On the Relation between Entropy and Kinetics

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Thermodynamic and kinetic properties of materials are usually thought of as unconnected. Relating them is a conceptual challenge with many practical benefits. Here, based on first principles, we derive a rigorous inequality relating entropy and diffusion coefficients. It is universal and applicable to equilibrium as well as non-equilibrium steady states. The relation can be used to obtain useful bounds for the diffusion coefficient (normal or anomalous) from the calculated thermodynamic entropy or, conversely, to estimate the entropy based on measured diffusion coefficients. We demonstrate the validity and usefulness of the relation through several examples. We discuss its broad range of applications, in particular, for non-equilibrium systems.

Materials are characterized by static thermodynamic properties (heat capacity, compressibility) and kinetic properties (viscosity, conductivity, diffusion coefficient). Indeed, to specify values of thermodynamic coefficients it is enough to define the units of energy and length, whereas values of kinetic coefficients require also a unit of time. It will be surprising, therefore, if a general relation is found between two properties belonging to these separate categories.

Such a relation would be very useful, because the abilities to calculate or measure these properties may differ significantly. On the one hand, the theory of materials in thermodynamic equilibrium is far more developed than the one for dynamical transport processes. On the other hand, in many cases, transport coefficients are easier to measure. For instance, consider a protein moving randomly inside the crowded environment of the cytoplasm. The entropy of its positions can be calculated theoretically, while entropy estimation from experimental data is often unreliable [11]. On the other hand, its diffusion coefficient can be directly measured by single-molecule tagging and tracking, while a theoretical prediction of the long-time diffusion coefficient in such a complex environment should be much harder to achieve. Clearly, the ability to infer one property from the other on general rigorous grounds is of tremendous benefit.

In the present work we derive and demonstrate a rigorous relation between a thermodynamic variable, the entropy, and a kinetic coefficient, the diffusion coefficient. The relation, in its most generality, is an inequality. It becomes an equality under specified assumptions.

Background. Several general relations between thermodynamic and kinetic properties were proposed over the years based on the equilibrium theory of fluids. The Adams-Gibbs relation between the entropy of a glass-forming liquid and its relaxation time [4] has inspired later theories of the glass transition [5,6]. Rosenfeld [7,8] and later, independently, Dzugutov [9] proposed a phenomenological relation between the entropy per particle of a fluid, \( s \), and the single-particle diffusion coefficient, \( D \). It reads

\[
\frac{D}{(v l)} = A \exp[b(s - s^{id})],
\]

where \( l \propto \rho^{-1/3} \) is the mean inter-particle distance (\( \rho \) being the mean density), \( v \propto T^{1/2} \) is the thermal velocity (\( T \) being the temperature), \( s^{id} \) is the entropy per particle of the ideal gas, and \( A \) and \( b \) are system-dependent phenomenological parameters to be found \textit{ad hoc} by experiment or simulation. Outside the realm of fluids, similar entropy-diffusion relations were obtained for the specific case of a single particle diffusing in a random external potential [10,11].

The phenomenological entropy-diffusion relation has been tested extensively in the last two decades against experiments and simulations. It has been used also in industrial applications to indirectly infer transport properties. For a recent review and literature survey, see Ref. [12]. The large variety of systems to which the relation has been applied includes simple and super-cooled liquids (e.g., Refs. [13,14]), electrolytes [16], ionic liquids [17], adsorbed gases [18], nano-confined liquids [19], hydration layers around ions and proteins [20,21], colloidal monolayers [22–25] and colloids in complex environments [26], active particles [27], rheology of glasses [28], plasticity of amorphous solids [29], transport coefficients of refrigerants [30], viscosity of oils [31], effect of model resolution on molecular dynamics simulations [32], and even transport properties of planetary cores [33].

The success of the phenomenological entropy-diffusion relation has been inconsistent, yielding good fits in some systems and poor ones in others. This indicates that the relation is neither exact nor universal [12]. The relation’s physical origin, and thus our ability to account for its successes and failures, has not been resolved; in Rosenfeld’s words, it is a “semi-empirical ‘universal’ corresponding-state relationship” [8]. In several cases the general scaling suggested by the relation has been confirmed, but not with the exponential function [12]. A theory based on a restrictive assumption concerning the inter-particle interaction has been developed in Refs. [12,34,35]. Overall,
Microscopic Dynamics

\[ \text{MSD} = 2dDt \]

\[ \text{SS} = -\int \tilde{P} \ln \tilde{P} dX \]

Steady State

\[ S = -\int \tilde{P} \ln \tilde{P} dX \]

\[ \text{MSD} = 2dDt \]

\[ \text{Ergodicity} \]

FIG. 1. Derivation outline. We assume the existence of a finite relaxation time, \( \tau \). For \( t \ll \tau \) (left) the particles follow microscopic dynamics (e.g., moving ballistically). For \( t > \tau \) (right) the system reaches a steady state. Two equivalent descriptions are considered. In the first (top row), particles are treated as indistinguishable. Their \( \tau \)-separated configurations are independent and drawn from the steady-state distribution \( \tilde{P}(X) \), with entropy \( S \). In the second description (bottom row), particles are treated as distinguishable (identifiable). Over time \( t > \tau \) each particle experiences many collisions, which (by the central limit theorem, CLT) leads to an effective diffusion with mean-squared displacement \( 2dDt \). Comparing the two statistics leads to a relation between the steady-state entropy (top right) and diffusion (bottom right).

the widespread use of the entropy-diffusion relation, even if it is empirical and inaccurate, attests to the far-reaching importance of relating thermodynamic and transport properties.

Below, we derive a relation between entropy and the diffusion coefficient based on first principles. It is an exact (under two commonly valid assumptions) universal inequality with no phenomenological parameters. Moreover, it is not restricted to materials at equilibrium. We first outline the derivation and present the central results, deferring technical details to the Supplementary Material (SM). We then proceed to give several examples demonstrating different aspects of the relation.

Derivation outline. We consider a material at steady state, consisting of \( N \) identical and indistinguishable particles whose microscopic configurations are given by \( X = \{x_1, x_2, \ldots, x_N\} \). The state \( x \) of each particle may include its position, orientation, velocity, etc. The many-particle configuration \( X \) changes with time \( t \) according to the case-specific microscopic laws of motion, defining a trajectory \( X(t) \) between \( t = 0 \) and \( t = t_{\text{obs}} \), the observation time. Our main assumption, valid for the vast majority of materials, is that the material has a finite relaxation time, \( \tau \). For times \( t > \tau \), the particle configurations are mixed, and the material reaches steady state. We discretize the trajectory \( X(t) \) into \( K + 1 \) consecutive 'snapshots' separated by time intervals \( \tau \), \( X^k = X(k\tau) \), \( k = 0, 1, \ldots, K = t_{\text{obs}}/\tau \). To relate the steady behavior to the kinetic one, we examine the discretized trajectories from two equivalent perspectives, regarding the particles as either indistinguishable or distinguishable (identifiable). Utilizing this distinction is at the core of the theory. See Fig. 1. We denote the probability to obtain a certain sequence of configurations by \( \tilde{P}_r(\{X^k\}) \) for indistinguishable particles, and by \( P_r(\{X^k\}) \) for identifiable ones.

From the first perspective (top row of Fig. 1), we consider configurations of the \( N \) indistinguishable particles. Over time intervals larger than \( \tau \), sufficiently many randomizing events (e.g., collisions) occur to mix the particles. Hence, the configurations at different instances along the discretized trajectory are independent, drawn each from the same steady-state probability distribution for indistinguishable particles, \( \tilde{P}(X) \). This implies the decomposition of \( \tilde{P}_r(X(t)) \) into a product of independent probabilities, \( \tilde{P}_r(\{X^k\}) = \tilde{P}(X^0) \times \tilde{P}(X^1) \times \cdots \times \tilde{P}(X^K) \). The thermodynamic entropy is the information content of \( \tilde{P}(X) \) [36], \( S = -\int dX \tilde{P}(X) \ln \tilde{P}(X) \).

From the second perspective (bottom row of Fig. 1), we treat particles as identifiable and follow their individual
dynamics. The configurations of the distinct particles, separated by time intervals $\tau$, are typically correlated, as each particle has traversed a negligible part of the total available space. However, the particle configuration at the end of a relaxation interval $\tau$ depends only on the configuration at the beginning of the interval and not on those at prior intervals. In other words, the sequence of configurations has no memory (a stationary Markov process). We denote the Markovian probability to change from configuration $X^{k-1}$ to configuration $X^k$ during time $\tau$ (also called the propagator) as $W_\tau(X^k|X^{k-1})$. Our second assumption is that the system is translation-invariant (on the time scale of $\tau$ and longer). This implies spatial homogeneity of the material in the case of positions, isotropy in the case of orientations, and Galilean invariance in the case of velocities. Under this assumption, $W_\tau$ depends only on the difference $\Delta X = X^k - X^{k-1}$ between the two configurations. This enables another decomposition of the trajectory probability, $Pr[X(t)] = P(X^0) \times W_\tau(\Delta X^1) \times \cdots \times W_\tau(\Delta X^K)$, where $P(X) = \tilde{P}(X)/N!$ is the steady-state distribution of configurations for indistinguishable particles.

Thus, we have decomposed the indistinguishable trajectory distribution $\tilde{P}_r[\{X^k\}]$ into steady-state distributions $\tilde{P}(X^k)$, and the identifiable trajectory distribution $Pr[\{X^k\}]$ into kinetic distributions $W_r(\Delta X^k)$. To relate these two results to entropy we define the following integral over all possible discretized trajectories:

$$H = -\frac{1}{K} \int d\{X^k\} Pr[\{X^k\}] \ln(Pr[\{X^k\}]).$$

(1)

When the decomposition of $Pr$ is substituted in Eq. (1), the integral becomes

$$H = (S + \ln N!)/K - \int d\Delta X W_r(\Delta X) \ln W_r(\Delta X),$$

see SM.

We now need a relation between the trajectory distributions $Pr$ and $\tilde{P}_r$. Here lies the main complication, because indistinguishable trajectories correspond to many possible permutations of identifiable ones. However, not all permutations are equally likely. For example, the probability that particles which start far apart will switch positions during time $\tau$ is negligibly small, whereas colliding particles may permute with high probability.

