Thermodynamic transport equations derived from first principles

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Practical analysis of complex systems currently relies on empirical transport laws because diffusion cannot be described by state functions alone, as assumed in Classical Thermodynamics and Statistical Mechanics. Lagrange mechanics emerge when diffusion is negligible; diffusion does not emerge in many-body Lagrange theory. I derive comprehensive transport equations directly from quantum mechanical principles by tallying particle motion individually, providing a concrete, seamless foundation for all applied physical science. This new approach resolves, without entropy or axiom, several critical issues that originally inspired the standard theories, and clarifies analysis of processes in mesoscopic and macroscopic systems.

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I. INTRODUCTION

Transport equations are the heart of science. Without them, theory can only describe static states, begging the question, of course, how such conditions came to be. Physics addresses how individual particles interact. Tallying the effect of countless interactions is the subject of thermodynamics and the basis for all applied physical sciences. Every field of applied science has grown from observations distilled into empirical natural laws. These empirical laws form the foundation for their respective fields because there is currently no concrete connection to physics, despite intense and prolonged investigation for over a century. This gap in understanding slows progress, particularly in mesoscopic and interdisciplinary science.

Without transport equations grounded in physics, persistent questions continue to confuse analysis. How can dissipation occur if underlying physics is symmetric in time? What then determines the direction of time? How can the Second Law be satisfied across the universe when the process of equilibration appears to be local? How can transport laws be defined in a consistent manner? And how are particle, energy and momentum flows related?

The standard theories of Classical thermodynamics and Statistical Mechanics were developed to fill this void by postulating the Second Law of thermodynamics and other laws from which empirical transport equations supposedly derive. The Second Law was originally formulated by Rudolf Clausius as a static condition comparing equilibrium states [1]. Josiah Gibbs later elevated entropy to a dynamic variable underlying his definition of equilibrium, giving the Second Law the appearance of a dynamic transport equation on par with energy conservation [2]. Ludwig Boltzmann and Gibbs separately proposed that entropy is related to the probability for a system to be in a specific state. These theories avoid detailed description of microscopic activity. Recent work continues this tradition by focusing on entropy production, yet no consistent formulation of entropy has been found out of equilibrium [3]. These issues persist in the relativistic regime as well [4]. Dynamic analysis of complex systems still relies on empirical laws and "first principles derivation of irreversibility remains a severe problem, as the 'first principles' at hand are all reversible" [5].

Theoretical attempts to prove that the Clausius, Boltzmann and Gibbs postulates obey physics principles generally employ Lagrangian theory. Molecular chaos in some form must be imposed arbitrarily, otherwise entropy does not increase [6]. All attempts have failed to prove the Second Law from first principles for a common reason: Lagrangian theory explicitly neglects microscopic forces and the work they do [7]. It is, therefore, appropriate for analyzing systems of a few well-defined bodies pushed by known forces, or in other words, for interaction between fundamental particles and for classical mechanics. Microscopic forces stem from individual particle motion, including resonant, state-collapsing quantum events. In neglecting them, friction and diffusion are neglected as well.

Standard thermodynamics supposedly overcomes this omission by relating diffusion to thermal fluctuation of bulk properties. But adding fluctuation to Lagrangian equations of motion does not suffice. The fluctuation-dissipation theorem is valid for a known force causing fluctuation in the trajectory of a body. However, microscopic force cannot be considered an applied force; diffusion has countless sources that migrate in and out of a body and render thermodynamic force unpredictable by position and time alone. Thermodynamic fluctuation is not related to dissipation.

Lars Onsager's arguments leading to his reciprocal relations are cited as justifying the use of empirical transport laws for analyzing irreversible (dissipative) processes. He assumes that fluctuations in equilibrium obey empirical transport laws [8]. He concludes that reciprocal flows are equal near equilibrium, as observed, because equilibrium fluctuations obey detailed balance. But fluctuations then must be considered irreversible processes as well, which would cause entropy to grow continually in equilibrium. Onsager's crucial assumption confuses mean variation, which dissipates by diffusion, with fluctu-

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ations, which are ever present and cannot drive a system out of equilibrium. Mean properties are uniform in equilibrium. Any variation, no matter how small, is out of equilibrium and cannot be in detailed balance, or else the system would not evolve from this state to equilibrium. There is no theoretical basis for Onsager's assumption [9].

Standard theory cannot be dynamic without understanding how fundamental physics produces diffusion. "One has to conclude that the heat equation and other transport equations simply do not belong to classical thermodynamics!"[10] The Second Law was adopted to act as a necessary dynamic constraint in order to determine an equilibrium state. But the Second Law remains vague and subject to many interpretations after 170 years [10, 11], largely because its premise is not generally valid [12]. By these arguments neither of the two essential assumptions in standard theory is true! Standard analysis of complex systems is not anchored in physics. It is inconsistent to estimate empirical transport coefficients by kinetic methods within the context of standard theory.

Max Planck recognized that any alternative theory must be derived from first principles [16]. Percy Bridgman speculated that, "Some of the other logical difficulties of the classical statistics, I believe, will also be surmounted by the adoption of the wave mechanics point of view, which assumes probability to be a primitive property of the elements of the model, rather than an emergent property resulting from the cooperation of great numbers."[17] The basis for a new theory of thermodynamics is derived here from quantum transition theory, avoiding multi-particle Lagrangian equations of motion by tallying individual particle activity directly. It is distinct from Quantum Thermodynamics approaches that focus on entropy growth [3, 13, 14].

II. GENERAL STATEMENTS

The following analysis treats all particles quantum mechanically, each being a quantum of excitation, not a point-like object. Reference [15] gives detailed explanation of comments here and in Sec. III. Stable particles exist in independent modes of motion under natural conditions. A particle may be a composite of more stable particles that persists during the process of interest. Modes may be represented as superpositions of eigenfunctions of quantum operators. These modes conform to all physical constraints on a system. Particles interact through emission an absorption of field bosons, whose influence may be approximated as force fields in the non-relativistic limit. These processes cause particle to transition into coupled modes at a specific inherent mean rate determined by quantum equations of motion, conserving energy, momentum and charge quantum numbers. This treatment applies as well to so-called active species with peculiar asymmetric rates [18, 19].

