Gauge optimization of time series for thermal-transport simulations

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Thermal and other transport coefficients were recently shown to be largely independent of the microscopic representation of the energy (current) densities or, more generally, of the relevant conserved densities/currents. In this paper we show how this gauge invariance, which is intimately related to the intrinsic indeterminacy of the energy of isolated atoms, can be exploited to optimize the statistical properties of the current time series from which the transport coefficients can be evaluated. To this end, we make use of a variational principle that relies on the metric properties of the conserved currents, treated as elements of an abstract linear space. Different metrics would result in different variational principles. We finally show how a recently proposed data-analysis methodology based on the theory of transport in multi-component systems can be recovered by a suitable choice of this metric.

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The concept of gauge invariance of transport coefficients was introduced and explored in recent works, in the particular case of thermal transport. In its utmost generality, this principle asserts that transport coefficients, such as thermal and electrical conductivity, are largely independent of the detailed form of the local representation of the conserved quantity (energy, charge, mass) being transported.

The marriage between first-principles simulations and the Green-Kubo (GK) theory of linear response for thermal conductivity calculations was quite recent, as it has long been believed that density-functional theory (DFT) was incompatible with the GK formalism. This misconception indeed originated from the observation that the energy density, from which the heat current and ultimately the thermal conductivity are derived, is ill-defined at the microscopic scale. In fact, any choice of a microscopic energy density that integrates to the same total energy is equivalent and defines a different gauge. Different gauges give rise to fluxes that differ from one to the other by the total time derivative of a bounded vector, which does not contribute to the thermal conductivity, thus making it gauge invariant, but ultimately affecting the statistical properties of its estimator. In a similar fashion, the gauge-invariance principle, together with topological quantisation of adiabatic charge transport, allows one to express the electrical conductivity of an insulating fluid in terms of integer, constant, scalar oxidation numbers, thus avoiding the use of real, time-dependent, tensor Born effective charges, which are cumbersome and expensive to compute.

In this contribution we introduce a general variational approach that can be leveraged to find an “optimal” gauge, that is a definition that optimizes the statistical properties of the estimator of the transport coefficient, thus reducing simulation times as much as possible. Such an operation reveals to be particularly useful when dealing with first-principles simulations, where “natural” definitions of the currents may lead to numerical hurdles. We focus on the estimation of thermal conductivity and we specialize our analysis to solids and one-component molecular liquids, thus neglecting multi-component liquid systems, where the total momenta of individual species should be considered to correctly define the heat current. In addition, we assume the materials to be electronic insulators. Our discussion will be otherwise as general as possible and will include examples from classical molecular dynamics (MD) and DFT. The latest will follow the GK formulation developed in Ref. 1, even if it is possible that different forms of the GK heat flux will be affected by the same numerical issues we are going to discuss to a larger or smaller extent. With this work we want to highlight some general phenomena and techniques that we believe must be taken into account and used either to develop new formulations of the GK current or to reduce the computational overhead of the existing ones.

The rest of the work is organized as follows. In Sec. I we introduce our general variational approach and discuss in a qualitative way the origin of the slowly-decaying signals, which can particularly affect first-principles simulations of transport coefficients. In Sec. II we discuss theoretically and numerically two implementations of the general theory, introducing a naive decorrelation technique and a more straightforward renormalization procedure, which shows some computational advantages. In Sec. III we show how a different implementation of our variational approach is conceptually equivalent to a framework naturally arising in the multi-component theory of heat transport, also providing novel insight into the known formulas. Finally, Sec. IV contains our conclusions.
I. THEORY

A. Variational formulation

In one-component isotropic systems the GK equation expresses the thermal conductivity in terms of the time autocorrelation function of the energy flux as:

\[ \kappa = \frac{1}{3V k_B T^2} \int_0^\infty \langle \mathbf{J}(t) \cdot \mathbf{J}(0) \rangle \, dt, \]  

where \( V \) is the system’s volume, \( k_B \) the Boltzmann constant, \( T \) the temperature, \( \mathbf{J} = \int \mathbf{j}(\mathbf{r}) \, d\mathbf{r} \) is the macroscopic energy current, usually referred to as the heat (or energy) flux, \( \mathbf{j}(\mathbf{r}) \) is the energy current density and \( \langle \cdot \rangle \) in this work indicates an equilibrium average over molecular trajectories in the microcanonical (NVE) ensemble. The integral of the autocorrelation function of the energy flux in Eq. 1 can also be interpreted as the zero-frequency component of its power spectrum, and is often called the GK integral. The energy flux \( \mathbf{J} \) is an example of a real observable, \( i.e. \) a function of the phase space \( \Omega \), described by instantaneous positions and velocities \( \Gamma \equiv (\mathbf{r}_i, \mathbf{v}_i) \) of all particles of the system. The set \( O \) of all such observables is naturally endowed with the structure of a real vector space, via pointwise addition and multiplication.

Particularly in \textit{ab initio} simulations, reaching convergence of the GK integral can pose serious challenges, as for example was observed in the case of liquid water\cite{H2O} or silica glass\cite{SiO2}. Whenever an energy-flux time series shows a slow convergence and high variance, one may suspect the presence of non-diffusive components. We say a signal is \textit{non diffusive} whenever its associated GK integral is equal to zero, corresponding to a vanishing conductivity. Interestingly, adding a non-diffusive energy flux to a diffusive one does not change the value of the transport coefficient, an intuitive result that was rigorously proven in Ref. \cite{H2O}. Nevertheless, non-diffusive terms may increase the power of the noise of the time series to a level that compromises its analysis or makes a numerical estimate too expensive. This suggests one to devise new “optimized” definitions of the energy flux, where signals known to be non-diffusive are hence subtracted. Identifying the sources of such “inert” fluxes is the first step either to develop novel definitions of the GK currents, where such contributions are reduced, or to devise \textit{ad hoc} post-processing techniques able to magnify the relevant signals.

We will discuss how formation and self-energy contributions, present in DFT calculations, are significant sources of inert signals. Let us suppose for the moment that a set of linearly independent non-diffusive signals \{\( \mathbf{Y}_n \), \( n = 1, \ldots, N \} \) can be identified. By induction, for every choice of some \{\( \lambda_n \)\} coefficients, a new time series:

\[ \mathbf{J}' = \mathbf{J} - \sum_n \lambda_n \mathbf{Y}_n, \]  

will provide, with infinite sampling, the same thermal conductivity as the one computed using the original heat flux \( \mathbf{J} \). In order to minimize the computational overhead, we should minimize the magnitude of inert signals included. To achieve this goal, let us introduce a generic scalar product \( \langle \cdot, \cdot \rangle \) on the vector space \( O \) of observables, inducing a norm \( \|A\| = \sqrt{\langle A, A \rangle} \). For the moment, we leave the scalar product generic. We now propose to choose as optimal coefficients the ones that minimize the function:

\[ f(\{\lambda_n\}) = \|\mathbf{J} - \sum_n \lambda_n \mathbf{Y}_n\|^2, \]  

which is the standard loss function used in a multiple-linear regression framework. From a geometrical point of view, the chosen \( \mathbf{J}' \) is the component of \( \mathbf{J} \) orthogonal to the subspace generated by the non-diffusive signals. We note that, as long as the scalar product is positive definite (\( i.e. \) \( \langle A, A \rangle > 0 \)), if \( A \neq 0 \) and the non-diffusive signals are linearly independent then the quadratic form in Eq. 3 is positive definite and has unique minimum.

