Anomalous Heat Diffusion

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Consider anomalous energy spread in solid phases, i.e., \( \langle \Delta x^2(t) \rangle_E \equiv \int (x - \langle x \rangle_E)^2 \rho_E(x, t) \, dx \propto t^\delta \), as induced by a small initial excess energy perturbation distribution \( \rho_E(x, t = 0) \) away from equilibrium. The second derivative of this variance of the nonequilibrium excess energy distribution is shown to rigorously obey the intriguing relation \( d^2 \langle \Delta x^2(t) \rangle_E / dt^2 = 2C_{JJ}(t) / (k_B T^2 c) \), where \( C_{JJ}(t) \) equals the thermal equilibrium total heat flux autocorrelation function and \( c \) is the specific volumetric heat capacity. Its integral assumes a time-local Helfand-like relation. Given that the averaged nonequilibrium heat flux is governed by an anomalous heat conductivity, the energy diffusion scaling determines a corresponding anomalous thermal conductivity scaling behavior.

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Fourier’s law of heat conduction states the relation between local heat flux and local temperature. In one dimension it assumes the familiar form \( j(x, t) = -\kappa \partial_x T(x, t) \), where \( j(x, t) \) is the local heat flux density, \( T(x, t) \) denotes the local equilibrium temperature, and \( \kappa \) is the (normal) thermal conductivity. Upon combining it with the local energy conservation law \( \partial_t \epsilon(x, t) + \partial_x j(x, t) = 0 \) and a local energy distribution relation \( \epsilon(x, t) = cT(x, t) \), we arrive at the heat equation describing the normal spread of energy, reading \( \partial_t \epsilon(x, t) = D_E \partial^2 \epsilon(x, t) \), wherein \( c \) denotes the specific volumetric heat capacity and \( D_E = \kappa / c \) is the thermal diffusivity [1].

Although Fourier’s law is obeyed ubiquitously in everyday experimental measurements for three-dimensional (3D) bulk materials possessing an inherent anharmonicity, it nevertheless remains an empirical law lacking a fundamental proof [2–5]. An open issue is its validity in the presence of spatial constraints caused by dimensionality. Indeed, a long-standing, mainly theoretical debate over the past two decades indicates that the Fourier law may fail in one- and two-dimensional momentum-conserving systems, thus giving rise to anomalous heat transport [4–8]. In such systems, given a temperature bias \( \Delta T \) across a sample of length \( L \), the nonequilibrium average heat flux typically scales not inversely with \( L \), but instead obeys a length-dependent scaling relation, i.e.,

\[
J = \sigma(L) \Delta T \equiv \kappa(L) \frac{\Delta T}{L}.
\]

Here, \( \sigma(L) \) denotes the heat conductance. Commonly, one then formally introduces \( \kappa(L) \equiv \sigma(L) L \) as an effective heat conductivity, which exhibits an anomalous length dependence [4,5]. Therefore, a strictly intensive material specific property such as heat conductivity generally does not exist, practically, at least, not on a finite length scale. A power-law divergence \( \kappa(L) \sim L^\alpha \) \((\alpha \neq 0)\) is typically observed for momentum-conserving 1D systems, while for 2D systems \( \kappa(L) \sim \log L \) [4,5]. It should be kept in mind, however, that such an effective thermal conductivity \( \kappa(L) \) then generally does not relate to the local heat flux density in terms of a local temperature gradient; consequently, Fourier’s law in its usual form no longer holds.

This intriguing length-dependent behavior has not only inspired a vivid theoretical activity [9–18] but also several intriguing recent experimental investigations [19–21] on low-dimensional materials such as polyethylene chains, single-walled carbon nanotubes, and, more generally, low-dimensional molecular chains. In all of these theoretical and experimental studies, an anomalous length dependence for \( \kappa(L) \) is clearly observed over extended length ranges. Here, our main objective is how such a length-dependent thermal conductivity behavior can be uniquely related to inherent, anomalous diffusive energy spread in solid phases.