The moment when a particle transitions is not predictable in principle and interrupts unitary evolution of its wave function. Resonant and non-resonant phase-changing transitions destroy quantum correlation among particles without breaking the time symmetry inherent in fundamental forces. The correlation time tends to be extremely short even in mesoscopic systems. Correlation tends to produce oscillatory behavior, which would be evident in fast measurements. When particles are completely uncorrelated over the duration of a measurement, the probability to transition from a given mode equals the sum of probabilities to transition to each coupled mode individually. Particles that are persistently correlated may be treated as a new species of composite quasiparticle occupying a distinct set of uncorrelated modes.

Particles must be contained in order to attain equilibrium, otherwise they would continue to disperse. Containment may be imposed by physical walls or by binding forces such as in a solid material. Consequently, the energy spectrum of modes is discrete in this analysis. Modes of subsystems within a continuous material may be constructed with periodic boundary conditions to allow movement through imaginary subsystem boundaries.

Modes evolve as the particle distribution changes. This greatly complicates analysis far out of equilibrium. Every system diffuses toward a steady state, though, such that the distribution and mode spectrum gradually stabilize. Active agents, such as Maxwell's demon, may steer and even thwart this relaxation by modifying the mode spectrum and transition rates. Quasi-equilibrium may then be defined as when the spectrum is stable enough to reveal the dynamics of interest. In more practical terms, this condition follows when net mean flow of particles, momentum and energy is small, regardless of what is outside. Such apparent macroscopic calm belies rampant activity of continuous opposing diffusive flows.

Dynamic analysis requires knowledge of particle, energy and momentum transformations. Each material phase is a stable configuration of particles with unique properties. Transformations involve transitions between phases, as well as reactants in a single phase. Therefore, a practical theory should identify particles not only by substance but also by the phase it is in. Each stable form of particle is considered a unique species in this theory. Consequently, all dynamics can be treated in a unified manner.

A system is any chosen collection of particles, which may exist within an arbitrarily defined boundary and may be select species of a mixture. Systems are implicitly subsystems that may exchange particles, energy and momentum with regions outside. The state of a system is the current configuration of particles. This configuration varies continually as particles transition among modes of motion due to their interaction. The energy of a system is the total kinetic and potential energy within its boundary.

Mode population and transition rates together determine the flux of particles, momentum and energy. Net flux then determines the force on a system and its rate of change in energy and particle number. This information is necessary and sufficient to determine how any system evolves.

Measurement of the current state is an interaction similar to what occurs continually between constituents. In the thermodynamic limit, measurement usually samples a small subsystem, with negligible flows if done ideally. The measurement apparatus may significantly influence the modes, and therefore the flows and equilibrium, of very small systems. Thermal fluctuation and quantum collapse both contribute to measurement uncertainty.

All measurements require finite duration. Therefore, define all system independent parameters and dependent properties as the average over a measurement period. When this period is longer than the correlation time of the system, then particle energy effectively separates into macroscopic (mode independent average) and microscopic parts. The latter includes the energy required to form each particle in its ground quantum state. Mean system energy U may be expressed as the sum of mean macroscopic energy E_{macro}, heat content Q and particle formation energy,

$$U = E_{\mathrm{macro}} + Q + \sum_{j}^{\text{species}} \varepsilon_{0j} N_j \ , \tag{1}$$

where ε_{0j} and N_j are the formation energy and mean number of particles in the system of the jth species. Ambient field energy is included in the macroscopic part so that U is the absolute total energy. (This property should not be confused with standard "internal energy," which does not recognize macroscopic energy or different species of the same substance and, therefore, cannot properly account for friction and latent heat.) Heat content can be inferred by subtracting the measured macroscopic energy from the computed values of U and formation energy.

Fluctuation in property values generally diminish relative to system size as size increases. The thermodynamic limit corresponds to when fluctuation in mean property values is sufficiently small for practical purposes. It is usually more accurate to evaluate simple systems by mechanical equation of motion, rather than by thermodynamic flows. The resulting mode population distribution and transition rates would be input directly in the defining rate equations developed below. These rate equations reduce to familiar form by assuming that all subsystems satisfy the thermodynamic limit. Mesoscopic systems may need a combination of both strategies.

III. EQUILIBRIUM

Quasi-equilibrium is defined as a steady state when all flows are practically zero on average over a measurement. The mode spectrum and mean occupation number must also be steady when net flow stops. A system can settle to equilibrium only if flow to the outside is negligible. Regions within a larger system can achieve these conditions locally and be described as thermalized subsystems with local equilibrium properties.

The number of system configurations Ω is sensitive to flows. This number can be formulated by common combinatorial methods assigning particles of the same energy ϵ and canonical momentum $\mathbf{p}$ to one "bucket," given that they are dynamically equivalent, with the result $\ln\Omega = \sum_i^{\text{buckets}} \ln\Omega_i$. Outside flow is made explicit by adding five terms that are identically zero: $\ln\tilde{\Omega} = \ln\Omega + W(N - \sum N_i) + \beta_{\mathrm{E}}(E - \sum \epsilon_i N_i) + \boldsymbol{\beta}_{\mathrm{p}} \cdot (\mathbf{P} - \sum \mathbf{p}_i N_i)$, with sums over all buckets. Coefficients W, β_{E} and $\boldsymbol{\beta}_{\mathrm{p}}$ evolve with the system. Equilibrium then corresponds to zero average rate of change of this number over a measurement: $\langle \partial_t \ln\tilde{\Omega}\rangle_t = 0$. Neglecting the very slow rate of change in these coefficients and mode energy and momentum near equilibrium, this condition is approximately

$$0 \approx \sum_{i}^{\text{Buckets}} \langle \partial_t \ln\Omega_i \rangle_t - (W + \beta_{\mathrm{E}}\epsilon_i + \boldsymbol{\beta}_{\mathrm{p}} \cdot \mathbf{p}_i) \langle \dot{N}_i \rangle_t \ , \tag{2}$$

if outside mean particle and energy flow and force applied on the system, $W\langle \dot{N}\rangle_t + \beta_{\mathrm{E}}\langle \dot{E}\rangle_t + \boldsymbol{\beta}_{\mathrm{p}} \cdot \langle \dot{\mathbf{P}}\rangle_t$, are far smaller. This is the criterion for quasi-equilibrium.