B. Origin of slow-decaying signals

One of the most important sources of inert signals that can be identified is related to the large formation energies considered in first-principles simulations. These energies do not influence the equilibrium dynamics of a system\cite{formation} and are defined up to a reference level describing the initial phase of its elemental constituents. In first-principles simulations, one is often forced to set the latter at the unphysical situation where all atoms are fully ionized and, as a consequence, the energy density is largely dominated by a term of the form \( \sum_i \epsilon S(i) \delta(\mathbf{r} - \mathbf{r}_i) \), \( \epsilon^A \) being the formation energy of species \( A \), \( S(i) \) the species of the \( i \)-th atom, and \( \mathbf{r}_i \) its position. This energy silently moves with the associated atom and does not contribute to the thermal conductivity, which instead is determined by the diffusive behavior of the energy exchanged between atoms. Nevertheless, when a formation energy is considered, a large and fluctuating term

\[ \mathbf{J}^A = \epsilon^A \mathbf{V}^A \]  

will be added to the energy current. Here \( \mathbf{V}^A = \sum_{i \in A} \mathbf{V}_i \) indicates the sum of the velocities of atoms of species \( A \), also referred as the macroscopic component of the \textit{particle current} of species \( A \). To fix notation, in this work capital Latin letters refer to atomic species, and Latin lowercase letters refer to atomic indexes; Greek letters are reserved for Cartesian coordinates, and a summation over repeated Cartesian indexes is implied. The GK formalism handles formation energies contributions in a correct way. In a mono-atomic fluid, \( \mathbf{J}^A \) is constant because of momentum conservation and it is equal to zero in the center-of-mass reference frame. It is clearly a non-zero, non-diffusive, signal in solids, since atoms individually do not diffuse. Furthermore, it can be proven that the
particle currents are non-diffusive in molecular fluids as well. We refer to Refs. [10,12] for the derivation of this result, which follows from the conservation of total momentum and the assumption that inter-molecular bonds do not break. In a DFT framework, the electrostatic self-interaction of electronic clouds can also introduce non-diffusive contributions. It is possible to show that all these phenomena do not contribute to the thermal conductivity, exploiting also the fact that the electronic current in an insulator is a non-diffusive signal. A more detailed discussion is reported in Appendix A.

In general the energy of isolated atoms is not considered in classical, semi-empirical Hamiltonians. Nevertheless, atomic energies are still defined by partitioning the interatomic energies, and their temporal mean is in general non-zero. As will become clearer later, mean atomic energies are several orders of magnitude lower than the typical first-principles formation energies, thus leading to smaller inert fluxes.

II. TECHNIQUES

The most common choice of scalar product between two real observables \( A, B \in \mathcal{O} \) is given by the static cross-correlation, which we refer to as the Boltzmann scalar product:

\[
(A, B)_{\text{B}} \equiv \langle AB \rangle = \int_{\Omega} P_{\text{NVE}}(\Gamma) A(\Gamma) B(\Gamma) \ d\Gamma,
\]

where \( P_{\text{NVE}} \) is the constant energy distribution of the microcanonical ensemble, explored ergodically via Hamiltonian dynamics. The last expression makes it clear that the Boltzmann scalar product is positive definite. In this section we will explore two different optimization techniques based on this choice of the metric.

A. Decorrelation

The projection onto the subspace orthogonal to the inert fluxes, Eq. (2), can be performed by simply differentiating Eq. (3) with respect to \( \lambda_m \) and obtaining the linear system:

\[
\langle \mathbf{J} \cdot \mathbf{Y}_n \rangle - \sum_m \lambda_m \langle \mathbf{Y}_m \cdot \mathbf{Y}_n \rangle = 0, \quad \forall n = 1, \ldots, N. \tag{6}
\]

The thermal conductivity can be then computed via the GK equation (1), by replacing \( \mathbf{J} \) with \( \mathbf{J}' \), that is defined in Eq. (2) using the \( \{\lambda_n\} \) coefficients that solve Eq. (6). The drawbacks of this procedure are two-fold. First, one needs to compute the coefficients \( \{\lambda_n\} \) numerically a posteriori. Second, the new energy current \( \mathbf{J}' \) is computed from the difference of the original current and the weighted inert fluxes, i.e. a difference of signals of large amplitude. This can pose practical challenges e.g. when choosing the simulation metaparameters, that need to be set \textit{a priori} for computation of the heat flux (e.g. density cutoffs). Nevertheless, this is the approach followed, under a more specialized setting, in Ref. [1] and we refer to it as the decorrelation technique, since the solution of Eq. (6) is equivalent to imposing that the current \( \mathbf{J}' \) is decorrelated with respect to each inert signal \( \{\mathbf{Y}_n\} \).

B. Velocity renormalization

Here we propose a more convenient renormalization procedure, which turns out to be numerically equivalent to the decorrelation technique when \( \mathbf{Y} = \{\mathbf{V}^A\}_{A \in S} \) (where \( S \) is the set of species of the system), but does not require the solution of any linear system and involves only operations with small-amplitude signals. From the discussion of the previous paragraph, the main sources of inert signals indeed appear to be of the form of Eq. (4). The renormalization technique applies to any heat current \( \mathbf{J}_{\text{bare}}(\{\mathbf{r}_i, \mathbf{v}_i\}) \), written as a function of the atomic coordinates \( \{\mathbf{r}_i, \mathbf{v}_i\} \). Let \( \mathbf{W}^A \) be the velocity of the center of mass of atoms of species \( A: \mathbf{W}^A = \mathbf{V}^A / N^A \). The renormalized heat current is then readily defined as:

\[
\mathbf{J}_{\text{ren}}(\{\mathbf{r}_i, \mathbf{v}_i\}) \equiv \mathbf{J}_{\text{bare}}(\{\mathbf{r}_i, \mathbf{v}_i - \mathbf{W}^{S(i)}\}). \tag{7}
\]