First, we consider an extreme case, which sets a strict lower bound on $H$, ignoring all the possible exchanges. Following this “undercounting”, we get $Pr \geq N! Pr$. Substituting the decomposition of $Pr$ in Eq. (1), we obtain $H \geq (S + \ln N!)/K + S$, where $S$ is the thermodynamic entropy defined above. Comparing the two expressions for $H$, we get

$$S \leq -\int d\Delta X W_r(\Delta X) \ln W_r(\Delta X).$$

(2)

Unfortunately, Eq. (2) is not very useful as is, because it depends on the propagator of the complete configurations of all $N$ particles, which is rarely known. Instead, one is typically interested in the transport properties of a much smaller number of particles, in particular, the effective diffusion coefficient of a single particle in the presence of the others. We notice that, if the particles are independent, then the propagator could be decomposed into single-particle ones, $W_r(\Delta X) = w_r(\Delta x_1) \times w_r(\Delta x_2) \times \cdots \times w_r(\Delta x_N)$, leading to $H = (S + \ln N!)/K - N \int d\Delta x w_r(\Delta x) \ln w_r(\Delta x)$. If particles are dependent, this relation sets another bound on $H$ (see SM). Overall, Eq. (2) becomes a bound on the entropy per particle, $s = S/N$:

$$s \leq -\int d\Delta x w_r(\Delta x) \ln w_r(\Delta x).$$

(3)

This rigorous inequality, which applies in general, is our first exact and universal relation between the thermodynamic entropy and a kinetic property (the single-particle propagator).

In most materials, due to the central limit theorem (CLT), the single-particle propagator converges to a Gaussian over intervals $\Delta t \geq \tau$, $w_{\Delta t}(\Delta x) = (4\pi D \Delta t)^{-d/2} \exp[-|\Delta x|^2/(4D \Delta t)]$, where $d$ is the number of dimensions. This limiting propagator describes random Brownian motion of a particle with diffusion coefficient $D$. Substitution into Eq. (3) gives

$$D \tau \geq (D\tau)^{\circ} \exp[(2/d) (s - s^\circ)],$$

(4a)

where the superscript $^{\circ\circ}$ denotes values for a known reference system (for which the bound is tighter). This is our first useful relation.

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2 The phase space for identifiable particles is $N!$ times larger than for indistinguishable ones, such that the integration of both sides over the larger space gives 1; see SM.

3 If the time discretization were made indefinitely fine (rather than by non-zero $\tau$-intervals), $H$ would quantify the complete information contained in the distribution of trajectories $Pr[X(t)]$ [39]. In this limit, $H/\tau$ is known as the Kolmogorov-Sinai entropy rate [37, 38]. Here we are not concerned with this limit.
While the bound \(^{4}\) always holds, we wish to improve it. We need to evaluate the contribution of the neglected permutations when relating indistinguishable and identifiable trajectories. Taking a ‘mean-field’ approach, we assume that during each time step \(\tau\), every particle can be exchanged with \(z\) nearby particles. Hence, \(\Pr \approx N! z^{N-K} \Pr\). As a result, Eq. (2) is replaced by

\[
S_z \text{particle has a ‘sphere of influence’ of radius } \sim \text{nearby particles with which a particle is likely to interchange paths during } \tau \text{. Estimating } z, \text{ the average number of nearby particles with which a particle is likely to inter-change paths during } \tau, \text{ requires kinetic considerations. Each particle has a ‘sphere of influence’ of radius } \sim (D_s \tau)^{1/2}, \text{ where } D_s \text{ is a short-time diffusion coefficient}^{39}. \text{ Therefore, } z \sim \rho(D_s \tau)^{d/2}. \text{ Repeating the same arguments as above (see SM), we arrive at our second useful relation,}
\]

\[
D \geq D_s \exp[(2/d) (s - s^{id})], \quad (4b)
\]

where \(s^{id} = -\ln \rho\) is the entropy per particle of the ideal gas. Equation \(^{4b}\) is not a rigorous bound because of the mean-field approximation involved; yet, under this assumption, it should provide an improved bound compared to Eq. \(^{4a}\).

Going back to the derivation, we note that Eq. (3) could be applied to any single-particle propagator \(w_r(\Delta X)\), not only the Gaussian one. For example, consider anomalous diffusion where the particle mean-squared displacement (MSD, the variance of \(\Delta X\)) is equal to \(d F\tau^\alpha\), with a ‘generalized diffusion coefficient’ \(F\). A modified derivation (see SM) leads to a generalized relation

\[
F \tau^\alpha \geq (F \tau^\alpha)^\rho \exp[(2/d) (s - s^\rho)]. \quad (5)
\]

Both inequalities \(^{4a}\) and \(^{5}\) become equalities when trajectories do not mix and the dynamics is well represented by single-particle diffusion.

Equations \(^{4}\) are reminiscent of the phenomenological entropy-diffusion relation proposed by Rosenfeld \(^{7,8}\) and Dzugutov \(^{9}\), with several crucial differences. (a) The relation is an inequality in general. (b) Since the derivation never assumed thermodynamic equilibrium, it is just as valid for materials at non-equilibrium steady states (e.g., fluids in steady flow or active matter at steady state). (c) We find an explicit value for the coefficient \(b, b = 2/d\). (d) In addition to the diffusion coefficient, the rigorous relations \(^{4a}\) and \(^{5}\) depend also on the relaxation time \(\tau\). In certain systems \(\tau\) is easily obtained, while in others it may require a separate measurement as shown below.

We now demonstrate the validity and usefulness of the relations in several examples.

**Previously tested examples.** Quite a few tests of the entropy-diffusion relation gave values of \(b\) close to or bounded by \(2/d\), as predicted by Eqs. \(^{4}\). Numerical studies of a 3D hard-sphere gas gave \(b = 0.65\) \(^{8}\). Molecular dynamics (MD) simulations of liquid metals gave \(b = 0.67-0.70\) \(^{33,31}\). Experiments on various colloidal monolayers \((d = 2)\) gave values bounded from above by \(b = 1\) \(^{22,25}\), and at least twice as high \(b\) values for the rotational diffusion coefficient, as expected for its lower dimension \((d = 1)\) \(^{24}\). Still, in other cases \(b\) was found larger than \(2/d\). Notably, recent extensive MD simulations of Lennard-Jones fluids gave \(b = 0.751\) \(^{42}\) (not far from Rosenfeld’s original report of \(b = 0.788\) \(^{7}\)).

The discrepancies between the phenomenological entropy-diffusion relation and observations can now be explained. First, the relation in general should be an inequality, not an equality. Indeed, the entropy-diffusion relation was more successful in cases where our bounds are expected to be tight — less correlated fluids (suspensions of hard spheres, simple molecular liquids, short-chain polymer melts), as compared to more correlated ones (liquids with hydrogen bonds such as water \(^{14}\) and methanol \(^{23}\), long-chain entangled polymer melts \(^{44}\)). Second, the relaxation time \(\tau\) in Eq. \(^{4a}\) and the short-time diffusion coefficient \(D_s\) in Eq. \(^{4b}\) contain additional dependencies on system parameters such as density and temperature. (This effect is seen in Fig. 2B below, and also in Fig. S1, where \(\tau\) has been underestimated.) Similarly, only if the short-time diffusion obeys \(D_s \propto \rho^{1/d} T^{1/2}\) does the bound of Eq. \(^{4b}\) coincide with the phenomenological entropy-diffusion relation. Any other dependence on \(\rho\) or \(T\) will be manifested as a deviation from that relation. The same explanation holds for the cases where \(b\) was found larger than \(2/d\).

**Example: Homogenized diffusion.** External potentials applied to diffusing particles typically break the assumption of homogeneity. However, under a periodic or random potential, after the particles have traversed a sufficiently long distance, their motions are accurately described by an effective (‘homogenized’) diffusion \(^{45}\). Calculations of the homogenized \(D\) even for a single particle in random \(^{10,11}\) and periodic \(^{45}\) potentials require elaborate mathematical analyses. In certain cases Eqs. \(^{4}\) offer a far simpler alternative. Indeed, for a particle in a random potential the elaborate analysis in Ref. \(^{10}\) arrives at a relation equivalent to Eq. \(^{4b}\). For a particle in a one-dimensional periodic potential, the known analytical result for the homogenized \(D\) \(^{45}\) agrees with Eq. \(^{4a}\). Moreover, Eq. \(^{4a}\) is found to be an equality for weak to moderate potentials. See SM for more details and a quantitative comparison.

**Example: Anomalous diffusion in a single file.** Single-file diffusion is relevant to a large variety of transport processes \(^{46}\), e.g., of molecules through nanoporous materials and membrane channels, of cargo along microtubules.

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\(^{4}\) The relation does not hold for anomalous-diffusion processes which do not have a finite relaxation time, e.g., non-ergodic sub-diffusions \(^{19}\).
in the cell, and of proteins along DNA or RNA. The model consists of \( N \) rigid particles of diameter \( a \), restricted to move along a line of length \( L \) without bypassing each other. An isolated particle would perform normal Brownian motion with diffusion coefficient \( D_a \). However, when put in a single file with others, its diffusion is strongly suppressed and becomes anomalous. The single-file constraint prevents mixing of particle trajectories (i.e., \( z = 1 \) exactly), suggesting that the bound in Eq. (5) should be tight. The exact solution of this problem \([47, 48]\) yields sub-diffusion with MSD(t) = \( F t^{1/2} \), where \( F = a(D_a/\pi)^{1/2}(1-\phi)/\phi \), where \( \phi = Na/L \) is the line fraction occupied by the particles. This \( \phi \)-dependence can be easily reproduced using Eq. (5). The total entropy per particle is \( s = \ln[(1-\phi)/\phi] \), and the relaxation time is proportional to the time between encounters of neighboring particles, \( \tau \propto l^2/D_a \), where \( l = a(\phi^{-1}-1) \) is the mean distance between neighbors. Substituting into Eq. (5) (with \( d = 1 \)), we obtain \( F \propto aD_s^{1/2}(1-\phi)/\phi \). Equation (5) turns out to be an equality in this case, despite the fact that the particle trajectories are dependent.

Example: Single-file diffusion in a periodic potential. To the best of our knowledge, there is no analytical result for the homogenized diffusion coefficient in this case \([49, 50]\). Here, point-like particles (\( a \to 0 \)) perform random walks without bypassing each other, under a potential with amplitude \( E \) (in units of \( k_B T \)) and periodicity \( \lambda \), \( U(x) = E [1 - \cos(2\pi x/\lambda)] \). This describes, for example, single-file diffusion occurring over a periodic (e.g., crystalline) substrate. The entropy per particle is \( s = -\ln \rho + f(E) \), where the function \( f(E) \) is given in the SM. Using Eq. (5), we predict that \( F \propto \rho^{1/2} = Ae^{2s(E)/\rho^2} \), where \( A \) is a reference constant. To verify this new analytical result, we performed Langevin Dynamics simulations with periodic boundary conditions for various particle densities \( \rho \) (the number of particles per wavelength \( \lambda \) and potential strengths \( E \)). We measured the MSD and extracted the homogenized diffusion coefficient \( F \). Obtaining the relaxation time \( \tau \) is intricate in this example because of its dependence on both \( \rho \) and \( E \). We assess it numerically from the crossover time between normal and anomalous diffusion. See SM. Figure 2A shows \( F\tau^\alpha \) as a function of \( \rho \) for fixed \( E = 0, 0.2, 1 \). The prediction \( F\tau^\alpha \propto \rho^{-2} \) with \( \alpha = 1/2 \) is verified. In Fig. 2B we plot \( F\tau^\alpha \) as a function of \( E \) for fixed \( \rho = 1, 2, 3 \). The prediction works well for small values of \( E \) but gets further from the numerical results as the potential strength is increased. This is due to an underestimation of \( \tau \) for large \( E \) (see SM). Alternatively, one can use these results together with the analytical expression to infer the relaxation time as a function of \( \rho \) and \( E \).