As modes of elemental particles transform smoothly in quantum field theory, the occupation number is invariant for all inertial reference frames. Because $\bar{p} = \{\epsilon, \mathbf{p}\}$ is a 4-vector, the β parameters must also transform as a 4-vector such that $\bar{\beta}_\nu \bar{p}^\nu = \beta_{\mathrm{E}}\epsilon_i + \boldsymbol{\beta}_{\mathrm{p}} \cdot \mathbf{p}_i$ is a 4-scalar. This is satisfied when $\bar{\beta} = \beta_0 \bar{u}/c$ is proportional to the 4-velocity $\bar{u} = \gamma_{\mathbf{u}}\{c, \mathbf{u}\}$ of one observer moving relative to another with velocity $\mathbf{u}$. The momentum parameters are practically zero and the energy parameter is conventionally defined as $\beta_{\mathrm{E}} = \beta_0 = 1/k_{\mathrm{B}}T$ in the observer's reference frame and other non-relativistic frames. In that case, all modes degenerate solely in energy are combined in one bucket and equally populated. Yet four "temperature" parameters are needed to infer an equilibrium distribution in a relativistically fast moving frame.

This reasoning applies to each subsystem of a specific species in a mixed system. In the observer frame, the mean equilibrium population of species j in mode indexed by i of energy ϵ_{ji} is

$$\langle N_{ji}\rangle_t \approx 1/\left(e^{\epsilon_{ji}/k_{\mathrm{B}}T + W_j} \pm 1\right) \ , \tag{3}$$

assuming that the measurement period is longer than the correlation time and that net exchange of energy and particles with the outside is negligible. The plus sign applies to fermions, because they cannot occupy the same mode, and minus for bosons. These formulas are valid for any interaction and mixture of species. Both distributions approximate $\langle N_{ji}\rangle_t \approx \langle N_j\rangle_t e^{-\epsilon_{ji}/k_{\mathrm{B}}T - W_j}$ at high temperature, defining the classical regime, when particles rarely exist in the same mode and so are effectively distinguishable.

Note that this steady state derivation only involves modes that are active over a finite period, and so avoids ergodicity issues [6], as well as ambiguity in defining probability. The average describes the actual system, not an ensemble. Also, the state of the outside environment is irrelevant so long as net flow across the boundary is negligible.

These results are reproduced by a general analytical method in which the time averaged likelihood for a system to be in a given particle configuration, called a state s, is assumed to be

$$P_s = \frac{1}{Z}\, e^{-E_s/k_\mathrm{B}T} \ , \tag{4}$$

where $E_s = \sum_j^{\text{species}} \sum_i^{\text{modes}} \epsilon_{ji} N_{ji}$ is the energy in that state. The time average brackets are implied for all parameters and properties from here on. This probability distribution is normalized by the partition function

$$Z(T, \{N_j\}, \cdot\cdot) \equiv \sum_s^{\text{states}} e^{-E_s/k_\mathrm{B}T}. \tag{5}$$

All mean properties are then computed statistically by summing over states of the state property value weighted by the probability to be in that state, or equivalently, as derivatives of $\ln Z$. Therefore, the partition function contains all information about an equilibrium state. It is evaluated with specific particle interaction models that determine the mode spectrum.

The system equilibrium state is uniquely identified by the set of independent parameters: temperature, particle numbers, either volume or stress parameters, and any applied fields. (The prior state from which it evolved is also necessary in cases of hysteresis.) The first derivative of the partition function with respect to each independent parameter is a system property called an equation of state (EOS). There is a process constraint associated with each EOS, namely conservation of energy for the temperature EOS property U, kinetic rate balance for the particle number EOS, balance of surface forces for volume EOS, and response to applied fields. Second derivatives of $\ln Z$ are the EOS sensitivities to change in each parameter. They are simply related when Z is an analytic function and its derivatives commute. The partition function is not analytic when a material ruptures or tears in a non-smooth manner.

The parameter W_j is closely related to the particle number EOS,

$$\begin{aligned}\eta_j(T, \{N_k\}, \cdot\cdot) &\equiv \ln Z(T, \{N_1, \cdot\cdot, N_j, \cdot\cdot\}, \cdot\cdot) \\ &\quad - \ln Z(T, \{N_1, \cdot\cdot, N_j - 1, \cdot\cdot\}, \cdot\cdot) \\ &= \partial_{N_j} \ln Z \ .\end{aligned} \tag{6}$$

Evidently, e^{η} is the partition contribution of one particle and η is called the particle partition logarithm (PPL). However, this PPL does not correspond exactly to the W parameter in (3). To very high accuracy, $W_j = \eta_j$ for fermions, and $W_j = \eta_j + 1/N_j$ for bosons. It is also consistent to assign $W_j = \eta_j - \ln N_j$ in the classical regime, when all particles are treated as effectively distinguishable in different modes.

The change in system energy between equilibrium states can be estimated by extrapolation. If the change is small then only the first order, linear terms in the Taylor series of U need be retained. In a system containing an isotropic fluid with an applied electric field, for example, the energy change is $\Delta U \approx C_\mathrm{V} \Delta T - (\partial_V U)\Delta V + (\partial_\varphi U)\Delta\varphi + \sum_j^{\text{species}} \varepsilon_j \, \Delta N_j$. Here φ is the electric potential and $\varepsilon_j = \partial_{N_j} U$ is the marginal particle energy of species j at constant volume. Marginal particle energy is the energy needed to maintain all other parameters in equilibrium when one particle is added, and is not equal to the average particle energy U/N_j. A single internal particle transformation releases or absorbs "latent energy" equal to $\sum_j x_j \varepsilon_j$, given stoichiometric coefficients x_j of the chemical reaction.

Conservation of energy implies that any change in system energy must be balanced by particle and energy flow through the boundary. For the above example,

$$\begin{aligned}\Delta U = -p\Delta V + \Delta Q_\text{outside} + \Delta E_\text{macro}^\text{inflow} \\ + \sum_j^{\text{species}} \varepsilon_{0j}\, \Delta N_j^\text{outside} + \int dV\, n_j q_j \,\Delta\varphi \ ,\end{aligned} \tag{7}$$

with particle number density n_j and electric charge q_j. Particles exchanged with the outside may carry macroscopic and formation energy as well as heat.