The renormalized current can be computed without any coding effort by any program providing an energy current, by replacing input velocities \( \mathbf{v}_i \) with their renormalized values \( \mathbf{v}_i' \equiv \mathbf{v}_i - \mathbf{W}^{S(i)} \) and leaving the positions unchanged. Despite its simplicity, this simple tweak has an impact on the convergence properties of the resulting energy current. A priori, the thermal conductivity computed from Eq. (1) using either the bare or renormalized currents can differ, but we will prove that in solids, mono-atomic and molecular fluids \( \kappa_{\text{ren}} = \kappa_{\text{bare}} \), thus formally justifying the renormalization procedure for these classes of systems. Let us notice that the renormalized current is not directly derived from a different decomposition of the energy density, therefore we cannot use the same arguments presented in the introduction and discussed in Ref. [1]. The non-diffusive behavior of the \( \mathbf{W}^A \) signal plays a central role in the derivation: at an intuitive level, the renormalization procedure, by setting the macroscopic particle currents to zero, is able to remove such a spurious signal from the original energy current. In this way, it provides a time series with reduced spectral power, i.e. a lower variance, that improves the convergence properties of the estimator of \( \kappa \). In particular, the renormalization method, differently from the decorrelation technique, does not require the intermediate computation of any ad hoc coefficients.

We demonstrate the effectiveness of this procedure by performing several classical simulations of liquid water at ambient conditions, adding a fictitious formation energy term to each species and studying the effects on
the resulting energy currents. Simulations were carried out using the LAMMPS molecular dynamics code\cite{plimpton1995fast} at ambient conditions, considering a flexible model of water\cite{grievink2011nonequilibrium} and an integration time step of 0.5 fs. A species-dependent shift was added to the instantaneous atomic energies: \( \epsilon_i \rightarrow \epsilon_i + \tau^{S(t)} \). We chose small values for the formation energies: \( \tau^{H} \approx -0.2, -0.4 \text{ eV} \), and \( \tau^{O} \approx -0.4, -0.9 \text{ eV} \), i.e., values that are higher than the typical interaction energies but much lower than the formation energies considered in DFT. Even such a small perturbation can have an impact on the convergence properties of the GK current. In Fig. 1(a) we plot the thermal conductivity estimated by a direct integration of Eq. (1), as a function of the upper integration limit, using the original definition of the energy current \( J^{(0,0)} \), several definitions with additional formation energies \( J^{(\epsilon_H, \epsilon_O)} \), and the latter after renormalization was applied \( J^{\text{ren}} \). The addition of formation energies increases the variance of the time series and slows down the convergence of the GK integral, thus requiring one to run longer simulations in order to converge the integral with similar accuracy. Nevertheless, as expected, all the integrals converge to the same value after a sufficient integration time. Once the renormalization procedure is performed, the convergence becomes much faster and the integral resembles to the one computed from \( J^{(0,0)} \). Notice that renormalizing any of the time series returns exactly the same \( J^{\text{ren}} \). Additional information can be inferred from the power spectrum of the energy current, defined as \( S(\omega) = \frac{1}{\tau} \left| \int_{0}^{\tau} J(t) e^{i\omega t} \, dt \right|^2 \) and plotted in Fig. 1(b), which clearly shows that formation energies lead to an increase in the power of the signal (the integral of the spectrum). The zero-frequency value of the spectrum, which is proportional to the thermal conductivity\cite{figgatt2013dynamical}, is not affected by the definition used, but becomes more and more difficult to estimate when larger formation energies are considered, due to the fast increase of \( S(\omega) \) at \( \omega \approx 0 \).

We now repeat the same kind of analysis in an \textit{ab initio} framework considering amorphous silica, a-SiO\(_2\), a multi-component solid, at \( \sim 350 \text{ K} \). For the scope of this calculation and to save computational time we considered a small cell of 72 atoms, we generated the trajectory via the classical BKS interatomic potential\cite{brenner1998bks} and for 10000 snapshots (corresponding to 100 ps of trajectory) we computed the energy current using the classical and \textit{ab initio} definitions. Finally, we applied the renormalization procedure to the latter. Let us remark that in order to compute \( \kappa \) from first principles one should generate the trajectory by \textit{ab initio} MD, nevertheless we use this expedient to observe the effects of the different energy-current definitions, without including the effects of the different dynamics. For the DFT calculations we used the QUA\textsc{ntum ESPRESSO} package\cite{giannozzi2009quantum} with a PBE functional\cite{kresse1993ab}, a plane-wave cutoff of 80 Ry, and optimized norm-conserving Vanderbilt pseudopotentials (ONCVP)\cite{gonze1997accurate}. In Fig. 2(a) we plot the GK integrals, which feature very large oscillations, making a direct estimate of \( \kappa \) extremely difficult. In particular, the integral of the DFT bare energy current \( J_{\text{bare}}^{\text{DFT}} \) is out of scale and is not shown. Much more information can be gained from the power spectra of the currents, reported in Fig. 2(b) on a logarithmic scale. We immediately notice the much larger power of the \( J_{\text{bare}}^{\text{DFT}} \) time series (solid green) with respect to the classical one (dotted blue). Indeed, the standard deviation of \( J_{\text{bare}}^{\text{DFT}} \) is 25 times larger than the classical one \( J_{\text{bare}}^{\text{cl}} \), and in both cases the renormalization reduces the standard deviations of a factor \( \approx 5 \). The huge power of the DFT current makes an estimate of \( \kappa \) impossible to converge to physical values with the trajectory lengths attainable with \textit{ab initio} MD. Renormalization allows one to solve this problem and to obtain meaningful results, which are also compatible with the classical values, as reported in Table I.

It is possible to prove formally the equivalence of the transport coefficients computed from the bare and renormalized currents, \( \kappa_{\text{bare}} = \kappa_{\text{ren}} \), starting with the follow-
Any atomic energy current, defined as the time derivative of the moment of an energy density, can be reduced to such a form, the matrices $\varepsilon_{\alpha,\beta}$ being functions of coordinates only (dependent on the local environment) and not of particle velocities. From Eq. (7) and after some manipulations, the renormalized current can be related to the bare one:

$$J_{\text{ren},\alpha} = J_{\text{bare},\alpha} - \sum_{A \in S} h^A_{\alpha,\beta} V^A_{\beta} + J'_{\alpha},$$

where the precise forms of the $h$-matrices and the residual current $J'$ are provided in Appendix B. Adding a non-diffusive signal does not change the transport coefficient: the desired result will thus follow from the non-diffusivity of the signal $\Delta J = J_{\text{bare}} - J_{\text{ren}} = \sum_{A \in S} h^A V^A - J'$. In Appendix B we show that this residual current $J'$ can be neglected in the thermodynamic limit, leading to the relation:

$$\frac{1}{V} \langle \Delta J(t) \cdot \Delta J(0) \rangle dt \sim \sum_{A, B \in S} h^A_{\alpha,\beta} h^B_{\alpha',\beta'} \frac{\langle V^A(t) V^B(0) \rangle}{V}.$$  

The expectation value $\frac{1}{V} \langle V^A(t) V^B(0) \rangle \sim O(1)$, thus bringing a non-vanishing contribution in the thermodynamic limit. However, as already observed, in solids, amorphous materials and one-component molecular liquids the signals $V^A$ are non-diffusive and therefore every cross-correlation $\langle V^A(t) V^B(0) \rangle$ has a vanishing zero-frequency component, as a consequence of the lemma in Ref. [1]. Therefore, even if the signal $\Delta J$ in general shows a non-zero autocorrelation function, its integral from zero to infinity has a vanishing value in the thermodynamic limit.