Because Fourier’s law is connected to normal energy diffusion (see above), this violation of Fourier’s law has been studied as well from the viewpoint of unbounded anomalous particle diffusion \( x_p(t) \) in 1D billiard models [22–25], obeying \( \langle x_p^2(t) \rangle \propto t^\beta \), \( \beta \neq 1 \). There, noninteracting particles diffuse and transport (kinetic) energy anomalously. A scaling relation \( \alpha = \beta - 1 \) was predicted for the billiard models following a Lévy walk dynamic [25,26].
Notably, such a relation was verified by several numerical investigations on energy diffusion in 1D lattice systems [27–31]. Explicit analytical studies are, however, available for noninteracting Lévy walk models only [25,26]. Therefore, the result $\alpha = \beta - 1$ is still restricted to cases with non-confined particle diffusion rather than with energy diffusion in solid phases. With the particles executing small displacements about fixed lattice sites, the energy transport in solids thus proceeds distinctly different from unconfined particle motion. In other words, the definition of a mean square deviation (MSD) of energy, i.e., $\langle (\Delta x^2(t))_E \rangle = \langle x^2(t) \rangle_E - \langle x \rangle_E^2$, along space $x$ has no direct meaning from an unconfined, diffusing particle dynamics viewpoint. As a consequence, although those previous efforts aimed at bridging energy diffusion and heat conduction from the viewpoint of particle diffusion are inspiring, the general scheme of nonequilibrium energy diffusion still remains an open issue.

Here, we study the general features of energy diffusion using linear response theory. We derive the evolution of the nonequilibrium excess energy density profile during energy diffusion processes [27,28,30,31]. Based on this, we derive a dynamical equality that relates the acceleration of non-equilibrium energy spread $\langle \Delta x^2(t) \rangle_E$ to the equilibrium autocorrelation function of total heat flux $C_{JJ}(t)$. This relation thus provides a sound and useful concept to investigate nonequilibrium, generally anomalous heat diffusion.

**Local excess energy distribution.**—In the following, we limit the study of energy diffusion to isolated 1D systems with no energy and particle exchange with heat baths. The generalization to higher-dimensional cases is straightforward.

Typically, the diffusion of energy refers to a relaxation process in which an initially nonequilibrium energy distribution evolves towards equilibrium, just as the relaxation of particle distribution in normal diffusion. We term this nonequilibrium distribution the excess energy distribution, which is proportional to the deviation [27–31] $\delta(h(x,t))_{\text{neq}} \equiv \langle h(x,t) \rangle_{\text{neq}} - \langle h(x) \rangle_{\text{eq}}$, where $\langle \cdot \rangle_{\text{neq}}$ denotes the expectation value in the nonequilibrium diffusion process, $\langle \cdot \rangle_{\text{eq}}$ denotes the equilibrium average, and $h(x,t)$ denotes the local Hamiltonian density. An illustration of this relaxation process is depicted in Figs. 1(a) and 1(b) for the arbitrary form of an initial distribution along a Fermi-Pasta-Ulam (FPU) chain [32,33].

Note that, for isolated, energy-conserving systems, this total excess energy, $\delta E = \int \delta(h(x,t))_{\text{neq}} \, dx$, remains conserved [35]. Therefore, the normalized fraction of excess energy at a certain position $x$ at time $t$ reads

$$\rho_E(x,t) = \frac{\delta(h(x,t))_{\text{neq}}}{\delta E} = \frac{\delta(h(x,t))_{\text{neq}}}{\int \delta(h(x,0))_{\text{neq}} \, dx}. \quad (2)$$

This quantity formally presents the analog of a probability density for particle diffusion. In distinct contrast, however, being a reference density, it can take on negative values, cf. Fig. 1(a). Although not being a manifest probability density, it nevertheless remains normalized during time evolution, i.e., $\int \rho_E(x,t) \, dx = 1$. The MSD for energy diffusion thus reads

$$\langle (\Delta x^2(t))_E \rangle = \int \langle x \rangle_{\text{neq}}^2 \rho_E(x,t) \, dx = \langle x^2(t) \rangle_E - \langle x \rangle_{\text{eq}}^2. \quad (3)$$

Here, its first mean, $\langle x \rangle_{\text{neq}} = \int x \rho_E(x,t) \, dx$, remains constant in time, cf. the Supplemental Material [35]. This MSD, $\langle (\Delta x^2(t))_E \rangle$, can also assume transient negative values, reflecting the fact that it is the variance $\langle (\Delta x^2(t))_E \rangle$ of this nonequilibrium excess energy distribution that spreads in time $t$ rather than the equilibrium average $\langle (x(t) - x(t_0))^2 \rangle_{\text{eq}}$ of the displacements of particle positions [1].