IV. PARTICLE REACTIONS

Fundamental particles are always stable. Metastable composite particles may transform into each other if energy, momentum and stoichiometry are conserved. Particle transformations within a material phase are generally called chemical reactions. First order phase transitions occur when a particle transformation involves species in coexisting material phases. Second order phase transitions, in contrast, are due to quantum constraints causing the properties of a single species to change dramatically.

Let Γ_{ck} be the quantum mechanical rate that a set of "reactant" particles existing in a specific configuration of modes c transitions to a set of "product" species in mode configuration k. While we typically think of chemical processes as consuming reactant to create products, these labels are in quotes because the transition rate is equal in both directions, reflecting the time symmetry of physical forces. (Symmetry breaking weak force interaction is a rare exception.) The aggregate rate from one reactant configuration c to any product configuration equals the sum over all product configurations, $\Gamma_c = \sum_k \Gamma_{ck}$.

Consider a generic transformation involving r reactant species $\{Y_1, \cdot\cdot, Y_r\}$ and s product species $\{Y_{r+1}, \cdot\cdot, Y_{r+s}\}$ in stoichiometric equation $(-x_1)\, Y_1 + \cdot\cdot + (-x_r)\, Y_r \leftrightarrow x_{r+1} Y_{r+1} + \cdot\cdot + x_{r+s} Y_{r+s}$. The reactant stoichiometric coefficients x_j are negative to indicate consumption in forward transformations. The transition rate is equal for all particles of the same species in the same mode. Therefore, the effective rate from configuration c is multiplied by as many factors as participating particles, each of which is the number of each reactant species in each mode of the configuration. The total forward rate is the sum over all reactant mode configurations,

$$R^{\text{forward}} = \sum_{c}^{\substack{\text{Reactant}\\ \text{config.}}} \Gamma_c \prod_{j=1}^{r} \prod_{m=1}^{-x_j} N_{j,cj(m)} \ , \tag{8}$$

where $N_{j,cj(m)}$ is the population of species j in mode m of configuration c. The reverse rate is likewise

$$R^{\text{reverse}} = \sum_{k}^{\substack{\text{Product}\\ \text{config.}}} \Gamma_k \prod_{j=r+1}^{s} \prod_{m=1}^{x_j} N_{j,kj(m)} \ , \tag{9}$$

given that $\Gamma_k = \sum_c \Gamma_{ck}$ is the sum over reactant configurations. Net transition rate is simply $R^{\text{net}} = R^{\text{forward}} - R^{\text{reverse}}$.

Out of equilibrium, particles continue to transform until either one of the participating species is exhausted, or the counter flows are balanced and net rate is zero. The latter case establishes an equilibrium kinetic condition,

$$R^{\text{forward}} = R^{\text{reverse}} \ , \tag{10}$$

that specifies the relative population between species in a reactive mixture. This condition is complementary to (3), which specifies intra-species kinetic balance. Designate this value as the equilibrium rate R^{eq}.

Section VIII concludes that all flows drive any system toward kinetic balance. Once balanced, the independent parameters describing the system must change for the system to evolve further to a different equilibrium state. Assume that this disruptive process occurs in two stages in order to make analysis practical as well as intelligible: First, particles thermalize quickly so that local parameters deviate from the prior equilibrium value by ΔT, etc. Second, these shifts drive particle transformations.

Assume, for clarity in this discussion, the typical case that all participating species are in the classical regime. The forward rate can then be written separating system properties from the rate information:

$$R^{\text{forward}} = \Psi_{\text{forward}} \prod_{j=1}^{r} \left(N_j e^{-\eta_j}\right)^{-x_j} \ , \tag{11}$$

defining the forward kinetic rate factor as

$$\Psi_{\text{forward}} \equiv \sum_{i}^{\substack{\text{Reactant}\\ \text{config.}}} \Gamma_i \prod_{j=1}^{r} \prod_{m=1}^{-x_j} e^{-\epsilon_{j,ij(m)}/k_{\text{B}}T} \ . \tag{12}$$

If the particle interaction model used to evaluate (5) does not accurately estimate local clustering deviating from system mean density, such as around ions, then a factor may be inserted in Ψ to account for this effect. Modes with high transition rate often group in a well-defined energy range, which establishes the activation energy required for significant transformation rate. Transformation rate (11) then has the form of the empirical Arrhenius and Eyring equations.

Factoring (9) similarly, (10) may be expressed as

$$\prod_{j=1}^{r+s} \left(N_j e^{-\eta_j}\right)^{x_j} = K \ , \tag{13}$$

defining the "rate quotient" specific to each transformation

$$K \equiv \frac{\Psi_{\text{forward}}}{\Psi_{\text{reverse}}} \ . \tag{14}$$

The rate quotient must not be confused with the standard reaction quotient, which contains no rate information. Equation (13) contradicts the Second Law of thermodynamics because $K \neq 1$ in complex systems [12, 20]. Consequently, dynamic balance can maintain coexisting phases above their ground states, possibly producing temporal oscillations under suitable conditions, such as observed in "time crystals" [21–23].

The rate quotient tends to be weakly dependent on temperature, density and pressure, because the activation energy cancels out. Note that the rate quotient is not equal to one except in trivial cases, such as for a unitary transformation within a single phase, when particles of the same species simply exchange modes.

There may be more than one transformation occurring at once, in which case distinguish each by index i. Extrapolating the change in forward rate (11) from equilibrium to first order yields

$$\begin{aligned}\Delta R_i^{\text{forward}} = R_i^{\text{eq}} \Bigg\{ &\frac{\Delta\Psi_i^{\text{forward}}}{\Psi_i^{\text{forward}}} \\ &+ \sum_{m}^{\text{reactants}} (-x_{im}) \left(\frac{\Delta N_m}{N_m} - \Delta\eta_m\right) \Bigg\} \ .\end{aligned} \tag{15}$$

The rate that particles of species j are produced by the ith transformation is $\dot{N}_{ij}^{\text{trans}} = x_{ij} R^{\text{net}}$. The total production rate due to all transformations is then

$$\begin{aligned}\dot{N}_j^{\text{trans}} = &\sum_{i}^{\text{trans}} R_i^{\text{eq}} x_{ij} \frac{\Delta K_i}{K_i} \\ &- \sum_{m}^{\substack{\text{all}\\ \text{species}}} \left[\sum_{i}^{\text{trans}} R_i^{\text{eq}} x_{ij} x_{im}\right] \left(\frac{\Delta N_m}{N_m} - \Delta\eta_m\right) \ .\end{aligned} \tag{16}$$