As a benchmark of our reasonings we plot the time integral of the autocorrelation function of $\Delta J$ computed for the classical water model presented before. We focus our attention on the thermodynamic scaling for large number of atoms $N_{\text{at}}$ of the function:

$$N_{\text{at}} \Delta \kappa(\tau) = \frac{N_{\text{at}}}{3 V k_B T^2} \int_0^\tau \langle \Delta J(t) \Delta J(0) \rangle dt,$$

plotted in Fig. [3]. From our previous arguments two different thermodynamic scaling regimes are expected and observed as a function of $\tau$: at short time lags $\Delta \kappa(\tau)$ tends to a finite value (in the thermodynamic limit) given by Eq. (10), thus $N_{\text{at}} \Delta \kappa(\tau)$ diverges linearly with $N_{\text{at}}$; at long time lags the contribution given by Eq. (10) integrates to zero and we observe that $N_{\text{at}} \Delta \kappa(\tau)$ tends to a finite limit, hence $\Delta \kappa(\tau) \sim O(1/N_{\text{at}})$. 

![Graph 1](image1.png)

**FIG. 2.** Analysis of different definitions of the energy current of a 72-atom sample of a-SiO$_2$. The original $J_{\text{bare}}$ classical (CL) and DFT definitions have been renormalized, obtaining $J_{\text{ren}}$. Also reported are the same currents decorrelated with respect to the particle current of one species (VD), the electronic current (ED), or both (VED). (a) Thermal conductivity computed from the GK equation, Eq. (1), as a function of the upper integration limit. The result of the bare DFT current is out of scale and has been omitted. (b) Power spectrum of the energy currents. The zero frequency corresponds to $\kappa$.

| $J$ definition | a-SiO$_2$ | H$_2$O |
|---------------|----------|--------|
| DFT bare      | 25.5 ± 5.9 | 740 ± 140 |
| DFT ren       | 1.31 ± 0.29 | 1.18 ± 0.17 |
| Classic bare  | 1.32 ± 0.29 | — |
| Classic ren   | 1.28 ± 0.26 | — |
| DFT bare, ED  | 1.30 ± 0.28 | 0.99 ± 0.15 |
| DFT bare, VD  | 2.79 ± 0.61 | 341 ± 46 |
| DFT bare, VED | 0.95 ± 0.21 | 0.82 ± 0.12 |
| DFT ren, ED   | 1.11 ± 0.24 | 1.03 ± 0.15 |

**TABLE I.** Thermal conductivities (W/mK) estimated via cepstral analysis from different definitions of the energy current. VD, ED, and VED indicate a current that has been decorrelated with respect to the particle current of a species $V^A$, the electronic current $J_{el}$, or both, respectively. Errors are one standard deviation.

ing generic expression of a component of a GK energy flux:

$$J_{\text{bare},\alpha} = \sum_i \left( \frac{1}{2} m_i v_i^2 \right) v_i, \alpha + \sum_i \varepsilon_{\alpha,\beta}^{i} \langle \{r\} \rangle v_i, \beta.$$  

(8)
be neglected, one has that \( \Delta \kappa (\tau) \) at fixed \( \tau \), as a function of \( N_\text{at} \). At short times the magnitude grows with \( N_\text{at} \), since \( \Delta \kappa (\tau) \) tends to a finite limit; instead, the converged value for large \( \tau \) remains stable and compatible with a \( O(1/N_\text{at}) \) decay of \( \Delta \kappa (\tau) \).

C. Comparison between decorrelated and renormalized currents

The theoretical relation between the two methodologies relies on the fact, proven in Appendix [C], that in the thermodynamic limit the coefficients \( h \) in Eq. (9) solve the same linear system derived by the decorrelation criterion, Eq. (6), when \( Y = \{ V^A \} \). According to Eq. (9), since in the thermodynamic limit the residual current can be neglected, one has that \( J^\text{ren} \sim J^\text{bare} - \sum A \epsilon h^A V^A \) and therefore the decorrelation becomes equivalent to the energy-flux renormalization. This result poses an application of both methods on solids grounds. The decorrelation technique, however, can also be performed with respect to other types of non-diffusive signals, such as the adiabatic electronic current \( J^\text{el} \).

We compare numerically the two techniques using the \textit{ab initio} energy currents of a-SiO\(_2\) and reporting all the estimated thermal conductivities in Table I. These values and their statistical errors have been obtained using the cepstral analysis technique\([23]\). As we previously noted, the bare current \( J^\text{DFT} \) leads to an overestimation of \( \kappa \) that can be corrected by applying the renormalization procedure. Equivalently, one could decorrelate \( J^\text{DFT} \) from one particle current \( \epsilon^\text{bare} \), i.e., \( V^\text{SI} \) or \( V^\text{O} \), thus obtaining a signal (VD) that gives a \( \kappa \) compatible with the one obtained from \( J^\text{ren} \). We also notice that the power spectra of these two signals are almost identical (dashed pink and solid red lines in Fig. 2(b)), confirming the equivalence of the decorrelation and renormalization methods. As one may suspect, the decorrelation has no effect when applied to \( J^\text{ren} \), in which the sum of all the renormalized velocities is zero by construction (see Appendix [C] for a formal justification). Furthermore, one can try to decorrelate a current with respect to other non-diffusive signals, such as the electronic current, \( J^\text{el} \). When applied to \( J^\text{DFT} \) or \( J^\text{bare,VD} \), we obtain a signal (labelled ED or VED, respectively) whose power is reduced by an additional factor of \( \approx 3 \), and that gives a compatible thermal conductivity. Instead, decorrelating the bare current \( J^\text{DFT} \) only with respect to \( J^\text{el} \) (ED, solid purple line) does not lead to a compatible value of \( \kappa \), a fact suggesting that the particle current is the largest source of inert signals in this system.