The first main objective is the evaluation of this very excess energy distribution $\rho_E(x,t)$. In doing so, we use (Kubo) linear response theory as put forward originally for an ensemble of isolated systems [36–40]. We prepare at the infinite past a nonequilibrium state $f_{\text{neq}}$ in terms of a quenched canonical ensemble at temperature $T$, $f_{\text{neq}} \propto \exp(-\beta_T H_T)$, with a total Hamiltonian $H_T = H + H'$, where $\beta_T = 1/(\kappa_B T)$, $H = \int h(x) \, dx$. Here, the part $H'$ accounts for the applied small perturbation to $H$ by substituting in $H_T$ the local Hamiltonian density by $h(x) \rightarrow [h(x) - \eta(x) h(x)]$, $\eta(x) \ll 1$. This perturbation is
then switched off suddenly at time $t = 0$ [35]. This so-quenched initial nonequilibrium state subsequently undergoes an ergodic, isolated nonequilibrium dynamics governed by the unperturbed Liouvillian containing $h(x)$ only, which relaxes in the long-time limit towards the manifest equilibrium statistics with the canonical phase space density $f_{eq} \propto \exp(-\beta_T H)$.

As detailed in the Supplemental Material [35], the corresponding response function is given in terms of the equilibrium spatiotemporal correlation of local Hamiltonian density $h(x, t)$. The result explicitly reads

$$\delta \langle h(x, t) \rangle_{eq} = \frac{1}{k_B T} \int C_{hh}(x, t; x', t') \eta(x') dx',$$

(4)

where, for any two local quantities $a(x)$ and $b(x)$, we define $C_{ab}(x, t; x', t') = \langle \Delta a(x, t) \Delta b(x', t') \rangle_{eq}$, with $\Delta a(x, t) = a(x, t) - \langle a(x) \rangle_{eq}$. Being in equilibrium, these spatial-temporal correlations obey time-translational invariance, i.e., $C_{ab}(x, t + s; x', t' + s) = C_{ab}(x, t; x', t')$, for arbitrary $s$. For a homogeneous system, these equilibrium correlations $C_{ab}(x, t; x', t')$ become spatially translation invariant, yielding $C_{ab}(x - x', t - t')$. Note that this requirement for homogeneity does not exclude disordered situations; tailored disordered systems are also homogeneous as long as the disorder strength is uniform. Consequently, the total excess energy $\delta E = \int \delta \langle h(x, 0) \rangle_{eq} dx$ can be simplified to read

$$\delta E = \int dx dx' C_{hh}(x - x', 0) \frac{\eta(x')}{k_B T} = c T \int \eta(x') dx',$n

(5)

where $c$ is the volumetric specific heat capacity and $\int C_{hh}(x, 0) dx = k_B T^2 c$ has been used [35]. The normalized excess energy distribution (2) then reads

$$\rho_E(x, t) = \frac{1}{\mathcal{N}} \int C_{hh}(x - x', t) \eta(x') dx',$$

(6)

where $\mathcal{N} = k_B T^2 c \int \eta(x) dx$ is the normalization constant.

For the nonequilibrium heat flow response, it was not necessary to make use of the concept of a spatially dependent temperature $T(x)$. Such a spatially dependent temperature $T(x)$, if indeed it exists, would enter the result via the initial preparation of the quenched, displaced thermal equilibrium upon identifying the quasiforce $\eta(x)$ as the response function $\delta T(x)/T \ll 1$. The energy distribution $h(x)$ then couples formally to the conjugate thermodynamic affinity $\delta T(x)/T$, implying that $\beta_T [1 - \delta T(x)/T] h(x) = \beta_T T(x) h(x)$, cf. Refs. [38–40]. Moreover, no time-dependent local equilibrium temperature $T(x, t)$ enters the derivation in Eq. (4).

**Anomalous energy diffusion versus equilibrium heat flux correlation.**—The main result relating arbitrary ergodic energy diffusion to the equilibrium heat flux autocorrelation function can be obtained as follows. With the conservation of local energy $\partial_t h(x, t) + \partial_x j(x, t) = 0$, we obtain [35]

$$\partial^2_t C_{hh}(x, t) = \partial^2_t C_{jj}(x, t).$$

(7)

Additionally, defining $J_L = \int_{-L/2}^{L/2} j(x, t) dx$ to be the total heat flux for a 1D system of length $L$, we have

$$C_{jj}(t) \equiv \lim_{L \to \infty} \frac{1}{L} \int_j (J_L(t) J_L(0))_{eq} = \int_{-\infty}^{\infty} C_{jj}(x, t) dx,$$

(8)

This autocorrelation function of total heat flux $C_{jj}$ is the central quantity that knowingly enters the Green-Kubo formula for normal heat conductivity [36–41].