Example: Momentum entropy. Finally, to demonstrate how general these results are, we apply them also to the entropy associated with the particles’ momenta. For momenta, the decomposition into single-particle dynamics is exact. When the momentum propagator is used in Eq. (3), \( Dr \) appearing in Eq. (4a) is replaced by the mean-square momentum. The latter is proportional to the mean kinetic energy, which in turn is proportional to the temperature \( T \). Equation (4a) for \( d = 3 \) then gives \( e^{s/3} \propto T \), in line with the known result from classical thermodynamics, \( s = \ln T^{3/2} + \text{const} \).

Summary. Equation (2) provides rigorous evidence that static properties of materials leave a generic mark on their dynamics. It offers a theoretical framework for relating thermodynamic and kinetic properties, even out of equilibrium. The only assumptions are the existence of a finite relaxation time and translation invariance. Thus, quite remarkably, quantitative predictions concerning kinetic coefficients could be obtained without a kinetic theory.

Equation (5) makes the general framework more applicable as it relates the entropy with the accessible dynamics of individual particles. We have used it to obtain relations between the entropy and the (generalized) long-time
diffusion, Eqs. (4) and (5). With additional knowledge of the material’s relaxation time (Eqs. (4a) and (5)) or short-time diffusion coefficient (Eq. (4b)), the relations can be used to obtain useful bounds for the long-time diffusion coefficient from entropy, and vice versa, as demonstrated in the examples above. Our results point at the main origins for the successes and failures of the widely used phenomenological entropy-diffusion relation. Indeed, the violation of the rigorous bound derived here might serve as an indicator of anomalous behaviors such as ergodicity breaking and aging [24].

The range of possible applications of Eqs. (4) and (5) is vast. Here are specific examples. The case of diffusion under an external potential analyzed above clearly shows how the relations could be used to infer binding parameters from measured diffusion. From the opposite direction, entropy is often fairly easy to find from equilibrium thermodynamics, and efficient methods of entropy estimation have been developed for non-equilibrium steady states [1, 3, 51–53]. Another example is the protein in a crowded environment, mentioned in the introduction. If the environment is regarded as an arrangement of stationary, rigid obstacles, the protein’s positional entropy is simply related to the free volume, $s = -\ln(1 - \phi)$, with $\phi$ the volume fraction of obstacles. This readily gives the $\phi$-dependence of the protein’s long-time kinetics. Lastly, out of equilibrium, the relation can be used to obtain the steady-state transport properties of active matter and collective motions in nature.

The theory can be extended to treat many-particle correlated diffusion and memory effects. It will be particularly important to derive similar relations for kinetic coefficients other than the diffusion coefficient, such as the heat conductivity and viscosity. This new theoretical framework, utilizing the distinction between the fast relaxation of indistinguishable particle configurations and the coarse-grained dynamics of identifiable particles, will hopefully be instrumental in the progress toward a consistent general theory of non-equilibrium thermodynamics.

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SUPPLEMENTARY MATERIALS

Supplementary text: detailed derivation and numerical methods
Figs. S1 to S4
References [54–57]

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ON THE RELATION BETWEEN ENTROPY AND KINETICS: SUPPLEMENTARY MATERIAL

Here we provide further technical information, which was not included in the main text. Section I details the analytical derivation of our central results. In Sec. II we give further details regarding the diffusion of a single particle under the effect of random or periodic potentials. In Sec. III we provide details on the numerical and analytical study of single-file diffusion under a periodic potential.

I. DETAILED DERIVATION

A. Steady-State Configurations of Indistinguishable Particles

We consider an ensemble of \( N \) identical and indistinguishable particles at steady state. We denote their microstates by \( \mathbf{X} = (x_1, \ldots, x_N) \). \( x \) may denote any single-particle variable, e.g., position, velocity or orientation. Since the system is at a steady state, its complete statistical-thermodynamical information is expressed by the steady-state \( N \)-particle probability density function (PDF), \( P(X) \). We denote the phase space (the support of \( P(X) \)) by \( \Phi = \Omega^N \) (with cardinality \( |\Omega| = \int \! dx \)). The particles were assumed identical, thus \( P \) remains invariant under any particle permutation, \( P(\sigma \mathbf{X}) = P(\mathbf{X}) \), where \( \sigma \) is an operator within the permutation group \( \mathcal{P} \); \( \sigma \mathbf{X} = (x_{m_1}, \ldots, x_{m_N}) \), with \( \{m_1, \ldots, m_N\} \) being the corresponding scrambled indices.

In order to explicitly take into account the indistinguishability of particles, it will be convenient to define a reduced (quotient) phase space, denoted \( \tilde{\Phi} \), in which every indistinguishable configuration is counted once. In other words, \( \mathbf{X} \) and all other permutations \( \sigma \mathbf{X} \) (for any \( \sigma \in \mathcal{P} \)) are identified as the same configuration. This cuts the available phase space \( \Phi \) by a factor of \( N! \). Without loss of generality, we still denote configurations in \( \tilde{\Phi} \) as \( \mathbf{X} \). The PDF of indistinguishable configurations is denoted \( \tilde{P}(\mathbf{X}) \). It is related to the PDF of distinguishable configurations \( P(\mathbf{X}) \) through a sum over all possible permutations,

\[
\tilde{P}(\mathbf{X}) = \sum_{\sigma \in \mathcal{P}} P(\sigma \mathbf{X}) = N! P(\mathbf{X}),
\]

where we used \( P \)'s invariance to particle permutation. Thus, while \( \int_{\tilde{\Phi}} \! d\mathbf{X} P(\mathbf{X}) = 1 \), the normalization of \( \tilde{P} \) is scaled,

\[
\int_{\tilde{\Phi}} \! d\mathbf{X} \tilde{P}(\mathbf{X}) = \frac{1}{N!} \int_{\tilde{\Phi}} \! d\mathbf{X} P(\mathbf{X}) = 1.
\]

The indistinguishable PDF \( \tilde{P} \) yields the thermodynamic entropy (the information content of the \( N \) indistinguishable particles' configuration [36]), which must account for the indistinguishable statistics,

\[
S = -\int_{\tilde{\Phi}} \! d\mathbf{X} \tilde{P}(\mathbf{X}) \ln(v^N \tilde{P}(\mathbf{X})) = -\frac{1}{N!} \int_{\Phi} \! d\mathbf{X} N! P(\mathbf{X}) \ln(v^N N! P(\mathbf{X})).
\]

\[
= -\int_{\Phi} \! d\mathbf{X} P(\mathbf{X}) \ln(v^N N! P(\mathbf{X})) = -\int_{\Phi} \! d\mathbf{X} P(\mathbf{X}) \ln(v^N P(\mathbf{X})) \ln N!
\]

Thus, \( S \) is the “usual” Shannon entropy entropy in the phase-space \( \tilde{\Phi} \), up to the entropy of permutations. Note that all continuous entropies are physically meaningful up to some additive reference constant, which is extensive in \( N \). The constant depends on the physical units and, if used, the discretization of phase space. We account for this arbitrary constant by including \( v^N \), where \( v \) bears the units of phase-space volume. Overall, the argument within the logarithm in Eq. (S3) is unitless.

In order to obtain our central results, we wish to relate Eq. (S3) to the asymptotic (long-time) dynamics occurring within that steady state. Consider the underlying microscopic trajectories \( \mathbf{X}(t) \) between times \( t = 0 \) and \( t = t_{\text{obs}} \). We divide the time interval \( t_{\text{obs}} \) into \( K \) steps of duration \( \Delta t = t_{\text{obs}}/K \) each, and denote \( \mathbf{X}^k \equiv \mathbf{X}(t = k\Delta t), k = 0, \ldots, K \), which is a collection of “consecutive snapshots” in that process. Let \( \tilde{P}([\mathbf{X}^k]) \) denote the PDF of observing the discrete sequence of \( K \) indistinguishable \( N \)-particle states \( \{\mathbf{X}^k\} \), defined over \( \tilde{\Phi}^{K+1} \) (i.e., how a collection of “gray points” evolves in time. See Fig. 1 of the main text).

A key assumption is that there exists a finite relaxation time \( \tau \), past which the system is guaranteed to converge to steady-state. Thus, if the ensemble began from some arbitrary PDF \( \tilde{P}^0 \) at \( t = 0 \) (not necessarily the steady-state \( \tilde{P} \)), then for \( \Delta t = M\tau \) (with \( M > 1 \)), the PDF of indistinguishable trajectories becomes a product of independent steady-state PDFs,

\[
\tilde{P}([\mathbf{X}^k]) = \tilde{P}^0(\mathbf{X}^0) \tilde{P}(\mathbf{X}^1) \cdots \tilde{P}(\mathbf{X}^K).
\]
\( \tau \) is specifically the relaxation time of the system to steady state (e.g., the inverse the intermediate scattering function’s rate of decay [24, 39]). An arbitrary \( M > 1 \) was put simply to further ensure the above “independent decomposition” (Eq. [S1]) and will not affect the derivation. A \( \Delta t \)-related subtlety will appear in Sec. I C 1.

### B. Dynamics of Distinguishable Particles

We now consider \( \Pr\{\{X^k\}\} \) — the PDF of observing the discrete sequence of \( K \) distinguishable \( N \)-particle states \( \{X^k\} \), defined over \( \Phi^{K+1} \) (i.e., how a collection of “colored points” evolves over time). Now the identity of particles must remain consistent across snapshots.

We write the information content of \( \Pr \) [36] as

\[
\mathcal{H} = - \int_{\Phi} \Pr[\{X^k\}] \ln(N^{K+1})\Pr[\{X^k\}], \tag{S5}
\]

where we accounted for the arbitrary entropic constant by including \( N^{K+1} \). No indistinguishability factor \( (N!)^{K+1} \) is necessary, since the particles are distinguishable in this picture. \( \mathcal{H} \) in Eq. (1) of the main text is related to \( \mathcal{H} \) through \( \mathcal{H} = \mathcal{H} / K \).