The matrix in square brackets is symmetric. Therefore, when the variation in rate quotient is negligible, there are reciprocal relations between the rate that one species is produced by an excess of another ($j \neq k$):

$$\frac{\dot{N}_j^{\mathrm{trans}}}{\Delta N_k} \approx \left[\sum_i^{\mathrm{trans}} R_i^{\mathrm{eq}} x_{ij} x_{ik}\right] \frac{\partial \eta_j}{\partial N_k} = \left[\sum_i^{\mathrm{Trans.}} R_i^{\mathrm{eq}} x_{ik} x_{ij}\right] \frac{\partial \eta_k}{\partial N_j} \approx \frac{\dot{N}_k^{\mathrm{trans}}}{\Delta N_j} \ , \quad (17)$$

so long as the partition function is analytic, implying

$$\left.\frac{\partial \eta_j}{\partial N_k}\right|_V = \frac{\partial}{\partial N_k}\left(\left.\frac{\partial \ln Z}{\partial N_j}\right|_V\right) = \frac{\partial}{\partial N_j}\left(\left.\frac{\partial \ln Z}{\partial N_k}\right|_V\right) = \left.\frac{\partial \eta_k}{\partial N_j}\right|_V \ . \quad (18)$$

The PPL in (16) must be expanded in terms of the independent parameters because it is not a directly measurable or controllable property. (Actually, neither Z nor PPL is a physical quantity.) While the direct expansion

$$\Delta \eta_j = \frac{\varepsilon_j}{k_{\mathrm{B}} T^2} \Delta T + \frac{\gamma_{\mathrm{p}j}}{\beta_{\mathrm{T}} k_{\mathrm{B}} T} \Delta V + \sum_k^{\mathrm{species}} \left.\frac{\partial \eta_j}{\partial N_k}\right|_V \Delta N_k + \left.\frac{\partial \eta_j}{\partial \varphi}\right|_V \Delta \varphi + \cdot\cdot \quad (19)$$

is generally valid, virial particle models reveal the dependence on number density $n_j = N_j/V$:

$$\frac{\Delta N_j}{N_j} - \Delta \eta_j = \frac{\Delta n_j}{n_j} - \sum_k^{\mathrm{species}} \left.\frac{\partial \eta_j}{\partial n_k}\right|_V \Delta n_k|_V - \frac{\varepsilon_j}{k_{\mathrm{B}} T^2} \Delta T - \left.\frac{\partial \eta_j}{\partial \varphi}\right|_V \Delta \varphi - \cdots \ . \quad (20)$$

Virial models, with general form $\eta_j = \ln[C_j V] + f_j(T, \{n_k\}, \varphi, \ldots)$, where C_j is a species specific constant, ensure that no more than three phases can coexist, as observed. The coefficients of expansion are defined as

$$\Delta V = V\left(\alpha \Delta T - \beta_{\mathrm{T}} \Delta p + \sum \gamma_{\mathrm{p}j} \Delta N_j + \cdot\cdot\right) \ . \quad (21)$$

In cases where pressure is measured or controlled as the independent parameter instead of volume,

$$\frac{\Delta N_j}{N_j} - \Delta \eta_j = \left.\frac{\Delta n_j}{n_j}\right|_p - \sum_k^{\mathrm{species}} \left.\frac{\partial \eta_j}{\partial n_k}\right|_p \left(1 - N_k \gamma_{\mathrm{p}k}\right) \Delta n_k|_p - \frac{\hat{\varepsilon}_j}{k_{\mathrm{B}} T^2} \Delta T + \frac{V \gamma_{\mathrm{p}j}}{k_{\mathrm{B}} T} \Delta p - \left.\frac{\partial \eta_j}{\partial \varphi}\right|_p \Delta \varphi - \cdots \ . \quad (22)$$

Here $\hat{\varepsilon}$ is the marginal particle energy at constant pressure. The density dependence cancels out in pure systems because when temperature and pressure are constant, then number density is too.

V. PARTICLE FLOW

Particle flow is essentially a unitary transformation between spatially dislocated modes. Forward and reverse, in this context, refer to mode transitions across an interface in the positive and negative directions. Define two adjacent subsystems on either side of the interface, each small enough to thermalize quickly into local quasi-equilibrium while still satisfying the thermodynamic limit. Let the interface be normal to the $\hat{\mathbf{z}}$ direction with subsystem a on the negative side and b on the positive side. Net flow may be derived by extrapolation if a and b represent the same phase. But if the interface lies on a phase boundary, this process is treated by (16), with $r = s = 1$.

From (8), the rate that particles transit the interface is

$$\dot{N}_j^{a \to b} = \sum_i^{a\text{ modes}} N_{ji} \sum_k^{b\text{ modes}} \Gamma_{j,ik} \ . \quad (23)$$

The mode rate $\Gamma_{j,ik}$ represents diffusive particle transfer and reflects all geometrical constraints such as walls and apertures at the interface. Ballistic particles rarely interact as they pass through either subsystem and are better treated separately in larger subsystems. Transition rates vary with direction in anisotropic materials, and so designate aggregate rate $\Gamma_{j,i}^{(z)} = \sum_k^{b\text{ modes}} \Gamma_{j,ik}$ by interface orientation.

Net flux through interface area A is then

$$J_{\mathrm{N}j}^{(z)} = \frac{1}{A}\left(\dot{N}_j^{a \to b} - \dot{N}_j^{b \to a}\right) \ . \quad (24)$$

When the interface is a phase boundary, regions a and b represent different material phases, usually with distinct properties. Transfer across a phase boundary is more consistently viewed as "particle exchange transformations" with net rate determined by the difference between (8) and (9) evaluated in each phase at their respective parameter values. For example, evaporation and condensation processes are the transformation and exchange of liquid and gas species of the same substance.

When regions a and b represent the same material phase, the terms in (24) are related by Taylor expansion. Setting $w_{ji} = \epsilon_{ji}/k_{\mathrm{B}}T + W_j$ in (3), linear extrapolation of each term from equilibrium produces

$$J_{\mathrm{N}j}^{(z)} \approx -\frac{1}{A} \sum_i^{\mathrm{eq\ modes}} \frac{\Delta_z \Gamma_{j,i}^{(z)}}{e^{w_{ji}} \pm 1} - \frac{\Gamma_{j,i}^{(z)}\, e^{w_{ji}}\, \Delta_z w_{ji}}{\left(e^{w_{ji}} \pm 1\right)^2} \ . \quad (25)$$

Here $\Delta_z f$ is the difference in adjacent subsystems in the positive z direction.