Upon combining Eqs. (3), (6), (7), and (8), we obtain the central result for the MSD:

$$\frac{d^2 \langle \Delta x^2(t) \rangle_E}{dt^2} = \frac{1}{N} \int x^2 \frac{\partial^2 C_{hh}(x - x', t)}{\partial x^2} \eta(x') dx dx'$$

$$= \frac{2C_{jj}(t)}{k_B T^2 c},$$

(9)

where an integration by parts has been used twice. This central equality constitutes an equation of motion for the MSD of general energy diffusion. The corresponding initial conditions are $\langle \Delta x^2(t = 0) \rangle_E = \int x^2 C_{hh}(x, 0) \eta(x') dx dx' / N - \int x \int C_{hh}(x, 0) \eta(x') dx dx' / N^2$ and $d \langle \Delta x^2(t) \rangle_E / dt|_{t = 0} = 0$. It is only the initial value for $\langle \Delta x^2(t) \rangle_E$ that exhibits a dependence on the initially chosen energy perturbation. The vanishing initial speed follows from the fact, that for an inertial dynamics, $C_{jj}(y, t)$ is an even function in time $t$, being continuously differentiable at time $t = 0$. Therefore, any physically realistic energy diffusion process will start out as a ballistic transport [42].

The numerical verification of the main finding in (9) is depicted in Fig. 1 for the theoretical archetype model of low-dimensional heat transfer, i.e., for a FPU chain, as detailed in [35]. Inset 1(a) is obtained by evaluating the linear response result (6) at dimensionless $T = 1$ from an initial small perturbation $\eta(x)$ with a positive and a negative Gaussian weight. In inset 1(b), the full nonequilibrium energy diffusion is simulated from an initial, near-equilibrium steady state using a preparation with heat baths of differing temperature. The energy diffusion proceeds after removing those heat baths. An ensemble of $4 \times 10^8$ realizations is used to obtain the depicted nonequilibrium energy density distribution $\rho_E(x, t)$ in Fig. 1(b). The total heat flux autocorrelation function $C_{jj}(t)$ is obtained in thermal equilibrium at a temperature $T = 1$ by averaging over an ensemble of $2 \times 10^9$ realizations. The specific heat, $c = 0.828$, is calculated analytically according to its definition. Very good agreement between theory and numerical experiments is obtained.

Let us recall the assumptions used in the derivation of this intriguing result: For the application of linear response
theory, the process is supposed to be sufficiently ergodic, implying that no nonstationary (i.e., ageing) phenomena for long-time correlations are at work, thus ensuring manifest relaxation towards thermal equilibrium. This crucial ergodicity assumption rules out all anomalous energy diffusion processes that undergo ageing, as it occurs in many continuous time random walk descriptions [43–47]. Those models, however, lack a microscopic Hamiltonian basis. There exists, however, ergodic anomalous diffusion dynamics stemming from a generalized Langevin equation [47–54]. Likewise, microscopic Hamiltonian models involving homogeneous disordered lattices exhibit subdiffusive heat conductivity [55,56]. Our result (9) is robust involving homogeneous disordered lattices exhibit subdiffusive heat conductivity [55,56]. Our result (9) is robust in the initial energy profile; it only affects fusive heat conductivity [55,56]. Our result (9) is robust in the initial energy profile; it only affects fusive heat conductivity [55,56]. Our result (9) is robust in the initial energy profile; it only affects fusive heat conductivity [55,56]. Our result (9) is robust in the initial energy profile; it only affects fusive heat conductivity [55,56]. Our result (9) is robust in the initial energy profile; it only affects fusive heat conductivity [55,56]. Our result (9) is robust in the initial energy profile; it only affects fusive heat conductivity [55,56].