In the limit \( \Delta t \rightarrow 0 \) (and also \( t_{\text{obs}} \rightarrow \infty \), i.e., much larger than any possible relaxation time), \( \mathcal{H} / t_{\text{obs}} \) is the Kolmogorov-Sinai entropy rate [37, 38]. However, as noted prior to Eq. (S4), we concentrate on the opposite limit, where \( \Delta t \gg \tau \) is the relaxation time (or bigger). While it implied Eq. (S4) for \( \tilde{\Pr} \), a similar “independent decomposition” does not hold for \( \Pr \) of the distinguishable particles. The typical time it takes \( N \) distinguishable particles to converge to the steady-state PDF, \( P \), diverges with system size, since each particle must traverse the entire phase-space. This contrasts the indistinguishable particles case, where the subspace that each particle has explored is a viable sample for every other particle (through permutations), cutting down phase-space from \( |\Phi| \) to \( |\tilde{\Phi}| = |\Phi| / N! \), with \( N \gg 1 \).

Although an independent decomposition is not possible, assuming \( \Delta t \) is longer than all memory effects (\( \tau \geq \tau_{\text{mem}} \)), the collection of consecutive \( N \)-particle configurations \( \{X^k\} \) is a stationary Markov chain. Hence,

\[
\Pr[\{X^k\}] = P_0(X^0) \prod_{k=1}^{K} W_N(X^k|X^{k-1}, \Delta t), \tag{S6}
\]

where \( W_N(X'|X, \Delta t) \) is the Markovian transition PDF (‘propagator’) to change from distinguishable \( N \)-particle state \( X \) at time \( k\Delta t \) to state \( X' \) at time \( (k + l)\Delta t \), which is assumed to be independent of \( k \) (i.e., this is a stationary propagator). Note that \( W_N \) is not a transition rate. \( P_0(X) \) is the initial distinguishable steady-state distribution, obeying \( P_0(X) = N!P_0(X) \) (see Eq. [S1]), supplying the possible initial configurations of the observed process.

Substituting Eq. (S6) in Eq. (S5), and using \( W_N(X'|X, 0) = \delta(X' - X) \) and the Markovian property \( \int dX' W_N(X'|X, k\Delta t)W_N(X'|X'', (k + l)\Delta t) = W_N(X'|X, (k + l)\Delta t) \) we obtain

\[
\mathcal{H} = S^0 + \ln N! - \int_{\Phi} dX^0 P_0(X^0) \int_{\Phi} dX \sum_{k=0}^{K-1} W_N(X|X^0, k\Delta t) \int_{\Phi} dX' W_N(X'|X, \Delta t) \ln(v^N W_N(X'|X, \Delta t)), \tag{S7}
\]

where the first two terms are the entropy of the initial state with statistics \( P_0 \) (Eq. [S3]), not necessarily being the steady-state \( P \).

We now assume translation invariance — homogeneity for positions, isotropy for orientations, Galilean invariance for velocities, etc. In this case, \( W_N(X'|X, \Delta t) \) depends on \( \Delta X \equiv X' - X \) only. Recalling the normalization conditions \( \int dX' W_N(X'|X, \Delta t) = \int dX P(X) = 1 \), we simplify Eq. (S7) to

\[
\mathcal{H} = S^0 + \ln N! + KS_N, \tag{S8a}
\]

\[
S_N = -\int_{\Phi} d\Delta X W_N(\Delta X, \Delta t) \ln(v^N W_N(\Delta X, \Delta t)). \tag{S8b}
\]

\( S_N \), the information content of the Markovian jump PDF during \( \Delta t \), obviously depends on \( \Delta t \). It is worth-mentioning that \( KS_N / t_{\text{obs}} = S_N / \Delta t \) is the Kolmogorov-Sinai entropy rate of a discrete-time Markov chain [37, 38]. In that context, the opposite limit of continuous-time (\( \Delta t \rightarrow 0 \)) Markov chain is a problematic limit (see Ref. [38] for possible remedies). As mentioned above, we are not taking this limit.
C. Central Step: Combining the Two Decompositions

The last step is to relate \( \Pr \) to \( \tilde{\Pr} \). The former includes the dynamical quantities within the Markov propagator (Eq. [S6]), while the latter separates into steady-state PDFs (Eq. [S4]). The two are related, as before, through permutations—to obtain \( \tilde{\Pr} \) (the PDF to find a sequence of indistinguishable snapshots) one needs to sum over all possible permutations at each time step in \( \Pr \) (the probability to observe sequence of distinguishable snapshots),

\[
\tilde{\Pr}[\mathbf{X}^0, \mathbf{X}^1, \ldots, \mathbf{X}^K] = \sum_{\sigma_0 \in \mathcal{P}} \sum_{\sigma_1 \in \mathcal{P}} \cdots \sum_{\sigma_K \in \mathcal{P}} \Pr[\sigma_0 \mathbf{X}^0, \sigma_1 \mathbf{X}^1, \ldots, \sigma_K \mathbf{X}^K].
\]  

(S9)

Note that performing the same permutation \( \sigma_0 \) at all steps does not change \( \Pr \), as it is independent of the identity of the particle that underwent a particular trajectory. Thus, renaming \( \sigma'_k = \sigma_k \sigma_0^{-1} \) (i.e., carrying the permutation \( \sigma_0 \) down the whole path), we are free to permute the identity of the particles in the initial state, without changing \( \Pr \),

\[
\tilde{\Pr}[\mathbf{X}^0, \mathbf{X}^1, \ldots, \mathbf{X}^K] = N! \sum_{\sigma'_0 \in \mathcal{P}} \cdots \sum_{\sigma'_K \in \mathcal{P}} \Pr[\mathbf{X}^0, \sigma'_1 \mathbf{X}^1, \ldots, \sigma'_K \mathbf{X}^K].
\]  

(S10)

We may not repeat this step, since the PDF for a jump from configuration \( \mathbf{X} \) to \( \mathbf{X}' \) may differ from the PDF for the jump \( \mathbf{X} \) to \( \sigma \mathbf{X}' \) (i.e., where the final particles’ positions are scrambled), or explicitly, \( W_N(\sigma \mathbf{X}' - \mathbf{X}, \Delta t) \neq W_N(\mathbf{X}' - \mathbf{X}, \Delta t) \) for \( \sigma \neq 1 \) (the unit permutation). (The permutations in the initial state were equality probable since, following the construction of the \( \sigma_k \)'s, \( W_N(\sigma_0 \mathbf{X}' - \sigma_0 \mathbf{X}, \Delta t) = W_N(\mathbf{X}' - \mathbf{X}, \Delta t) \) for any \( \sigma_0 \in \mathcal{P} \).) We offer below three possible inequalities and approximations, building upon this realization.

1. Exact Inequality

Since Eq. (S10) is a sum of non-negative quantities, we may write the crude yet rigorous bound by only including the unit-permutations, \( \sigma'_1 = \cdots = \sigma'_K = 1 \),

\[
\tilde{\Pr}[\mathbf{X}^0, \mathbf{X}^1, \ldots, \mathbf{X}^K] \geq N! \Pr[\mathbf{X}^0, \mathbf{X}^1, \ldots, \mathbf{X}^K].
\]  

(S11a)

Equality only occurs when trajectories do not mix (see Sec. I C 2). Using Eqs. (S4) and (S1),

\[
-\ln(\nu^N(K+1) \Pr([\mathbf{X}^k])) \geq \ln N! - \ln(\nu^N(K+1) \tilde{\Pr}([\mathbf{X}^k])) = \ln N! - \ln[\nu^N N! \mathcal{P}(\mathbf{X}^k)] - \sum_{k=1}^{N} \ln[\nu^N N! \mathcal{P}(\mathbf{X}^k)].
\]  

(S11b)

Thus, utilizing Eqs. (S11b) and (S3), Eq. (S5) yields

\[
\mathcal{H} \geq S^0 + \ln N! + KS.
\]  

(S12)

Comparing Eq. (S12) with Eq. (S8), we get a rigorous bound on the entropy from kinetics,

\[
S \leq S_N = - \int_{\phi} d\Delta \mathbf{X} W_N(\Delta \mathbf{X}, \Delta t) \ln(\nu^N W_N(\Delta \mathbf{X}, \Delta t)).
\]  

(S13)

Equation (S13) is Eq. (2) of the main text. This expression depends on \( \Delta t \). On the one hand, the bigger \( \Delta t/\tau = M \), the worse is the bound (as more mixing events might occur during each step). Thus, smaller \( \Delta t \) is preferable. On the other hand, we may not choose \( \Delta t < \tau \), as the “independent decomposition” (Eq. (S1)), and perhaps even the Markovian decomposition (Eq. (S6)), would not be valid. However, comparing different states with a similarly bigger \( \Delta t \) than their corresponding \( \tau \), the underestimation of both \( \tilde{\Pr} \) is “bad” to the same extent, as \( \Delta t_1/\Delta t_2 = \tau_1/\tau_2 \). See Sec. I D.

2. Special Case: Equality for Non-Mixing Trajectories

All the inequalities appearing in Sec. I C 1 become equalities for a particular scenario, namely, when \( \Pr[\mathbf{X}^0, \sigma'_1 \mathbf{X}^1, \ldots, \sigma'_K \mathbf{X}^K] = 0 \), unless \( \sigma'_1 = \cdots = \sigma'_K = 1 \). It applies for systems which still converge to steady state during a finite time, but whose particles may not mix, so later permutations are prohibited.
An example that obeys this rule is single-file diffusion \[46\], and its analogues. These are usually one-dimensional systems, where the particles follow some kinetic law (diffusion, ballistic motion, etc.), but may not cross each other. In these systems, the \(n\)th particle “from the left” always remains the \(n\)th one, regardless of how big \(\tau\) or \(t_{\text{obs}}\) are. Thus, while the \(N!\) permutations over the initial conditions in Eq. \((S10)\) are still permitted, all later permutations are forbidden.

To conclude, in such systems,

\[
\tilde{P}_t[X^0, X^1, \ldots, X^K] = N!P_t[X^0, X^1, \ldots, X^K].
\]

This results in the equality

\[
S = S_N = -\int_{\Phi} d\Delta X W_N(\Delta X, \Delta t) \ln(\nu^N W_N(\Delta X, \Delta t)).
\]

Here, the only restriction on \(\Delta t/\tau = M\) is that Eq. \((S4)\) will remain valid.

### 3. General Case: Equality within ‘Mean-Field Approximation’

There is no generic way to express \(W_N(\sigma X' - X, \Delta t)\) in terms of \(W_N(X' - X, \Delta t)\) only. We do note, however, that the vast majority of permutations lead to very unlikely trajectories, requiring some particles to go to the other end of phase-space during time \(\Delta t\). Such trajectories do not contribute much to the PDF. Thus, only “neighboring” particles may interchange trajectories with non-zero PDF. The Markov property additionally suggests that indeed the mixing at every step is independent of the exchanges of the previous step; the only dependence is on the current arrangement.