The sum of N_{ji} over modes equals the subsystem population N_j in equilibrium. Label the sum over derivative distribution $N_j^{'} = \sum_i e^{w_{ji}}/\left(e^{w_{ji}} \pm 1\right)^2$, which, in the quantum regime, selects fermion modes within $k_{\mathrm{B}}T$ of the Fermi energy or over weights low energy boson modes, and approaches N_j in the classical regime. Define the weighted average transition rate over the normal distribution as $\langle\Gamma_j\rangle_\mathrm{N} \equiv (1/N_j)\sum_i \Gamma_{j,i}/\left(e^{w_{ji}} \pm 1\right)$, and similarly over the derivative distribution $\langle\cdot\cdot\rangle_{\mathrm{N}'}$. Net flux may then be expressed as

$$\mathbf{J}_{\mathrm{N}j}^{(z)} \approx -\frac{1}{A}\Big(N_j\,\langle\Delta_z\Gamma_j^{(z)}\rangle_\mathrm{N} - N_j'\langle\Gamma_j^{(z)}\,\Delta_z w_j\rangle_{\mathrm{N}'}\Big)\ . \qquad (26)$$

Define the equilibrium diffusion velocity $\overline{v}_{\mathrm{N}j}^{(z)} = L_z\langle\Gamma_j\rangle_\mathrm{N}$, where L_z is the distance between subsystem centers. Flux then is the product of equilibrium flux and relative gradient in properties between subsystems:

$$J_{\mathrm{N}j}^{(z)} \approx -n_j\overline{v}_{\mathrm{N}j}^{(z)}L_z\left(\frac{\langle\partial_z\Gamma_j^{(z)}\rangle_\mathrm{N}}{\langle\Gamma_j^{(z)}\rangle_\mathrm{N}} - \frac{N_j'}{N_j}\frac{\langle\Gamma_j^{(z)}\,\partial_z w_j\rangle_{\mathrm{N}'}}{\langle\Gamma_j^{(z)}\rangle_\mathrm{N}}\right)\ , \qquad (27)$$

Differential notation here is understood to represent a finite difference $\partial_f f = \Delta_z f/L_z$.

Further define the mean energy of flowing particles $\langle\epsilon_j\rangle_\mathrm{N}^{(z)} \equiv \langle\Gamma_j^{(z)}\epsilon_j\rangle_{\mathrm{N}'}/\langle\Gamma_j^{(z)}\rangle_\mathrm{N}$, and define the gradient in mean energy of flowing particles similarly. The latter right hand average in (27) may be expressed to first order as

$$\frac{\langle\Gamma_j^{(z)}\,\partial_z w_j\rangle_{\mathrm{N}'}}{\langle\Gamma_j^{(z)}\rangle_\mathrm{N}} = \frac{\langle\partial_z\epsilon_j\rangle_\mathrm{N}^{(z)}}{k_\mathrm{B}T} - \frac{\langle\epsilon_j\rangle_\mathrm{N}^{(z)}}{k_\mathrm{B}T}\frac{\partial_z T}{T} + \frac{\langle\Gamma_j\rangle_{\mathrm{N}'}^{(z)}}{\langle\Gamma_j\rangle_\mathrm{N}^{(z)}}\partial_z W_j \qquad (28)$$

Equation (27) is the flux in the co-moving frame of the material if the interface is stationary relative to the modes. In equilibrium, bulk velocity is uniform and there exist three principal axes about which modes are symmetric such that flux is parallel to the axes: $\mathbf{J}_{\mathrm{N}j}^{\text{co-moving}} = \hat{\mathbf{x}}\,J_{\mathrm{N}j}^{(x)} + \hat{\mathbf{y}}\,J_{\mathrm{N}j}^{(y)} + \hat{\mathbf{z}}\,J_{\mathrm{N}j}^{(z)}$ if $\{\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}\}$ are the principal axes. Recognizing the factor in parentheses in (27) as one component of a vector, define the particle diffusivity tensor

$$\overleftrightarrow{D}_{\mathrm{N}j} \equiv \hat{\mathbf{x}}\hat{\mathbf{x}}\overline{v}_{\mathrm{N}j}^{(x)}L_x + \hat{\mathbf{y}}\hat{\mathbf{y}}\overline{v}_{\mathrm{N}j}^{(y)}L_y + \hat{\mathbf{z}}\hat{\mathbf{z}}\overline{v}_{\mathrm{N}j}^{(z)}L_z\ . \qquad (29)$$

Flux then is

$$\mathbf{J}_{\mathrm{N}j}^{\text{co-moving}} \approx -n_j\overleftrightarrow{D}_{\mathrm{N}j}\cdot \sum_k^{x,y,z}\hat{\mathbf{k}}\left(\frac{\langle\partial_k\Gamma_j^{(k)}\rangle_\mathrm{N}}{\langle\Gamma_j^{(k)}\rangle_\mathrm{N}} - \frac{N_j'}{N_j}\frac{\langle\Gamma_j^{(k)}\,\partial_k w_j\rangle_{\mathrm{N}'}}{\langle\Gamma_j^{(k)}\rangle_\mathrm{N}}\right). \qquad (30)$$

Material may move locally with bulk velocity $\mathbf{v}_j$ relative to an observer, who may also choose a system boundary moving at velocity $\mathbf{u}$. The boundary interface then sweeps through the material with speed $\mathbf{v}_j - \mathbf{u}$ and the designation of a and b modes in (23) changes with time. Diffusive flux retains the same form but with effective diffusion velocity $\mathbf{v}_{\mathrm{N}j}$ through the moving interface. Spatially varying bulk velocity and strain between subsystems produce second order effects. Therefore, to first order, flux through a boundary in the observer's frame is

$$\mathbf{J}_{\mathrm{N}j}^{\text{boundary}} \approx n_j\left(\mathbf{v}_j - \mathbf{u}\right) + \mathbf{J}_{\mathrm{N}j}^{\text{co-moving}}\Big|_{\overline{\mathbf{v}}_{\mathrm{N}j}\to\mathbf{v}_{\mathrm{N}j}}\ . \qquad (31)$$