Relation to the Helfand scenario.—Inspired by the Green-Kubo relation [36,41] for normal transport, Helfand showed that the average over the canonical initial thermal equilibrium of all phase space coordinates of the squared displacement of the appropriate “Helfand moment,” i.e., \( G_L(t) = \frac{1}{2} \int_0^L \langle x^2 \rangle dt \), obeys

\[
\langle G_L(t) - G_L(0) \rangle_{eq} / L = 2 \int_0^t (t - u) C_{JJ}(u) \, du.
\]

Therefore, taking the second time derivative, it follows with \( L \to \infty \) that

\[
\lim_{L \to \infty} \frac{d^2}{dt^2} \langle G_L(t) - G_L(0) \rangle_{eq} / L = 2C_{JJ}(t).
\]

(10)

Here, the initial conditions are \( \langle \Delta G^2(t = 0) \rangle_{eq} = 0 \) and \( d\langle \Delta G^2(t) \rangle_{eq} / dt \big|_{t=0} = 0 \). Consequently, the scaled equilibrium average of the squared displacement of the Helfand moment, i.e., \( \langle \Delta G^2(t) \rangle_{eq} / k_B T c \), differs from \( \langle \Delta x^2(t) \rangle_{E} \) by a constant shift, as determined by the initially chosen excess energy profile. In the absence of the main relation in (9), the mere result in (10) (with dimension [length(energy)\(^2\)]) alone cannot provide the result for the spread \( \langle \Delta x^2(t) \rangle_{E} \) of (anomalous) nonequilibrium energy diffusion. Observing the stated initial conditions, we next integrate (9) to yield the corollary

\[
\frac{d\langle \Delta x^2(t) \rangle_{E}}{dt} = \int_0^t \frac{2C_{JJ}(t')}{k_B T c} \, dt' = \frac{1}{k_B T c} \frac{d\langle \Delta G^2(t) \rangle_{eq}}{dt}.
\]

(11)

This finding can be interpreted as a time-local Helfand-like relation. This is true because, in contrast to the ordinary Helfand relation for normal heat conductivity, i.e., \( \kappa_{\text{normal}} = \langle \Delta G^2(t) \rangle_{eq} / \langle 2k_B T^2 \rangle \), no explicit time derivative enters [1,57,58]. In other words, Eq. (11) involves the time-local quantity \( d\langle \Delta x^2(t) \rangle_{E} / dt \) or \( d\langle \Delta G^2(t) \rangle_{eq} / dt \) rather than a finite-time version \( \langle \Delta x^2(t) \rangle_{E} / t \) or \( \langle \Delta G^2(t) \rangle_{eq} / t \).

This intriguing corollary (11) assumes an appealing form to establish the relationship between anomalous energy diffusion scaling and a generally anomalous scaling for the thermal conductivity \( \kappa(L) \) obeying \( J \sim \kappa(L) \Delta T / L \).

Normal energy diffusion.—For normal energy diffusion the MSD increases asymptotically linearly in time; i.e., \( \lim_{t \to \infty} \langle \Delta x^2(t) \rangle_{E} / t = 2D_E \). \( D_E \) is termed the thermal diffusivity. With time \( t \to \infty \) in (11), we find

\[
\kappa_{\text{normal}} = \int_0^{\infty} \frac{C_{JJ}(t)}{k_B T^2} \, dt = \frac{c}{2} \lim_{t \to \infty} \frac{d\langle \Delta x^2(t) \rangle_{E}}{dt} = c D_E.
\]

(12)

This is just the familiar Green-Kubo expression for normal heat conduction [1,36–41]. Arriving at this Green-Kubo relation, it is important to recall that, in all these cited derivations, one implicitly or explicitly uses the validity of Fourier’s law, together with local thermal equilibrium, i.e., a transport behavior for steady-state heat flux \( j(x) = -\kappa \nabla T(x) \). For a small thermal bias \( \Delta T \), the spatially constant gradient scales as \( \nabla T(x) = \Delta T / L \). This in turn implies a length scaling for normal heat conductivity, \( \kappa(L) = k L \Delta T / L \equiv \kappa_{\text{normal}} \), which is independent of system size. Normal heat diffusion being proportional to time \( t \) thus implies, with \( \beta = 1 \), the self-consistent scaling relation \( \alpha = \beta - 1 = 0 \).