As a mean-field approximation, we argue that all paths that a particle may adopt are obtained regardless of the detailed arrangement of the background particles, and it “sees” \(z(\Delta t)\) particles (on average) for a potential exchange during \(\Delta t\). Therefore,

\[
\tilde{P}_t[\{X^K\}] \simeq N!z(\Delta t)^N K \tilde{P}_t[\{X^K\}].
\]

Following the same steps as in Sec. \(1C.1\) we get

\[
S + N \ln z(\Delta t) \simeq S_N = -\int_{\Phi} d\Delta X W_N(\Delta X, \Delta t) \ln(\nu^N W_N(\Delta X, \Delta t)),
\]

where the approximation sign arose from the mean-field treatment of path exchanges. Note that since every particle can mix “with itself”, \(z(\Delta t) \geq 1\), and Eq. \((S17)\) yields Eq. \((S13)\) (without approximation sign). In contrast to Eq. \((S13)\), the arbitrary \(\Delta t/\tau = M\) will cancel out explicitly.

### D. Useful Relations

Equations \((S13)\) and \((S17)\) are rigorous relations between thermodynamics (entropy) and dynamics. Eq. \((S13)\) is an exact inequality, which becomes an equality for well-defined, yet rare systems. On the other hand, Eq. \((S17)\) is an equality within mean-field approximation. However, notice that \(W_N(\Delta x_1, \ldots, \Delta x_n, \Delta t)\) is the propagator of \(N \gg 1\) particles, which is inaccessible experimentally and rarely known analytically.

A salutary step towards a useful relation would be to track a (much) smaller number of particles, \(N \gg n \geq 1\), for which the propagator \(W_n(\Delta x_1, \ldots, \Delta x_n, \Delta t)\) is accessible. Below, we consider the single-particle \((n = 1)\) propagator. It is the PDF that during \(\Delta t\), the 1st particle moved \(\Delta x_1\), the 2nd — \(\Delta x_2\), and so on for \(n\) particles. For that purpose, we could label only \(n\) particles to begin with (already at Eq. \((S4)\) while carefully taking care of the remaining \((N - n)\) indistinguishable particles and their statistics. Alternatively, we use the well known subextensivity property for the entropy,

\[
\frac{S_N}{N} \leq \frac{S_{N-1}}{N-1} \leq \cdots \leq \frac{S_2}{2} \leq S_1,
\]

\((S18a)\)

This is an overestimation, as each particle is a neighbor for \(z\) other particles. To leading order in \(z(\Delta t) \ll N\), this ‘combinatorial’ double-counting is negligible, and we remain with \(z(\Delta t)^N\) options in total.
where \( S_n \) is the information content of the \( n \)-particle propagator, \( W_n \),

\[
S_n = -\int_{\Omega} d\Delta x_1 \cdots d\Delta x_n W_n(\Delta x_1, \ldots, \Delta x_n, \Delta t) \ln[v^n W_n(\Delta x_1, \ldots, \Delta x_n, \Delta t)].
\]  

(S18b)

Eq. (S18a) becomes a set of equalities if particle trajectories are independent, that is,

\[
W_N(\Delta x_1, \ldots, \Delta x_N, \Delta t) = \prod_{n=1}^{N} W_1(\Delta x_n, \Delta t).
\]  

(S19)

For completeness, the subextensivity property (Eq. (S18a)) is proven in Sec. I E.

Next, define the thermodynamic entropy per particle, \( s = S/N \). Together with Eq. (S13), we obtain,

\[
s \leq S_N/N \leq S_1,
\]  

(S20a)

This is Eq. (3) of the main text. Similarly, the equality (within mean-field approximation) that was Eq. (S17) becomes an inequality as well,

\[
s + \ln \varpi(\Delta t) \simeq S_N/N \leq S_1.
\]  

(S20b)

We proceed to write our final proven relations in two common cases — normal and anomalous diffusion.

1. Normal Diffusion

We start with the case of a Brownian particle. While the complete \( N \)-particle propagator may include complex hydrodynamical and direct interactions, upon integration over \((N-1)\) particles (which is consistent with the assumption underlying Eq. (S18a)), we are left with an effective single-particle propagator of the form:

\[
W_1(\Delta x, \Delta t) = \frac{1}{(4\pi D \Delta t)^{d/2}} \exp\left(-\frac{|\Delta x|^2}{4D \Delta t}\right),
\]  

(S21)

where \( D \) is the asymptotic, single-particle diffusion coefficient; \( \langle \Delta x \cdot \Delta x \rangle(\Delta t) = 2dD \Delta t \), and \( d \) is the dimensionality. Inserting \( W_1 \) into Eq. (S18b), we obtain,

\[
S_1 = \frac{d}{2} \left[ 1 + \ln \left( \frac{4\pi D \varpi}{\varpi^{2/d}} \right) \right].
\]  

(S22)

This is the entropy of a Gaussian random variable [53].

Equation (S20a), combined with Eq. (S22), gives the exact inequality,

\[
D\tau \geq Ae^{2s/d},
\]  

(S23a)

where \( A \) is some proportionality constant (into which we absorbed the arbitrary \( \Delta t/\tau = M \) and \( v; A = v^{2/d}/(4\pi e M) \)). At lower density, while Eq. (S18a) has tighter inequalities (the particles’ motion is less correlated), the undercounting of Eq. (S11a) is not necessarily less severe (as \( \tau \) would increase with density). Thus, in order for this inequality to remain consistent, one should estimate how the extend of mixing changes with system parameters. Once estimated, one may consider a reference whose entropy, diffusion coefficient, and relaxation time are known; \( s^o \), \( D^o \), and \( \tau^o \), respectively. Then, one could write

\[
D\tau \geq D^o \tau^o e^{2(s-s^o)/d}.
\]  

(S23b)

Thus, it is important to determine the trends regarding the extent of mixing first. (Alternatively, one could infer them with a few data-points based on whether the direction of inequality is the correct one.)

Note that for systems with non-mixing trajectories, Eq. (S23) is a tighter inequality (recall the two inequality steps in Eq. (S20a)) — while the undercounting of trajectories is no longer an issue, the particles may exhibit correlated motion which are integrated out in Eq. (S18a). For instance, even in the case of non-interacting single-file particles, the sole fact that they are non-passing leads to complex many-body effects which the coarse-graining of Eq. (S18a) might ignore. For example, the single particle even undergoes sub-diffusion, thus requiring the adjustments presented in Sec. I D 2.
Equations \((S20b)\) and \((S22)\), within mean-field approximation, give a tighter inequality. However, we should relate \(z(\Delta t)\) to physical parameters first. We argue from basic kinetic considerations that, at the relaxation time, the number of neighbors a particle encounters is \(z(\tau) \sim \xi^d \rho\), where \(\xi\) is the system’s correlation length, and \(\rho = N/\int dx\). This is because \(\xi^d\) is the phase-space volume that was explored during the relaxation time. For example, in the case of an ideal gas with positional DOFs, \(\xi\) is the mean-free path. For electrolytes, it is the Debye length. Now, the number of encounters by time \(\Delta t = M\tau\) \((M > 1)\) is \(z(\Delta t) = z(\tau) \cdot (\Delta t/\tau)^{d/2} = M^{d/2} z(\tau)\), as the particle’s motion past \(\tau\) is diffusive, and the covered area increases linearly with \(\Delta t\). Inserting the estimated \(z(\Delta t)\) and Eq. \((S22)\) in Eq. \((S20b)\), we find

\[
D \geq D_s e^{2(s-s_{id})/d},
\]

which is the relation proposed by Rosenfeld [7] and Dzugutov [9], with some crucial modifications whose origins are now apparent. See main text for extensive comparison. In this expression, \(s_{id} = -\ln(\nu \rho)\) is the entropy per particle of the ideal gas (in the units and discretization that gave the constant reference \(\upsilon\)), \(\xi\) is the mean-free path. For electrolytes, \(\nu = M\). It may too depend on density, temperature, and other thermodynamic parameters, similar to \(s_{id}\) and \(D\). In simple liquids, \(D_s\) is just the diffusion coefficient of the ideal gas, whose explicit dependence on density and temperature is known. Indeed, even prior to our present paper, \(D\) was rescaled according to \(D_s \sim (k_B T/m)^{1/2} \rho^{1/4} \approx D_{\text{kin}}\) [8]. However, building upon the argument of Ref. [12], if there is a hidden scale-invariance, then one may expect the excess entropy \(s-s_{id}\) and the short-time diffusion coefficient \(D_s\) to depend on the same rescaled parameter, thus showing a data collapse for \(D\) even beyond the simple line \(\ln(D/D_{\text{kin}}) \sim 2\delta s/d\). In more complex cases, there was no such data collapse (see examples in Ref. [12]). On top of this discussion, direct interaction among particles couples the motions, thus the relation should be, in fact, an inequality (Eq. \((S24)\)). Equation \((S24)\) becomes an approximate equality for independent particles (recall Eq. \((S20b)\)).

Since we never assumed equilibrium, all relations presented here are also valid out of equilibrium, without any additional assumptions. Similarly, equilibrium does not necessarily imply that the above inequalities would be tighter.

2. Anomalous Diffusion

Equations \((S20a)\) and \((S20b)\) can be applied to more complicated cases than regular Brownian diffusion. For example, consider a single-particle anomalous-diffusion propagator. To this end, we replace the (Fourier-transformed) normal Gaussian propagator,

\[
\tilde{W}_1(q, \Delta t) = \exp \left[ -D|q|^2 \Delta t \right],
\]

with a more general, possibly non-Gaussian, one

\[
\tilde{W}_1(q, \Delta t) = \exp \left[ - (F|q|^2 \Delta t^\alpha /2)^{\nu/2} \right].
\]

Here, \(F\) is the generalized anomalous diffusion coefficient, \(\alpha\) is the anomalous diffusion exponent, and \(\nu\) is a stretching exponent. The propagator of Eq. \((S25)\) is obtained for \(\alpha = 1, \nu = 2\), and \(F = 2D\).

Such propagators appear as a result of the generalized central limit theorem for anomalous diffusion [33]. Equation \((S26)\) is the Fourier transform of a general elliptically-contoured multidimensional centered (zero mean) stable distribution [55]. On time scale \(\tau\) on which the appropriate diffusive propagation has already been adopted, the non-stable part of any general propagator would vanish. This means that a sum of diffusive displacements occurring for time \(\Delta t\), up to parameters rescale (namely, division by \(M^\alpha\)), will converge to one of the stable distributions of Eq. \((S26)\). Therefore, the results should be applicable to any anomalous diffusive propagator, provided that a finite mean relaxation time \(\tau\) exists.

