges due to an initial overshoot in $v_1^2(t)$. However, in this case, the difference in velocities implies that the pathway taken during heating is fundamentally different from the pathway followed during the reciprocal cooling process.

Near equilibrium, heating and cooling become symmetric Finally, we show that for quenches near equilibrium heating and cooling are indeed almost symmetric, in agreement with linear non-equilibrium thermodynamics [1]. First, for $T_+ = (1 + \varepsilon)T_w$ with $0 < \varepsilon \ll 1$, we find that $T_-(T_+) = (1 - \varepsilon + \mathcal{O}(\varepsilon^2))T_w$ (see Eq. (S33) in SM), i.e., near equilibrium, TE temperatures are approximately equidistant from the ambient temperature T_w . Second, we find in this limit (see SM, Corollary 4) that $\varphi_w^i(t) = \varphi_i^w(t) = 1 - e^{-2(\kappa/\gamma)t} + \mathcal{O}(\varepsilon)$ and

$$\varphi_w^c(t) = \varphi_w^h(t) + \mathcal{O}(\varepsilon) \text{ and } \varphi_h^w(t) = \varphi_c^w(t) + \mathcal{O}(\varepsilon).$$
 (6)

That is, for near-equilibrium quenches heating and cooling are approximately symmetric and the asymmetry is thus a genuinely far-from-equilibrium phenomenon, as claimed.

Discussion Detailed experiments on colloidal particles corroborated by analytical theory revealed a fundamental asymmetry in thermal relaxation upon a rapid change of temperature; for thermodynamically equidistant temperature quenches as well as between two fixed temperatures, heating is always faster than cooling. Moreover, the microscopic pathways followed by a system during heating and cooling, respectively, are fundamentally different. Therefore, except very near to thermodynamic equilibrium, thermal relaxation, in general, does *not* evolve quasistatically through quasi-equilibria even for systems with a single energy minimum. We, therefore, witness a breakdown of the "near equilibrium" paradigm of classical non-equilibrium thermodynamics [1].

Namely, when the system is brought rapidly out of equilibrium, such as upon a temperature quench, the probability density of the system cannot follow the temperature change quasi-statically and a lag develops between the instantaneous $P_i^w(x,t)$ and the new equilibrium $P_{eq}^w(x)$ [25]. This lag, which here corresponds to $D[P_i^w(x,t)||P_{eq}^w(x)]$, is nominally smaller during heating than during cooling. This is so because for short times heating essentially corresponds to a free expansion [15], which is materialized as an overshoot of statistical velocity and is characterized by a smaller dissipated work. The latter in turn bounds from above the maximal lag that can develop [36]. Initial free expansion during heating also explains the faster departure from the initial equilibrium within the backward protocol, as well as for heating and cooling between any two fixed temperatures.

Our work further underscores that there is a fundamental difference between equidistant temperatures, thermodynamically equidistant temperatures, and kinematically equidistant temperatures. The existence of a zero temperature and the $e^{-1/T}$ -dependence of Boltzmann-Gibbs equilibrium statistics readily imply that raising and lowering the temperature by the same amount pushes the system differently far from equilibrium. However, even when temperatures are chosen to be thermodynamically equidistant, the colder system is kinematically farther from equilibrium than the hotter one, and yet it reaches equilibrium faster.

Thermal relaxation, therefore, seems to be much more complex than originally thought and our results only scratch at the surface. Relaxation in systems with multiple energy minima [3, 8, 15, 16], time-dependent potentials [22, 23, 37–40], driven relaxation processes [41, 42], and in the presence of time-irreversible, detailedbalance violating dynamics [31, 43–45] still remains poorly understood, and calls for a systematic analysis through the lens of thermal kinematics.

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