In the classical regime, the mean rate factors into particle partition and a kinetic rate factor analogous to (12), $\langle\Gamma_j^{(z)}\rangle_\mathrm{N} \approx e^{-\eta_j}\Psi_{\mathrm{N}j}^{(z)}$, and $\langle\epsilon_j\rangle_\mathrm{N}^{(z)} \approx k_\mathrm{B}T^2\partial_T\ln\Psi_{\mathrm{N}j}^{(z)}$. Flux in the co-moving frame then may be expressed as

$$J_{\mathrm{N}j}^{(z)} \approx -n_j\overline{v}_{\mathrm{N}j}^{(z)}L_z\left(\frac{\partial_z\Psi_{\mathrm{N}j}^{(z)}}{\Psi_{\mathrm{N}j}^{(z)}} + \frac{\partial_z N_j}{N_j} - \partial_z\eta_j\right)\ , \qquad (32)$$

and, in an isotropic material,

$$\mathbf{J}_{\mathrm{N}j}^{\text{co-moving}} \approx -n_j\overline{v}_{\mathrm{N}j}L\left(\frac{\nabla\Psi_{\mathrm{N}j}}{\Psi_{\mathrm{N}j}} + \frac{\nabla N_j}{N_j} - \nabla\eta_j\right)\ . \qquad (33)$$

The PPL expands in the same form as (19), (20) and (22), except with the gradient operator ∇ replacing Δ.

This formula produces Fick's laws and exhibits mutual particle diffusion, which causes Brownian motion of colloidal particles. Ohm's law follows for an applied electric field $\mathbf{E} = -\nabla\varphi$. The temperature gradient term produces the Soret effect. The Seebeck effect appears when a temperature gradient exists with an electric field, $q_j\mathbf{J}_{\mathrm{N}j} = \sigma_j(-\nabla\varphi - S_j\nabla T)$ in an isotropic material. The Seebeck coefficient then equals

$$S_j \equiv \frac{1}{k_\mathrm{B}T^2}\frac{\varepsilon_j - \langle\epsilon_j\rangle_\mathrm{N}}{\partial\eta_j/\partial\varphi|_V}\ . \qquad (34)$$

The first term in the numerator is due to increased number of modes to transition into, driving particles toward higher temperature regions. The second term is due to increased average particle speed with temperature, driving particles toward lower temperature regions. Thermal diffusion may flow with or against the temperature gradient, depending on the relative strength of these two trends. Many other thermodynamic effects occur between pairs or even triplets of terms in (30).

VI. MOMENTUM FLOW

Momentum flows with particles and by remote interaction mediated by force fields. Distinguish these as convective and conductive flow, respectively. The total rate of momentum flow through an interface between subsystems a and b is then

$$\dot{\mathbf{\Pi}}^{a\to b} = \dot{\mathbf{\Pi}}_\text{conv}^{a\to b} + \dot{\mathbf{\Pi}}_\text{cond}^{a\to b}\ . \qquad (35)$$

The convective component includes all particles transiting the interface in the positive direction. The mean rate of transit in the observer's frame is

$$\hat{\mathbf{z}}\cdot\left(\mathbf{v}_j - \mathbf{u}\right)\left(N_j/L_z\right) + \sum_i^{\substack{a\\\text{modes}}} N_{ji}\Gamma_{j,i}\ , \qquad (36)$$

with interface axis $\hat{\mathbf{z}}$. Define the mode diffusion velocity $\hat{\mathbf{z}} \cdot \mathbf{v}^{a\to b}_{\mathrm{N}j,i} = L_z \Gamma_{j,i}$. Mean mechanical momentum flow for particles of rest mass m_j is then

$$\dot{\mathbf{\Pi}}^{a\to b}_{\mathrm{conv}} = \sum_{j}^{\mathrm{species}} \sum_{i}^{\substack{a\\ \mathrm{modes}}} N_{ji} \left[\hat{\mathbf{z}} \cdot \left(\mathbf{v}_j - \mathbf{u} + \mathbf{v}^{a\to b}_{\mathrm{N}j,i}\right)/L_z\right] \times \gamma_{j,i} m_j \left(\mathbf{v}_j + \mathbf{v}^{a\to b}_{\mathrm{N}j,i}\right) \ . \quad (37)$$

Lorentz factor $\gamma_{j,i}$ significantly complicates further reduction for a relativistic range of mode diffusion velocity; the non-relativistic limit $\gamma_{j,i} \to 1$ is assumed here to simplify the following derivation. The mode summation is limited here to positive net velocity particles, $\hat{\mathbf{z}} \cdot \left(\mathbf{v}_j - \mathbf{u} + \mathbf{v}^{a\to b}_{\mathrm{N}j,i}\right) > 0$. This vector is a projection of a rank two tensor:

$$\dot{\mathbf{\Pi}}^{a\to b}_{\mathrm{conv}} = A_z \hat{\mathbf{z}} \cdot \sum_{j}^{\mathrm{species}} m_j n_{aj} \Big\{ \left(\mathbf{v}_j - \mathbf{u}\right) \mathbf{v}_j + \mathbf{v}^{a\to b}_{\mathrm{N}j} \mathbf{v}_j + \left(\mathbf{v}_j - \mathbf{u}\right) \mathbf{v}^{a\to b}_{\mathrm{N}j} + \overleftrightarrow{V}^{a\to b}_{j} \Big\} \ . \quad (38)$$

The effective diffusion velocity is $\mathbf{v}^{a\to b}_{\mathrm{N}j} = \left(1/N_{aj}\right) \sum_i N_{ji} \mathbf{v}^{a\to b}_{\mathrm{N}j,i}$ and diffusion velocity tensor defined as

$$\overleftrightarrow{V}^{a\to b}_{j} \equiv \frac{1}{N_{aj}} \sum_{i}^{\substack{a\\ \mathrm{modes}}} N_{ji}\, \mathbf{v}^{a\to b}_{\mathrm{N}j,i}\, \mathbf{v}^{a\to b}_{\mathrm{N}j,i} \ , \quad (39)$$

again with the positive net velocity condition.