Finally, we performed the same analysis on \textit{ab initio} heavy water at ambient conditions. The simulation was performed with the same setting of Ref. [1]. Similarly to silica, an analysis of the bare current \( J^\text{DFT} \) returns an unphysical value of \( \kappa \), reported in Table I. The renormalization procedure or the decorrelation with respect to a particle signal should be applied in order to obtain a physical value of \( \kappa \), which is compatible with the one originally estimated by [Marcolongo et al.]. Moreover, a decorrelation with respect to the electronic current \( J^\text{el} \) can also be applied, thus giving compatible results. The GK integrals and the power spectra of the energy current for the different definitions are displayed in Fig. 3.
III. RELATION WITH THE MULTI-COMPONENT FORMALISM

The variational framework presented in this work can be exploited to rederive, in an alternative way, the formulas for thermal conductivity presented in Ref. [7] for multi-component systems. This derivation will provide a different interpretation and novel insight. Let us use in Eq. (3) the following Green-Kubo scalar product between two generic fluxes $A, B$:

\[ (A, B)_{\text{GK}, \omega} \equiv \frac{1}{2} \int_{-\infty}^{\infty} (A(t)B(0)) e^{i\omega t} dt, \tag{12} \]

which is symmetric, bilinear and real. The symmetry property follows from the identity $\langle A(t)B(0) \rangle = \langle B(t)A(0) \rangle$, while the scalar product is real because $\langle A(t)B(0) \rangle = \langle A(t)B(0) \rangle$. Both identities follow from Onsager’s principle of microscopic reversibility\(^{(21)}\) and reminding that fluxes are odd under time reversal. $(A, B)_{\text{GK}, \omega}$ is also known as the cross-power spectrum, and $(A, A)_{\text{GK}, \omega}$ is the power spectrum of $A$, which is always $\geq 0$ for stationary signals. We note that the GK scalar product is well defined on the subspace generated by a set of signals that are odd under time reversal, and it depends parametrically on the chosen frequency $\omega$. For small $\omega \neq 0$ we can assume the scalar product to be positive definite, whereas any non-diffusive signal has zero norm at $\omega = 0$. Later we will discuss the limit $\omega \to 0$.

Following Ref. [7] let us consider a multi-component system characterized by $M$ linearly independent, conserved fluxes $J_i$, $i = 0, \ldots, M - 1$, individually diffusive and where $J_0$ is the energy flux. We shall show that, by taking $\mathbf{Y} = \{J_i\}_{i=1}^{M-1}$ and applying the variational framework with respect to the GK scalar product Eq. (12), we can recover the formulas of the multi-component theory. To this purpose let us define the (frequency-dependent) matrices:

\[
\Lambda_{i,j}(\omega) \equiv \langle J_i, J_j \rangle_{\text{GK}, \omega}, \quad i, j = 0, \ldots, M - 1, \tag{13} \\
\Sigma_{i,j}(\omega) \equiv \Lambda_{i,j}, \quad i, j = 1, \ldots, M - 1, \tag{14} \\
K_i(\omega) \equiv \Lambda_{i,0} - \Lambda_{0,i}, \quad i = 1, \ldots, M - 1, \tag{15}
\]

where $\Lambda$ and $\Sigma$ are symmetric and $K$ is a column vector. We now define: $J_0'(\omega) = J_0 - \sum_{i=1}^{M-1} \lambda_i(\omega)J_i$. For each $\omega$, the vector of coefficients $\{\lambda_i(\omega)\}_{i=1, \ldots, M-1}$ that minimizes Eq. (3) (i.e. the power spectrum $\|J_0 - \sum_{i=1}^{M-1} \lambda_i(\omega)J_i\|_{\text{GK}, \omega}$) is then obtained by decorrelating the energy flux $J_0$ with respect to the other particle fluxes and solving the linear system: $\lambda(\omega) = \Sigma(\omega)^{-1}K(\omega)$. If we apply the (frequency dependent) GK formula, Eq. (1), to the optimized energy flux $J_0'(\omega)$, we obtain:

\[
\kappa(\omega) = \frac{1}{3V k_B T^2} \left( \mathbf{J}_0 - \sum_{i=1}^{M-1} \lambda_i(\omega)\mathbf{J}_i \right)_{\text{GK}, \omega}.
\]

An explicit computation leads to:

\[
\kappa(\omega) = \frac{1}{3V k_B T^2} \left( \Lambda(\omega)_{0,0} - K(\omega)^\top \Sigma(\omega)^{-1} K(\omega) \right) = \frac{1}{3V k_B T^2} \left( \Lambda(\omega)_{0,0}^{-1} \right), \tag{17}
\]

where the last equality follows from writing the inverse of the $\Lambda$ matrix in a block form. Interestingly, in the $\omega \to 0$ limit Eq. (17) becomes exactly the expression of the thermal conductivity for multi-component systems, which is usually derived from the Onsager relations by imposing the vanishing of all the mass fluxes\(^{(62)}\). The matrix $\Lambda_{i,j}(\omega = 0) = \langle J_i, J_j \rangle_{\text{GK}, \omega=0}$ can be assumed to be invertible in a multi-component setting. Furthermore, $\kappa(\omega)$ is proportional to the so-called reduced spectrum that was defined in Ref. [7]. As a bonus, our derivation from a general variational principle shows that the reduced spectrum is always lower than the power spectrum of both the original and the decorrelated signal.

In Ref. [7] the multi-component formalism was also applied as a tool to remove spurious signals in polyatomic liquids, by considering the energy flux $J_0$ and a generic set of inert signals $\{J_i\}_{i=1, \ldots, M-1}$. In this case the only non-zero element of $\Lambda(\omega = 0)$ is $\Lambda(\omega = 0)_{0,0} = \langle J_0, J_0 \rangle_{\text{GK}, \omega=0}$ and the matrix is obviously non-invertible. Nevertheless, the limit $\omega \to 0$ can be taken after the matrix inversion, leading to a well defined scheme. The cepstral analysis technique described in Ref. [7] provides a statistically correct way to obtain the $\omega \to 0$ limit after the matrix inversion.

Overall, our analysis shows that formulas and techniques originating from the multi-component framework follow from a general variational principle and the GK scalar product in the $\omega \to 0$ limit. On the opposite side, the decorrelation and renormalization techniques follow from the same variational principle and the Boltzmann scalar product, namely from correlation functions computed in the $t \to 0$ limit. Besides, it is possible to exploit the numerical advantages of the renormalization procedure (i.e. dealing exclusively with the smaller renormalized energy fluxes) and on top of that applying the multi-component formalism. At the present moment, it remains unclear which technique can be more effective in the general case and we leave this question open for future work.