In real space, the propagator takes the form,

\[
W_1(\Delta x, \Delta t) = \frac{1}{(2\pi F \Delta t^{\alpha})^{d/2}} \Phi_{d,\nu} \left( \frac{|\Delta x|}{\sqrt{2F \Delta t^\alpha}} \right),
\]

\[
\Phi_{d,\nu} (z) = \frac{2}{z^{d/2-1}} \int_0^\infty dR R^{d/2} e^{-R^\nu} J_{d/2-1} (2Rz),
\]

where \(J_j(u)\) is the \(j\)th Bessel function of the first kind. Indeed, we obtain a Gaussian for \(\nu = 2, \Phi_{d,2}(z) = \exp(-z^2)\), where one can see the anomalous time scaling through \(\langle \Delta x \cdot \Delta x \rangle / (\Delta t) = dF \Delta t^\alpha\). Other important 1D examples
include the Cauchy distribution (with $\nu = 1$) and Lévy distribution ($\nu = 1/2$, with slight adjustments) [50]. Now that we have constructed the general propagator, we insert it in Eq. (S18b) and obtain

$$S_1 = \frac{d}{2} \left[ \Lambda_{d,\nu} + \ln \left( \frac{2\pi F \Delta t^\alpha}{\nu^{2/d}} \right) \right],$$

$$\Lambda_{d,\nu} = -\frac{2}{\Gamma(d/2 + 1)} \int_0^\infty dz z^{d-1} \Phi_{d,\nu}(z) \ln [\Phi_{d,\nu}(z)]. \quad (S28)$$

For a Gaussian ($\nu = 2$), $\Lambda_{d,2} = 1$ as before. What has made the integration possible in this non-Gaussian case is the self-similar form of the propagator (its dependence on the combination $|q|^2 \Delta t^\alpha$ rather than on $q$ and $\Delta t$ separately).

Similar to Eq. (S23), Eqs. (S20a) and (S28) give the loose inequality

$$F^\tau s \geq Ae^{2s/d}.$$  \quad (S29a)

where $A$ is again some proportionality constant. Note that there is no dependence on $\nu$. Relative to a reference point (with $s^\circ$, $F^\circ$, and $\tau^\circ$),

$$F^\tau s = F^\circ (\tau^\circ)^\alpha e^{2(s-s^\circ)/d}. \quad (S29b)$$

In general, the exponents $\alpha$ and $\nu$ may be different than in the reference. In this case, the corresponding $\alpha^\circ$ should also be included.

As mentioned in Sec. 1D, equality is obtained if the particles do not interchange paths and move independently. In single-file diffusion, particles are strongly correlated due to their inability to pass each other, and therefore, we expect Eq. (S29) to be a (tighter) inequality. To our surprise, as shown in the main text, the relation seems to be an equality for two single-file examples.

As to the bound within mean-field approximation, due to the anomalous diffusion, we must modify $z(\Delta t) = z(\tau) M^{\alpha n/2}$. With that, Eqs. (S20b) and (S28) give

$$F \leq F_s e^{2(s-s^d)/d}, \quad (S30)$$

which suggests that a modified relation (Eq. (S24)) applies for anomalous diffusion, too. $F_s \sim \xi^2 / \tau^\alpha$ is then the “short-time anomalous diffusion coefficient”. A consistent definition of $F_s$ may not exist (by the reason that the preceding collisions, which are usually what leads to the long-time anomalous diffusion, most commonly occur within normal-diffusive regime). In this case, it can be replaced with an expression of the form $F_s = D_s \tau^{1-\alpha}$.

3. Toy Model for Many-Particle Diffusion

As seen above, undercounting particle permutations and coarse graining the dynamics lead to inequalities. A possible remedy for the former was the mean-field counting of mixed trajectories. With the hierarchical structure of Eq. (S18a), we now demonstrate how one could improve the inequalities coming from the latter.

Consider, as toy model, a Gaussian process of identical $N$ variables $X_N$. This implies that, for any subset of variables $X_n$, the $n$-variable diffusive propagator is given by

$$W_n(\Delta X_n, \Delta t) = \mathcal{N}_n e^{-(4\pi \Delta t)^{-1/2} \Delta X_n \cdot D_n \cdot \Delta X_n}, \quad \mathcal{N}_n = \left[ (4\pi \Delta t)^{dn} \det(D_n) \right]^{-1/2}, \quad (S31)$$

where $D_n$ is a constant ($X_n$-independent) $dn \times dn$ matrix. Inserting Eq. (S31) for the $N$-particle propagator in Eqs. (S13) and (S17) (with the previously estimated $z(\Delta t)$), we get

$$[\det(D_N)]^{1/(N^d)} \tau \geq Ae^{2s/d}, \quad (S32a)$$

$$[\det(D_N)]^{1/(N^d)} \simeq D_se^{2(s-s^d)/d}, \quad (S32b)$$

where $s_n = S_n / n$, and $A$ is the proportionality constant. As a consequence of the hierarchy of Eq. (S18a), we obtain a set of inequalities,

$$D \tau \geq \cdots \geq [\det(D_n)]^{1/n^d} \tau \geq \cdots \geq [\det(D_N)]^{1/N^d} \tau \geq Ae^{2s/d}, \quad (S33a)$$

$$D \geq \cdots \geq [\det(D_n)]^{1/n^d} \geq \cdots \geq [\det(D_N)]^{1/N^d} \simeq D_se^{2(s-s^d)/d}. \quad (S33b)$$

Thus, if the asymptotic many-particle diffusion tensor is known, following these steps, one could find a relation with a tighter inequality, depending on how many additional particles were considered.
E. Entropy is Subextensive

We present a proof that the entropy is a subextensive quantity. This key property is the reason why all the relations appearing in the main text and in Sec. [D] include an inequality.

Consider \( N \) identical, continuous, dependent, and distinguishable degrees of freedom (DOFs) we denote by \( \{x_1, \ldots, x_N\} \). They are drawn from a PDF \( P_N(x_1, \ldots, x_N) \). The continuous entropy (information content) of this PDF \( \text{(S34)} \) is

\[
H_N = - \int dx_1 \cdots \int dx_N P_N(x_1, \ldots, x_N) \ln[v^n P_N(x_1, \ldots, x_N)].
\]

Since the DOFs are identical, without loss of generality, we may integrate the “last” \((N - n)\) DOFs to obtain the marginal PDF of \( 1 \leq n \leq N \) DOFs,

\[
P_n(x_1, \ldots, x_n) = \int dx_{n+1} \cdots \int dx_N P_n(x_1, \ldots, x_N).
\]

Its entropy is also

\[
H_n = - \int dx_1 \cdots \int dx_n P_n(x_1, \ldots, x_n) \ln[v^n P_n(x_1, \ldots, x_n)].
\]

Using the chain rule for conditional PDFs, we rewrite the entropy of \( n \) DOFs as

\[
H_n = - \int dx_1 \cdots \int dx_n P_n(x_1, \ldots, x_n) \ln \left[ v^n \prod_{m=1}^{n} P_m(x_m|x_1, \ldots, x_{m-1}) \right] = \sum_{m=1}^{n} H^\text{cond}_m,
\]

where \( P_m(x_m|x_1, \ldots, x_{m-1}) = P_m(x_1, \ldots, x_{m-1}, x_m)/P_{m-1}(x_1, \ldots, x_{m-1}) \) is the conditional PDF of \( x_m \) under a given configuration of \( m - 1 \) other DOFs, and its (conditional) entropy, upon relabeling the identical variables \( x_1 \leftrightarrow x_m \), is

\[
H^\text{cond}_m = - \int dx_1 \int dx_2 \cdots \int dx_m P_m(x_1, x_2, \ldots, x_m) \ln[v P_m(x_1|x_2, \ldots, x_m)].
\]

We now use Jensen inequality for the logarithm, \( \langle \ln(\cdot) \rangle = \ln(\langle \cdot \rangle) \); in our case \( \langle \cdot \rangle = \int dx_m P_m(x_1|x_2, \ldots, x_m) \).

We denote for compactness \( Y = \{x_2, \ldots, x_m\} \), and prove that conditional entropy increases with less conditioned DOFs:

\[
H^\text{cond}_m = - \int dx_1 \int dY \int dx_m P_m(x_1, Y, x_m) \ln[v P_m(x_1|Y, x_m)]
\]

\[
= \int dY P_{m-2}(Y) \int dx_1 P_{m-1}(x_1|Y) \int dx_m P_m(x_m|x_1, Y) \ln \left[ \frac{1}{v P_m(x_1|Y, x_m)} \right]
\]

\[
\leq \int dY P_{m-2}(Y) \int dx_1 P_{m-1}(x_1|Y) \ln \left[ \frac{1}{v} \int dx_m P_m(x_m|x_1, Y) \frac{1}{P_{m-1}(x_1, Y)} P_m(x_1, Y) \right]
\]

\[
= \int dY P_{m-2}(Y) \int dx_1 P_{m-1}(x_1|Y) \ln \left[ \frac{1}{v} \frac{P_m(x_1, Y, x_m)}{P_{m-1}(x_1, Y)} \right] = H^\text{cond}_{m-1}.
\]

Thus, we may establish the following hierarchy,

\[
H_N^\text{cond} \leq H_{N-1}^\text{cond} \leq \cdots \leq H_2^\text{cond} \leq H_1^\text{cond} = H_1.
\]

Using Eq. \( \text{(S37a)} \) and \( \text{(S38)} \), we find

\[
\frac{H_n}{n} = H_n^\text{cond} + \sum_{m=1}^{n-1} H_m^\text{cond} \leq \frac{1}{n-1} \sum_{m=1}^{n-1} + \sum_{m=1}^{n-1} H_m^\text{cond} = \frac{\sum_{m=1}^{n-1} n - 1}{n - 1} = \frac{H_{n-1}}{n - 1}.
\]

This shows that entropy is subextensive,

\[
\frac{H_N}{N} \leq \frac{H_{N-1}}{N - 1} \leq \cdots \leq \frac{H_2}{2} \leq H_1.
\]

In the thermodynamic limit, \( N \gg 1 \), entropy is regarded as extensive. The subextensivity appears in finite-sized systems \( (n \geq 1) \). Equations \( \text{(S39)} \) DOFs.
II. HOMOGENIZATION

Here, we give further details regarding the diffusion of a single particle under the effect of either a random or periodic potentials. Both cases, in the long-time limit, obey translation invariance, as the obtained effective diffusion coefficient "homogenizes" these potentials past the relaxation time.

A. Random Potentials

The authors of Ref. [10] considered non-Gaussian potentials in general dimensions, originating from a Gaussian field. The formula for the long-time effective diffusion coefficient was found using self-similar renormalization group. In one of the examples, this formalism was applied to a system of many particles, where the total force acting on a single particle by the others was modeled as a random potential. Their formula for a tagged-particle diffusion coefficient led to an equation \( \frac{D}{D_0} = \exp(2\Delta s/d) \), in agreement with our derivation (Eq. (S24)). We believe that the coarse graining of the inter-particle forces is what led them to the equality.