Superdiffusive energy diffusion.—With ergodic superdiffusive energy diffusion obeying \( \langle \Delta x^2(t) \rangle_{E} \sim t^\beta \), \( 1 < \beta \leq 2 \), the time-local Helfand relation (11) possesses no long-time limit and the integral of \( C_{JJ} \) diverges as well. Therefore, no finite superdiffusive heat conductivity exists. The typical way out in practice [4,5,59,60], however, is to consider a finite system of length \( L \) and formally introduce an upper cutoff signal time \( t_c \) for heat transfer across the sample. In terms of a characteristic scale for the speed \( v_s \) of phonon transport, one sets \( t_s \sim L / v_s \); \( v_s \) is commonly approximated by the speed of sound, which is renormalized for nonlinearity [29]. By adopting this reasoning, the use of the time-local Helfand relation (11) then implies an asymptotic behavior:

\[
\kappa_{\text{super}}^L \sim \frac{1}{k_B T^2} \int_0^{L/v_s} C_{JJ}(t) \, dt = \frac{c}{2} \lim_{t \to \infty} \frac{d\langle \Delta x^2(t) \rangle_{E}}{dt} \bigg|_{t \to L/v_s}.
\]

(13)

This finite-time Green-Kubo relation implies for the length-dependent superdiffusive heat conductivity \( \kappa_{\text{super}}^L \sim L^\alpha \) the scaling relation

\[
\alpha = \beta - 1.
\]

(14)

This result corroborates the relation derived for a specific case of a billiard model where the particles undergo an \( a \text{ priori} \) assumed Lévy walk process [25,26].

Subdiffusive energy diffusion.—Let us next consider an ergodic energy subdiffusion with \( \langle \Delta x^2(t) \rangle_{E} \sim t^\beta \), \( 0 < \beta < 1 \). From the main relation in (9), it follows that
the total heat flux correlation $C_{JJ}(t) \sim \beta(\beta - 1)\beta^{-2}$. With the relation for the exponent, i.e., $\delta = \beta - 2 < -1$, we find that $C_{JJ}(t)$ remains integrable over the total time $[0, \infty)$. The time-local Helfand formula in (11) is thus applicable for $t \to \infty$, yielding

$$\kappa_{\text{sub}} = \lim_{t \to \infty} \frac{c \langle \Delta x^2(t) \rangle_{E}}{dt} \sim \lim_{t \to \infty} \beta^{-1} = 0,$$

which indicates a perfect thermal insulator. How does this vanishing of subdiffusive heat conductivity occur with increasing size $L$? If we likewise may impose in (11) a finite cutoff time scale $t_{c} \propto L$, we find that ergodic heat subdiffusion occurs with $\kappa_{\text{sub}} \sim L^{\alpha}$, $-1 < \alpha = \beta - 1 < 0$.

Conclusion.—In this work we studied anomalous heat diffusion in the absence of ergodicity breaking. The main finding in (9) relates dynamically the acceleration of the nonequilibrium energy MSD directly to the equilibrium autocorrelation $C_{JJ}(t)$ of the total heat flux. Equivalently, this result assumes the form of a time-local Helfand relation as specified with (11). Given the premise that anomalous stationary heat flux follows a behavior in terms of an anomalous heat conductivity, i.e., $k(L) \sim L^{\alpha}$, then implies the scaling $\alpha = \beta - 1$. Because (9) applies for all times $t$, it can be invoked as well for those intermediate cases where an anomalous, length-dependent heat conductivity occurs over a finite size [10–18].

The similarity between the global Helfand moment scenario used for normal diffusion in Ref. [1] with the time-local result in (11) suggests analogous relations as in (9) to hold for other anomalous diffusion processes. Particularly, what comes to mind is unbiased, anomalous particle diffusion $x_{p}(t)$. Unlike for energy diffusion in solid phases, the position increments, i.e., $\langle x_{p}(t) - x_{p}(s) \rangle = \int_{s}^{t} x_{p}(t') dt'$, are now given in terms of the particle velocity $v_{p}(t)$. Indeed, with ergodic anomalous diffusion obtained from an equilibrium generalized Langevin equation dynamic [47,50–54], with $x_{p}(t)$ and $\langle v(t) \rangle_{eq}$, $m\langle v^{2}(t) \rangle_{eq} = k_{B}T$, it readily follows that (9) implies $d^{2}\langle x^{2}(t) \rangle/dt^{2} = 2\langle v(t)v(0) \rangle_{eq}$ for all times $t$ [61].

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