IV. CONCLUSIONS

In this work we presented a general framework, based on a variational principle, able to optimize a generic energy-flux time series by removing inert signals that do not contribute to the thermal conductivity. Our method
is general and it can be generalized to the computation of other transport coefficients as well, whenever a non-diffusive signal can be identified. In the case of thermal transport, we highlighted why formation and self-energy contributions can pose serious convergence problems to Green-Kubo thermal conductivity simulations, especially in \textit{ab initio} frameworks and in polyatomic systems. We investigated numerically two solutions to this problem, that use the static cross-correlation as a scalar product between observables in our general framework. The first approach is based on the concept of decorrelation of the energy-current time series, and the second on renormalization of velocities. In the thermodynamic limit the two procedures are shown to be equivalent both from a theoretical and numerical point of view, when the decorrelation technique is used in combination with the particle currents. The decorrelation technique can indeed be applied when a generic slowly-decaying signal makes a direct application of the GK formulas impossible or extremely expensive. The renormalization technique, instead, decorrelates the energy flux with respect to the particle current, but it is more straightforward to apply and can be used to detect whether formation energy contributions are correctly handled. As we demonstrated numerically, ignoring formation energy contributions can lead to wrong results, which cannot be detected by any standard statistical analysis of the heat currents. We therefore propose that both procedures should be performed to ensure that the simulation is not affected by convergence problems due to slowly-decaying signals. Finally, we proved formally the equivalence between our general framework and the GK theory of heat transport in multi-component systems, by identifying a scalar product that formalizes the dynamical decoupling between the fluxes that are associated to the different transport mechanisms in such systems. We think that this work will help to interpret and analyze future applications of the GK theory to the computation of thermal conductivity.

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Appendix A: Non-diffusive signals in DFT

As discussed in the main text, one source of inert signals in DFT calculations is given by formation energy contributions. We first note that the zero of energy changes according to which electrons are considered core electrons and which are instead pseudized. In an all-electron calculation the energy density would show contributions from the formation energy of all the valence and core electrons, leading to larger formation energy contributions and spurious non-diffusive signals. As a second example we identify, in the specific formulation of the GK currents of Ref. 1 the following term which explicitly depends on the arbitrary choice of the zero of the one-electron energy levels:

$$J_{KS}^{el} = \sum_{\nu} \left( \langle \phi_{\nu} | r H_{KS} | \phi_{\nu} \rangle + \varepsilon_{\nu} \langle \phi_{\nu} | r | \phi_{\nu} \rangle \right)$$  \hspace{1cm} (A1)

where $\varepsilon_{\nu}$ and $\phi_{\nu}$ are the eigenvalues and eigenfunctions of the Kohn-Sham Hamiltonian $H_{KS}$, respectively, and the sum runs over the occupied orbitals. A shift of the $\varepsilon_{\nu}$ levels by a quantity $\Delta \varepsilon$ results in a shift of the energy current by $\Delta \varepsilon J_{el}$, where $J_{el}$ is the adiabatic electronic current.\textsuperscript{22} Analogously to the particle current, in the electronically insulating systems considered in this work the electronic current $J_{el}$ is a non-diffusive signal\textsuperscript{2}

The second source of inert signals that we want to highlight is related to the subtle balance between ionic and electronic contributions taking place in first-principles calculations. Indeed, total energy and forces are computed as a sum of terms of large magnitude, each one having often a clear electronic or ionic origin, yielding a smaller net sum due to the screening of the Coulomb interactions. Nevertheless, the Coulombic interaction of electronic clouds with themselves leads to some energy contributions which cannot be counterbalanced by ionic terms. In fact, terms describing the (classical) Coulomb interaction of ions with themselves are divergent and therefore excluded from any total energy computation. The corresponding electronic terms therefore lead to an overall shift of the total energy, which is unimportant when evaluating energy differences or forces, but can lead to non-diffusive inert fluxes when computing GK currents. Again, we can exemplify this state of affairs with a concrete example from a specific definition of the GK current, by considering every atom $i$ as surrounded by a species-dependent and localized electronic cloud $\rho^{S(i)}$. At a zero-order approximation the latter do not depend on time and we call $\nu^{S(i)}(r)$ the corresponding Hartree potential. The contribution to the “Hartree current” defined in Ref. 1 then reads:

$$J_{H,i} = \sum_{i,j} \sum_{i,j} \nu_{i,j} \frac{\varepsilon_{i,j}}{4 \pi} \int \frac{d^{3}r}{\partial r_{\alpha} \partial r_{\beta}} \frac{\delta^{3}(r - r_{i})}{\nu^{S(i)}(r - r_{j})} dr.$$  \hspace{1cm} (A2)

The integral contained in the terms with $i \neq j$ describes the electrostatic interaction between the electronic clouds surrounding the $i$ and $j$-atoms. In the limit of localized electronic clouds, i.e. $\nu^{S(i)} \sim \frac{1}{|r - R_{i}|}$, these terms have a finite limit able to screen the current generated by the electrostatic interaction between the respective ionic cores. Instead, terms with $i = j$ describe the self-interaction of an electronic cloud. In such a case the
integrals do not depend on the position of the atom anymore and it is easy to see that the integrand tends to zero as \( r^{-2} \). This contribution then diverges, as it would its classical ionic counter-term, and brings a spurious electronic contribution which cannot be counterbalanced by ionic terms. Nevertheless, this contribution features the general form of a current derived by a formation energy, Eq. (4), the only difference being the tensorial form of the atomic energy. Therefore, this spurious term is non-diffusive as well and does not contribute to the thermal conductivity, but introduces large oscillating signals that are highly correlated with the particle currents \( \mathbf{V}^A \).

### Appendix B: General relation between bare and renormalized currents

We prove here Eq. (9) of the main text, showing the explicit form of the \( h \)-matrices and of \( J' \). Let us therefore monitor how the GK current changes when velocities are replaced with their renormalized values. We introduce the fluctuation linear operator \( \delta \), acting on a phase-space observable \( X \) as \( 6X \equiv X - \langle X \rangle \). Under renormalization, the term linear with the velocities transforms in the following way:

\[
\sum_i \langle \epsilon_{a,\beta}(\{r\})v_{i,\beta} \rangle \rightarrow \sum_i \langle \epsilon_{a,\beta}(\{r\})v_{i,\beta} \rangle - \sum_{A \in S} \left[ \langle \delta \epsilon_{a,\beta} \rangle + \frac{1}{N_A} \sum_{i \in A} \delta \epsilon_{i,a,\beta} \right] V^A_{\beta},
\]

where, with a slight abuse of notation, we called \( \langle \delta \epsilon_{a,\beta} \rangle \) the ensemble mean of \( \langle \epsilon_{a,\beta} \rangle \) over all atoms of species \( A \), supposed to be equivalent. The kinetic term instead transforms like this:

\[
\sum_i \left( \frac{1}{2} m_i v_i^2 \right) v_{i,a} \rightarrow \sum_i \left( \frac{1}{2} m_i v_i^2 \right) v_{i,a} - \sum_{A \in S} \frac{1}{N_A} \sum_{i \in A} v_{i,a} v_{i,\beta} V^A_{\beta} N_A - m_A \left( \sum_{i \in A} v_{i,a} v_{i,\beta} \right) \frac{V^A_{\beta}}{N_A} + \sum_{A \in S} m_A V^A_{\alpha} \frac{(V^A)^2}{N_A^2},
\]