We briefly mention Ref. [11], which deals with single-particle diffusion on a randomly-rugged potential following the Zwanzig model. Their work only seems to agree with our result (and the result of Ref. [10]) for one- and two-dimensional systems.

B. Periodic Potential

A rigorous homogenization procedure for a periodic potential is outlined in Ref. [45]. To our knowledge, its prediction is never compared to the Rosenfeld relation.

For simplicity, consider a one-dimensional system of size \( L \) with a periodic potential \( U(x) = U_0 u(x/\lambda) \), \( u(x+1) = u(x) \), having wavelength \( \lambda \ll L \) and strength \( E = U_0/(k_B T) \). The ‘homogenized’ diffusion coefficient is \[ D = \frac{D_0}{\zeta(E)/\zeta(-E)}, \quad \zeta(E) = \int_0^1 dy e^{-E u(y)}, \] (S40)

where \( D_0 \) is the diffusion coefficient in the absence of the potential. Assume now that \( N \) non-interacting particles are free to diffuse on that energy landscape. The equilibrium Boltzmann distribution is \( P(X) \propto \exp(-E \sum_{n=1}^N u(x_n)) \). The entropy is

\[ s = -\ln(\rho) + \ln \zeta(E) + E \langle u(x) \rangle = -\ln(\rho) + \left( 1 - E \frac{d}{dE} \right) \ln \zeta(E), \] (S41)

where \( \rho = N/L \) is the density. These equations may be generalized to many dimensions.

Equations (S40) and (S41) may be used in Eq. (S24) to find the diffusion coefficient of possibly interacting particles (as they are exactly \( D_0 \) and \( s^{id} \), respectively). With the above, except for the usual dependencies of \( D_0 \) and \( s^{id}(E = 0) \) on \( \rho \) and \( T \) (namely, \( D_{\text{kin}} \) and \( -\ln \rho \) respectively), the dependence on the potential depth is taken into account.

We can also check whether Eqs. (S40) and (S41) are in line with the exact-inequality variant of our relation — Eq. (S23). The reference is chosen to be the one in the absence of a potential \( (E = 0) \), where \( D^\circ = D_0 \), \( \tau^\circ = \tau_{\text{col}} \) (the average collision time), and \( s^\circ = -\ln(\rho) \).

In the limit of weak potentials \( (E \ll 1) \), the diffusion coefficient and entropy to order \( E^2 \) are

\[ D/D^\circ \approx 1 - \left[ (\ln \zeta') \right]_{E=0} E^2 - \left[ \frac{(\ln \zeta')'}{12} - \frac{(\ln \zeta')''}{2} \right]_{E=0} E^4, \] (S42a)

\[ e^{2(s-s^\circ)} \approx 1 - \left[ (\ln \zeta') \right]_{E=0} E^2 - \left[ \frac{2(\ln \zeta')'}{3} \right]_{E=0} E^3 \left[ \frac{(\ln \zeta')''}{8} - \frac{(\ln \zeta')'''}{2} \right]_{E=0} E^4, \] (S42b)

where \( \zeta' = d\zeta/dE \), and so on for higher-order derivatives. We see that \( D/D^\circ = e^{2(s-s^\circ)} \) up to order \( E^2 \). While the diffusion coefficient and entropy are available from Eqs. (S40) and (S41), respectively, we cannot estimate the relaxation time accurately. Nevertheless, we know that \( \tau/\tau^\circ \geq 1 \) for certain, as some time is wasted between collisions to overcome potential wells (\( \tau = \tau^\circ \) only occurs for \( E = 0 \)). Thus, we find \( D\tau \geq D^\circ \tau^\circ e^{2(s-s^\circ)} \) to order \( E^2 \), as dictated by Eq. (S23).

For increasing potential strength \( E \), the higher-order terms might be either positive or negative. In some cases, as in the example of Fig. S1, we might even get \( D/D^\circ < e^{2(s-s^\circ)} \) for stronger potentials. Following Eq. (S23), we may now give a more informative bound on \( \tau \) than \( \tau/\tau^\circ \geq 1 \), namely, \( \tau/\tau^\circ \geq D^\circ e^{2(s-s^\circ)}/D \).
FIG. S1. Homogenized diffusion of a particle in a periodic potential. The arbitrarily selected potential (in units of the thermal energy $k_B T$) is $U(x) = E \cos x$. The curves show the long-time diffusion coefficient $D(E)$, normalized by its value in the absence of potential $D^0 = D(0)$, as a function of the potential strength $E$. The full orange curve shows the result of an analytic asymptotic expansion \[45\]. The dashed blue curve is the prediction of Eq. (S23) in one dimension, $D/D^0 = e^{2(s-s^0)}$, assuming that the relaxation time is unaffected by the potential. Inset: An illustration of a particle moving on the above periodic potential.

In the limit of strong potentials ($E \gg 1$), we obtain from a saddle-point approximation,

\[
\zeta(E) = \int_0^1 dy e^{-Eu(y)} \simeq \int_\infty^\infty dy e^{-Eu_{\text{min}} + \frac{1}{2}u''_{\text{min}} y^2} = e^{-Eu_{\text{min}}} \sqrt{\frac{2\pi}{Eu''_{\text{min}}}},
\]

\[
\zeta(-E) = \int_0^1 dy e^{Eu(y)} \simeq \int_\infty^\infty dy e^{Eu_{\text{max}} - \frac{1}{2}u''_{\text{min}} |y|^2} = e^{Eu_{\text{max}}} \sqrt{\frac{2\pi}{Eu''_{\text{max}}}},
\]

where $u_{\text{max}}$, $u_{\text{min}}$, $u''_{\text{max}}$, and $u''_{\text{min}}$ are the values of $u$ and its curvature at the top and bottom of the potential. Substitution in Eq. (S40) and (S41) leads to

\[
D/D^0 \simeq \frac{\sqrt{u''_{\text{min}} u''_{\text{max}}}}{2\pi} e^{-E(u_{\text{max}} - u_{\text{min}})},
\]

\[
e^{2(s-s^0)} \simeq \frac{2\pi e}{Eu''_{\text{min}}}.
\]

For sufficiently large potential strengths $E$, the limiting process is the escape time rather than collisions, so we may say that $\tau \simeq \tau_{\text{esc}}$, which is exactly the inverse of the Kramers escape rate \[57\]. Noting that $\tau \propto D^{-1}$ obtained above, we obtain $DT/(D^0 \tau^0) \simeq \text{const}$, while $e^{2(s-s^0)} \propto E^{-1}$. In the aforementioned limit $E \gg 1$, Eq. (S23) is a loose bound in the correct direction.

III. SINGLE-FILE DIFFUSION IN A PERIODIC POTENTIAL

Here we provide further technical information regarding the example of single-file diffusion in a periodic potential, which is presented in the main text. The system consists of $N$ point particles, restricted to move along a line of length $L$ without bypassing each other. Thus, following Sec. I C 2, Eqs. (S23) and (S29) are the relevant relations for this case (being, in particular, tight inequalities), rather than Eqs. (S24) and (S30) as in Sec. II B.

The particles move with diffusion coefficient $D_0$. In addition, they are subjected to external periodic potential of amplitude $E$ and wavelength $\lambda$, $U(x)/(k_B T) = E[1 - \cos(2\pi x/\lambda)]$ ($k_B$ — Boltzmann constant, $T$ — temperature). This model was studied in Ref. \[49\] (see also Ref. \[50\]). There are two control parameters: the potential strength $E$ and the density (number of particles per period) $\rho$. In Sec. III A we describe the Langevin Dynamics simulations. In Sec. \[41\] we show analytically that the entropy per particle $s$ is equal to the entropy of a single, labeled particle, giving some insight as to why Eq. (S29) is an equality for this unusual system.
A. Numerics

We choose the units of length, time, and energy such that $\lambda = 1$, $D_0 = 1/2$, and $k_B T = 1$. We perform Langevin dynamics simulations. At each time step we pick a particle at random, $N$ times (with possible repetitions). Each selected particle is moved according to

$$x_n(t + dt) \sim x_n(t) - \pi E \sin(2\pi x_n(t))dt + \eta \sqrt{dt}, \quad \eta \sim \mathcal{N}(0,1),$$

where $\eta$ is a random force drawn from a normal distribution with zero mean and unit variance. If the obtained $x_n(t + dt)$ is such that the particle bypasses its neighbor(s), then $n$ inherits the location of its neighbor, and the neighbor moves to $x_n(t + dt)$. This is repeated for every conflicting neighbor. The simulation runs until $t_{\text{obs}} = 10^3$ with $dt = 10^{-3}$, and the box size is $L = 10^4$ with periodic boundary conditions. We extract the anomalous-diffusion coefficient $F$ and the anomalous exponent $\alpha$ from the asymptotic limits of the mean-square displacements (MSD),

$$F t^\alpha = \langle (\Delta x)^2 \rangle = \frac{1}{N} \sum_{n=1}^{N} (x_n(t) - x_n(0))^2.$$  

(S46)

As in many one-dimensional single-file problems [46], we find $\alpha = 1/2$. See Fig. S2.

While $F$ is readily obtained from a log-log plot of the MSD, inferring the relaxation time in this system is intricate because of an interplay between two typical time scales. The first is the mean time between collisions, i.e., the time it takes a particle to “notice” that it cannot bypass its neighbors. This density-dependent time scale, denoted $\tau^\pm(\rho)$, is given by the crossover from normal diffusion ($MSD \propto D_0 t$) to anomalous diffusion ($MSD \propto F t^{1/2}$). It is the only time scale in the absence of a potential. We will measure the relaxation times for $E > 0$ relative to $\tau^\pm(\rho)$.

The other time scale is the mean time of escape out of a potential well into a neighboring one, $\tau_{\text{esc}}$. We estimate it from the simulation as the mean time it takes a particle, starting inside a well centered at $x = k\lambda, k \in \mathbb{Z}$, to arrive at $x = (k \pm 3/4)\lambda$. In the high-barrier limit ($E \gg 1$), we expect $\tau_{\text{esc}}^{-1}$ to be proportional to Kramers’ escape rate [47]

$$\tau_{\text{esc}}^{-1} = \frac{D_0/(2\pi k_B T)}{(U''_{\text{obs}}/\sqrt{U''(0)})^{1/2}} \exp\left[-(U_{\text{max}} - U_{\text{min}})/(k_B T)\right] = 2\pi(D_0/\lambda^2)Ee^{-2E}.$$  

This large-$E$ limit is confirmed in Fig. S3A, regardless of whether the single-file constraint is imposed. In the absence of the constraint, the asymptotic (normal) diffusion coefficient, ‘homogenizing’ the periodic potential, is known analytically [45], $D_s = D_0/(I_0(E))^2$, where $I_j(u)$ is the $j$th modified Bessel function of the first kind. (See Sec. I B.) In the presence of the constraint, the escape time increases with increasing density, as particles block each other (Fig. S3A).