By using the \( \delta \) operator we can separate the fluctuations from the mean values, which are determined by the equipartition theorem, as:

\[
\frac{1}{2} m_i v_i^2 = \frac{3}{2} k_B T + \frac{1}{2} m_i \langle v_i^2 \rangle, \quad v_{i,a} v_{i,\beta} = \frac{k_B T}{m_A} \delta_{\alpha,\beta} + \delta(v_{i,a} v_{i,\beta}),
\]

thus leading to the following substitutions in Eq. (B2):

\[
- \sum_{A \in S} \left( \frac{1}{2} m_i v_i^2 \right) \frac{V^A_{\beta}}{N_A} = - \sum_{A \in S} \left[ \frac{3}{2} k_B T + \frac{1}{2} m_A \frac{1}{N_A} \sum_{i \in A} \delta(v_i^2) \right] V^A_{\alpha},
\]

and

\[
- \sum_{A \in S} m_A \left( \sum_{i \in A} v_{i,a} v_{i,\beta} \right) V^A_{\beta}/N_A = - \sum_{A \in S} \left[ k_B T \delta_{\alpha,\beta} + m_A \frac{1}{N_A} \sum_{i \in A} \delta(v_{i,a} v_{i,\beta}) \right] V^A_{\beta}.
\]

Combining Eqs. (B1), (B2), (B5), and (B6) we finally derive Eq. (9) by defining the following \( h \)-matrices:

\[
h^A_{\alpha,\beta} = \langle \epsilon_{a,\beta} \rangle + \frac{5}{2} k_B T \delta_{\alpha,\beta}.
\]

The residual current \( J' \) has the following form:

\[
J'_\alpha = - \sum_{A \in S} \left[ \left( \frac{1}{N_A} \sum_{i \in A} \delta f_{a,\beta} \right) + m_A \left( \frac{1}{N_A} \sum_{i \in A} \delta(v_{i,a} v_{i,\beta}) \right) \right] + \frac{1}{2} m_A \left( \frac{1}{N_A} \sum_{i \in A} \delta(v_i^2) \right) \delta_{\alpha,\beta} - m_A \frac{(V^A)^2}{N_A^2} \delta_{\alpha,\beta} V^A_{\beta}.
\]

By inspection, the residual current \( J' \) can now be identified as a sum of terms, each one given by a product of signals, \( (S_1 \times \cdots \times S_p)/N_A^q \), with \( (p,q) = (2,1) \) or \( (p,q) = (3,2) \), depending on the term considered. In Eq. (B8), each of these signals is written as a sum of fluctuations \( \delta f \), \( S = \sum \delta f \langle r_i, v_i \rangle \), i.e. a sum of local variables with zero mean. The precise form of the function \( f \) depends on the particular \( S \)-signal and the sum over \( i \) is restricted to a certain atomic species: in order to keep the notation light, in the following we leave out these indexes. We call \( S \)-decomposition of \( J' \) the one obtained in formula (B8).

The decomposition characterizing the \( S \)-signals makes it convenient to analyze the thermodynamic scaling of the autocorrelation functions formed by a finite product of them. In the following we check the scalings of \( S \)-signals: \( \langle S_1 S_2 \rangle \sim \mathcal{O}(N) \), \( \langle S_1 S_2 S_3 \rangle \sim \mathcal{O}(N) \), \( \langle S_1 S_2 S_3 S_4 \rangle \sim \mathcal{O}(N^2) \), \( \langle S_1 S_2 S_3 S_4 S_5 \rangle \sim \mathcal{O}(N^3) \). The first case, involving the product of two \( S \)-signals, is well known and leads to the usual thermodynamic scaling of the standard GK formula for thermal conductivity, Eq. (1). These scalings can be verified in a naive way by expanding the summations defining the \( S \)-signals and noticing that fluctuations among particles at large distances are uncorrelated. In the following we formalize this procedure using indicator functions and the law of total expectation. We first embody the concept of decorrelation at large distances considering the \( n \)-particle autocorrelation functions:

\[
\langle \prod_{i=1}^n \delta f(r_i, v_i) \rangle,
\]
where $1, \ldots, n$ are $n$ tagged particles. When we consider the set of configurations $\{r_i\} = \{(r_1, \ldots, r_n) ||r_1 - r_k|| \gg 0, k \neq 1\}$ where one particle, say the first, is far from the other $n-1$, the fluctuations are uncorrelated and factorize leading to a vanishing contribution:

$$\langle \prod_{i=1}^n \delta f(r_i, v_i) | r_i \rangle = \langle \prod_{i=2}^n \delta f(r_i, v_i) | r_1 \rangle \delta f(r_1, v_1) | r_1 \rangle = 0. \quad (B10)$$

This property has several consequences. For example, the 2-particle autocorrelation function can be decomposed via the law of total expectation in the following way:

$$\langle \delta f(r_i, v_i) \delta f(r_j, v_j) \rangle = P(|r_i - r_j| \leq a_c) \langle \delta f(r_i, v_i) \delta f(r_j, v_j) | r_i - r_j| \leq a_c \rangle + P(|r_i - r_j| > a_c) \langle \delta f(r_i, v_i) \delta f(r_j, v_j) | r_i - r_j| > a_c \rangle \sim P(|r_i - r_j| \leq a_c) \langle \delta f(r_i, v_i) \delta f(r_j, v_j) | r_i - r_j| \leq a_c \rangle \quad (B11)$$

where $P(|r_i - r_j| \leq a)$ is the probability that particle $i$ and particle $j$ are closer than a cutoff $a$, and $P(|r_i - r_j| > a)$ is the probability of being farther apart.

The existence of a critical distance $a_c$ where the autocorrelation function involving distant particles can be neglected is the condition for the cited scalings to hold. Let us indicate $P(|r_i - r_j| \leq a_c)$ symbolically as $P(r_i \sim r_j)$, and a similar notation holds in the case of many particles. We then have:

$$\langle S_i S_j \rangle \sim \sum_{r_i, r_j} P(r_i \sim r_j) \langle \delta f(r_i, v_i) \delta f(r_j, v_j) | r_i \sim r_j \rangle \sim \sum_i \langle \sum_j C_{i,j} 1_{(r_j \sim r_i)} \rangle = O(N). \quad (B12)$$

Given a subset $A$ of the phase-space, the indicator function $1_A(\{r, v\})$ is equal to 1 if the configuration belongs to the subset and 0 otherwise. In particular, $P(A) = \langle 1_A \rangle$. For example, $\sum_j 1_{(r_j \sim r_i)}$ counts the number of atoms close to atom $i$, which is an intensive quantity. Here and in the following we indicate with $C$ some generic bounded constants, whose form can be explicitly written in terms of constrained autocorrelation functions. For every fixed atom $i$, their weighted sum is still intensive because only a finite number of neighbouring particles is involved in the summation.

For the 3-particle autocorrelation function it is possible to proceed in a similar fashion. In this case $r_i, r_j, j$ and $r_k$ all need to belong to the same neighbourhood in order to lead to a non-vanishing contribution: $r_i \sim r_j \sim r_k$.

Therefore:

$$\langle S_i S_j S_k \rangle = \sum_{r_i, r_j, r_k} P(r_i \sim r_j \sim r_k) \times \langle \delta f(r_i, v_i) \delta f(r_j, v_j) \delta f(r_k, v_k) | r_i \sim r_j \sim r_k \rangle \sim \sum_i \langle \sum_{j,k} C_{i,j,k} 1_{(r_j \sim r_i, r_k)} \rangle = O(N). \quad (B13)$$

The indicator function in this case selects non-zero contributions only from pairs of atoms $j, k$ both belonging to the neighbourhood of the $i$-atom, yielding again a finite, intensive quantity. As a last example, for the 4-particle autocorrelation function the condition that no particle is far from all the other three leads to the condition that either $r_i \sim r_j$ and $r_k \sim r_l$ (or permutations), or $r_i \sim r_j \sim r_k \sim r_l$. One can consider only one of the equivalent permutations for the first case:

$$\langle S_i S_j S_k S_l \rangle \sim 6 \sum_{i,k} \langle \sum_{j,l} C_{i,j,k,l} 1_{(r_j \sim r_i, r_l \sim r_i)} \rangle + \sum_i \langle \sum_{j,k,l} C_{i,j,k,l} 1_{(r_j \sim r_k \sim r_i)} \rangle = O(N^2), \quad (B14)$$

where the product of indicator functions selects the number of pair of atoms $j, l$ such that the $j$-atom is close to atom $i$ and the $l$-atom is close to atom $k$. The second indicator function with coefficients $C'$ selects the triplets $j, k, l$ such that all three atoms are close to the atom $i$, but leads to a weaker $O(N)$ scaling.

In an analogous way one can derive all the cited scalings and generalize the results to any product of $n$ signals $S$. The relevant scaling turns out to be given by configurations where $r_i \sim r_{i+1} \sim r_{i+2} \ldots r_{n-1} \sim r_{n}$ if $n$ is even, and $r_i \sim r_{i+2} \sim r_{i+4} \ldots r_{n-2} \sim r_{n-1} \sim r_{n}$ if $n$ is odd. Therefore

$$\langle S_1 \ldots S_n \rangle \sim O(N^{n/2}), \quad n \geq 2. \quad (B15)$$

where $[\cdot]$ is the floor function.

Finally, one can use the S-decomposition of $J'$, eq. [B8] combined with the scaling of the individual $S$-signals, eq. [B15] to show that the terms neglected in Eq. [10] are indeed negligible in the thermodynamic limit. As an example, let us consider the scalar product of $S_0 \equiv \sum_{A} h_{\alpha,\beta}^{A} V_{\beta}^{A}$ with one of the addends of $J'$, with $(p, q) = (2, 1)$. In such a case we have that $\frac{1}{\langle S_0 \times S_1 S_2 \rangle} \sim O(\frac{1}{N}),$ i.e. the contribution vanishes in the thermodynamic limit, all other terms in Eq. [10] being of order $O(1)$. Upon inspection, all terms involving the residual current give a negligible contribution.

**Appendix C: Equivalence between renormalization and decorrelation**

Let us consider only isotropic systems, such as $h_{\alpha,\beta}^{A} = h_{\alpha,\beta}^{A} \delta_{\alpha,\beta}$. In this section we use different brackets $\langle \cdot \rangle$ and $\langle \cdot \rangle_{\text{can}}$ to indicate an equilibrium average in the microcanonical and the canonical ensemble, respectively. From the explicit form of the canonical Boltzmann distribution:

$$P_{\text{can}} \{ \{r, v\} \} \sim \exp \left[ -\frac{U(\{r\})}{k_B T} \right] \prod_i \exp \left[ -\frac{m_i v_i^2}{2 k_B T} \right], \quad (C1)$$

one can explicitly verify that each renormalized velocity $v_i^{\prime} = v_i - W^{S(i)}$ is independent of $V^A$. For example, given the linearity of the transformation and the Gaussian velocity distribution, it is sufficient to check that $\langle v_i^{\prime} V^A \rangle_{\text{can}} = 0$. As a consequence $\langle J_{\text{ren}} V^A \rangle_{\text{can}} = 0$, the current $J_{\text{ren}}$ being sum of functions of $v_i^{\prime}$ and therefore
uncorrelated with $V^A$. This result holds exactly for every finite number of particles and not only in the thermodynamic limit.

The standard formula relating the expectation values of fluctuations in different ensembles\textsuperscript{23,25} now reads:

$$
\langle J_{\text{ren}}^A V^A \rangle = \sum_{\alpha, \beta} \partial (\beta w_{\alpha}) \left( \frac{\partial (J_{\text{ren}}^A)}{\partial \beta} \right) \partial (V^A) \alpha \beta
$$

$$
+ \frac{\partial \beta}{\partial E} \left( \frac{\partial (J_{\text{ren}}^A)}{\partial \beta} \right) \frac{\partial (V^A) \alpha \beta}{\partial \beta} + o(N), \quad (C2)
$$

where $E$ and $M$ are the total energy and momentum, whose conjugate quantities are $\beta$ and $\beta w$, $w$ being the mean centre of mass velocity. The renormalized current has a zero expectation value for every temperature and is by construction independent of any global drift of the system. Therefore all derivatives of $J_{\text{ren}}$ are zero and $\langle J_{\text{ren}}^A V^A \rangle \sim o(N)$. Let us exploit this result and calculate the scalar product of $J_{\text{ren}}$ and a generic $V^B$. Using Eq. (9), in the thermodynamic limit one finds the following formal set of relations satisfied by $h^A$:

$$
\left\langle \left( J_{\text{bare}} - \sum_{A \in S} h^A V^A \right) V^B \right\rangle = 0, \quad B \in S, \quad (C3)
$$

which is exactly the same linear system used for the decorrelation technique. As discussed in the text, this implies the equivalence, in the thermodynamic limit, between the decorrelation and renormalization techniques.

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