In the limit of low density and weak potential, the collision time is the longer time scale, and in the opposite limit the escape time is the longer one. In all cases, however, the relaxation — i.e., reaching the asymptotic dynamics of homogenized anomalous diffusion — requires escapes as well as collisions. In Fig. S2 we see how, with increasing $E$, this asymptotic regime (with $\alpha = 1/2$) is reached after an increasingly long time. For large $E$ the MSD exhibits a
plateau (Fig. S2), reflecting the long trapping inside the potential well. In such a case, determining \( \tau \) from a crossover time becomes problematic. We chose to estimate it from the equation \( 2D_0 \tau = F \tau^{1/2} \), using the value of \( F \) as extracted from the simulation for each set of parameters.

In Fig. S3B, we plot the estimated relaxation time alongside the relaxation time as predicted by Eq. (S29) as an equality. The relaxation time becomes problematic. We chose to estimate it from the equation \( 2D_0 \tau = F \tau^{1/2} \), using the value of \( F \) as extracted from the simulation for each set of parameters. This explains the deviation at large \( E \) seen in Fig. 2b of the main text.

### B. Analytics

We begin with single-file diffusion in the absence of a potential (\( E = 0 \)). In this limit we consider particles of non-zero diameter \( a \). We shall subsequently treat the case of \( E \neq 0 \) and \( a = 0 \).

#### 1. No potential

Consider first the many-particle picture. The probability distribution to find the particles at some available configuration is uniform, \( P(X) = Z^{-1} \), where \( Z \) is the partition function. The single-file constraint leads to configurations with ordered particles: \( 0 \leq x_1 \leq x_2 - a \leq \cdots \leq x_N - (N - 1)a \leq L - Na \). Since the distribution is uniform, the integrals here are simple. The partition function and the entropy per particle are

\[
Z = \int_{(N-1)a}^{L-a} dx_N \int_{(N-2)a}^{x_N-a} dx_{N-1} \cdots \int_{0}^{x_2-a} dx_1 = \frac{(L - Na)^N}{N!},
\]

\[
s = N^{-1} \ln(Z/\nu) = -\ln(\nu N) + \ln(1 - \phi),
\]

where \( \rho = N/L \) and \( \phi = Na/L \).

We now switch to the single-particle picture. The \( m \)th particle’s marginal distribution is not uniform (even for \( a = 0 \)), but rather

\[
P_1^m(x) = \langle \delta(x - x_m) \rangle = \frac{1}{Z} \int_{x+(N-m)a}^{L-a} dx_N \int_{x+(N-m-1)a}^{x_N-a} dx_{N-1} \cdots \int_{x+m+1}^{x_{m+2}-a} dx_{m+1} \int_{(n-2)a}^{x_{m+1}} dx_{m} \cdots \int_{0}^{x_{m+1}} dx_{1}
\]

\[
= \frac{\rho}{(1-\phi)^N} \binom{N-1}{m-1} \left( 1 - \frac{x + (N-m+1)a}{L} \right)^{N-m} \left( \frac{x - (m-1)a}{L} \right)^{m-1},
\]

\[\text{(S48)}\]
where \((m-1)a \leq x \leq L - (N-m+1)a\), as before.

\(P_1^m(x)\) is drawn in Fig. S4. Its mean and variance are \(\langle x \rangle_m = n(L + a)/(N + 1) - a\) and \(\langle x^2 \rangle_m - \langle x \rangle_m^2 = m(N + 1 - m)(Na - L)^2/[(N + 1)^2(N + 2)]\), respectively. To leading order, they are linear in system size: \(mL/N\) and \(m(1-m/N)(\phi - 1)^2/\rho^2\), respectively. In that sense, these particles behave as a solid — distinguishable particles occupy well-defined cells of size \(L/N\). However, contrary to the solid, where the width of the single-particle distribution is roughly of the cell size, here, the width of \(P_1^m(x)\) goes as \(N^{1/2}\). Nevertheless, since \(s_1^m\) below is intensive (Eq. (S49)), it means that a Gaussian with width \(\sim N^{1/2}\) is a bad model.

The effective single-particle entropy is

\[
s_1^m = - \int_{x+(N-m)a}^{L-a} dx P_1^m(x) \ln[vP_1^m(x)]
\]

\[
= - \ln(v\rho) + N \ln(1 - \phi) - \ln\left(\frac{N - 1}{m - 1}\right) - (N - m)[\text{Har}_{m-1} - \text{Har}_N + \ln(1 - \phi)]
\]

\[
- (m - 1)[\text{Har}_{m-1} - \text{Har}_N + \ln(1 - \phi)]
\]

\[
= - \ln(v\rho) + \ln(1 - \phi),
\]

where we have used Stirling’s approximation, \(\ln n! \simeq n \ln n - n\), and the approximation for the \(n\)th harmonic number, \(\text{Har}_n = \sum_{k=1}^{n} k^{-1} \simeq \gamma + \ln n\) (\(\gamma \simeq 0.58\) being the Euler-Mascheroni constant). The dependence on \(m\) and \(N\) vanishes, so \(s_1\) is found to be an intensive quantity as expected. Comparing Eqs. (S47b) and (S49), we get \(s = s_1^m\). This may give a hint as to why an equality holds — no many body effects raise the entropy per particle, compared to the entropy of a single labelled particle.

2. With potential

As in the preceding section, we consider first the many-particle picture. The probability distribution to find the particles in some available configuration is the Boltzmann distribution, \(P(X) = Z^{-1} \exp(-\sum_{n=1}^{N} U(x_n)/k_B T)\), with \(Z\) being the partition function. The actual statistics is of distinguishable (ordered) particles, such that an average is of the form \(\langle \cdot \rangle = \int_{x_0}^{L} dx_N \int_{x_0}^{x_N} dx_{N-1} \cdots \int_{x_0}^{x_{N-1}} dx_1 P_N(X_N)(\cdot)\). However, through permutations of particle labels, we may switch to an equivalent scheme of indistinguishable-particles, where the averaging is given by \(\langle \cdot \rangle = (N!)^{-1} \int_{x_0}^{L} dx_N \int_{x_0}^{L} dx_N \cdots \int_{x_0}^{L} dx_1 P_N(X_N)(\cdot)\). The partition function is then

\[
Z = \frac{[L\zeta(L)]^N}{N!}, \quad \zeta(y) = \frac{1}{y} \int_{0}^{y} dx e^{-U(x)/(k_B T)},
\]

\[
\zeta(L) = \frac{1}{L} \int_{0}^{L} dx e^{-E[1 - \cos(2\pi x/L)]} = \zeta(\lambda) = e^{-E I_0(E)},
\]

where \(I_j(u)\) is the \(j\)th modified Bessel function of the first kind. For \(\zeta(L)\), we have implicitly assumed \(L/\lambda \in \mathbb{N}\). If this condition is not satisfied, there are corrections of order \(O(\lambda/L)\), which vanish in the thermodynamic limit. The
entropy is

\[ s = \frac{1}{N} \left( \ln \left( \frac{Z}{\nu} \right) - \frac{\langle U \rangle}{k_b T} \right) = -\ln(\nu \rho) + \ln I_0(E) - \frac{E I_1(E)}{I_0(E)}. \]  

(S51)

Obtaining the single-particle entropy, \( s^m \), is more complicated. Considering the \( m \)th particle, we split the system into two sub-systems which, following the argument above, can be regarded as made of indistinguishable particles, separately. Therefore, the marginal distribution of the \( m \)th particle is

\[
P^m_I(x) = \langle \delta(x-x_m) \rangle = \int_x^L dx_N \int_x^{x_N} dx_{N-1} \cdots \int_x^{x_{m+2}} dx_{m+1} \int_0^x dx_m \cdots \int_0^{x_3} dx_2 \times \]

\[
P_N(x_1, x_m, x, x_{m+1}, \ldots, x_N)
\]

where \( \zeta(y) \) is the same as in Eq. (S50), and \( 0 \leq x \leq L \).

In the thermodynamic limit, we can take advantage of scale separation, \( \lambda \ll L \rightarrow \infty \). Define \( x = k\lambda + \epsilon, 0 \leq k < L/\lambda = \Lambda \in \mathbb{N}, 0 \leq \epsilon \leq \lambda \). Eq. (S52) is rewritten as

\[
P^m_I(k, \epsilon) = \frac{\rho}{\zeta(L)} \left( \frac{N-1}{m-1} \right) \left[ 1 - \frac{k\lambda}{\zeta(L)} \right]^{N-m} \left[ \frac{x\zeta(L)}{\zeta(L)} \right]^{m-1} e^{-U(x)/(k_b T)},
\]

(S53)

and the entropy becomes \( s^m_I = -\sum_{k=0}^{\Lambda-1} \int_0^L dy P^m_I(k, \epsilon) \ln[v P^m_I(k, \epsilon)] \). Treating \( k \) as continuous and defining \( y = k\lambda \), we approximate (with an error \( O(\lambda/L) \)) the sum by an integral, \( \sum_{k=0}^{\Lambda-1} \rightarrow \lambda^{-1} \int_0^L dy \). Following another change of variables, \( u = y + \epsilon\zeta(L)/\zeta(L) \), we have \( u \) ranging from 0 to \( L \) (also up to an error \( O(\lambda/L) \)). This results in \( P^m_I(u, \epsilon) \) separating into a product of independent distributions for \( u \) (identical to Eq. (S48)) and for \( \epsilon \),

\[
P^m_I(u, \epsilon) = \rho \left( \frac{N-1}{m-1} \right) \left( 1 - \frac{u}{\lambda} \right)^{N-m} \left( \frac{u}{\lambda} \right)^{m-1} e^{-U(\epsilon)/(k_b T)},
\]

(S54)

The entropy becomes a sum of entropies,

\[
s^m_I = -\int_0^L du \int_0^\lambda d\epsilon P^m_I(u, \epsilon) \ln[v P^m_I(u, \epsilon)] + O \left( \frac{\lambda}{L} \right)
\]

\[= -\ln(\nu \rho) + \ln I_0(E) - \frac{E I_1(E)}{I_0(E)}. \]  

(S55)

Comparing Eqs. (S51) and (S55), \( s = s^m_I \), again giving some insight as to why Eq. (S29) is an equality. This conclusion applies for any periodic potential with \( \lambda \ll L \); for a periodic potential which is not sinusoidal, the \( \ln I_0(E) - EI_1(E)/I_0(E) \) terms will be different, but still the same in both Eqs. (S51) and (S55).