By Newton's third law of motion, any transition changing a particle's momentum occurs with another transition producing equal and opposite momentum change. The conductive component of momentum flow represents pairs of transitions occurring on either side of the interface:

$$\dot{\mathbf{\Pi}}^{a\to b}_{\mathrm{cond}} = \sum_{j,j'}^{\mathrm{species}} \sum_{i,k}^{\substack{a\\ \mathrm{modes}}} \sum_{l,m}^{\substack{b\\ \mathrm{modes}}} N_{ji}\, N_{j'l} \times \mathbf{\Pi}_{j,ik}\, \Gamma_{jj',ik,lm} \ . \quad (40)$$

Here $\Gamma_{jj',ik,lm}$ is the probability per unit time for such transition pairs to occur from mode i to mode k, for one of the particles of species j, and mode l to mode m for the other of species j'. The difference in momentum of a particle in mode k to one in mode i is $\mathbf{\Pi}_{ik}$. This result includes long range "body" forces $\boldsymbol{\mathcal{F}}_{\mathrm{body}}$ and short range "contact" forces proportional to the interface area. High frequency body forces represent internal radiant emission and absorption, even if corresponding outside events do not occur during a measurement. Let $\mathbf{J}^{a\to b}_{\Pi}$ be the momentum flow per unit interface of all short range interactions in (40). Further define the set of rank two tensors $\overleftrightarrow{J}_{\Pi,j}$ such that $\mathbf{J}^{(\hat{\mathbf{n}})}_{\Pi} = \hat{\mathbf{n}} \cdot \sum_j \overleftrightarrow{J}_{\Pi,j}$ for interface axis $\hat{\mathbf{n}}$.

Force on a system is related to the rate of inward momentum flow through its boundary. Representing integral notation for the sum of finite interface area elements of subsystems inside and outside the boundary, total inward flow is

$$\dot{\mathbf{\Pi}} = \boldsymbol{\mathcal{F}}_{\mathrm{body}} + \int_V dA \left(-\hat{\mathbf{n}}\right) \cdot \sum_{j}^{\mathrm{species}} \Big\{ m_j n_j \Big[\left(\mathbf{v}_j - \mathbf{u}\right) \mathbf{v}_j + \mathbf{v}_{\mathrm{N}j} \mathbf{v}_j + \left(\mathbf{v}_j - \mathbf{u}\right) \mathbf{v}_{\mathrm{N}j} + \overleftrightarrow{V}_{j} \Big] + \overleftrightarrow{J}_{\Pi,j} \Big\} \ . \quad (41)$$

Normal vector $\hat{\mathbf{n}}$ to the local surface points outward by convention. The diffusion velocity and tensors are evaluated with subsystem a outside and b inside.

The classical picture, neglecting microscopic activity, assumes material moves as a laminar field. There is no diffusion in this case ($\mathbf{v}_{\mathrm{N}j}, \overleftrightarrow{V}_{j}, \overleftrightarrow{J}_{\Pi,j}$ are zero) and

$$\dot{\mathbf{\Pi}} = \partial_t \int_V dV \sum_{j}^{\mathrm{species}} m_j n_j \mathbf{v}_j \ . \quad (42)$$

In this case, (41) reduces to the Euler equation of motion with the aid of Reynold's transport and divergence theorems. The Euler equation is Galilean invariant because precise cancellation occurs between acceleration and convection terms, and invariant gravity and electromagnetic fields exert body forces.

According to Euler, the force on a volume is the total momentum inflow less that due to laminar bulk flow. Therefore, define the thermodynamic force as (41) less the first (macroscopic) term:

$$\boldsymbol{\mathcal{F}}_{\mathrm{TD}} \equiv \boldsymbol{\mathcal{F}}_{\mathrm{body}} + \int_V dA\, \hat{\mathbf{n}} \cdot \boldsymbol{\sigma}(\mathbf{r}, t) \ , \quad (43)$$

with stress tensor is defined as

$$\boldsymbol{\sigma}\left(\mathbf{r}, t\right) \equiv - \sum_{j}^{\mathrm{species}} \Big\{ m_j n_j \Big[\mathbf{v}_{\mathrm{N}j} \mathbf{v}_j + \left(\mathbf{v}_j - \mathbf{u}\right) \mathbf{v}_{\mathrm{N}j} + \overleftrightarrow{V}_{j} \Big] + \overleftrightarrow{J}_{\Pi,j} \Big\} \ . \quad (44)$$

The latter term in (43) evidently is the surface force. The thermodynamic equation of motion,

$$\dot{\mathbf{\Pi}} + \int_V dA\, \hat{\mathbf{n}} \cdot \sum_j m_j n_j \left(\mathbf{v}_j - \mathbf{u}\right) \mathbf{v}_j = \boldsymbol{\mathcal{F}}_{\mathrm{TD}} \ , \quad (45)$$

allows an observer unaware of microscopic activity to determine the acceleration of a body of material.

The left side of (45) is not Galilean invariant because the diffusive component does not cancel completely. Neither is thermodynamic force, because the first stress term depends on the absolute bulk velocity in the observer frame, while all other terms involve relative position and velocity. The apparent contradiction produced by inserting classical friction in the Euler equation is resolved by this quantum approach. Thermodynamic force must be computed in the frame of the observer.

The stress tensor pertains to the local conditions of a subsystem in quasi-equilibrium. Mode structure is sensitive to strain and strain rate relative to neighboring subsystems. Consequently, transition rate and displacement are as well. Extrapolating diffusion velocity to first order in strain and strain rate yields a general form of stress encompassing the entire range of materials from Newtonian fluid to elasticoviscous to viscoelastic to Hookean solid, depending on the relative strengths of the extrapolation coefficients. Mobile particle species contribute to viscosity through convective and conductive momentum exchange. Classical friction is the conductive momentum exchange between adjacent regions with different bulk velocity, and always converts macroscopic kinetic energy into microscopic motion.

Opposing forces balance everywhere in equilibrium, requiring all net diffusive flow to be zero. Viscosity damps out spatial variation in bulk velocity as well. The stress tensor is then symmetric, implying that there is a principal coordinate system in which the tensor is diagonal. Stress in a stationary system ($\mathbf{v}_j = \mathbf{u} = 0$, i.e. the co-moving frame) in equilibrium is

$$\boldsymbol{\sigma}^{\mathrm{eq}} = -\sum_{j}^{\text{species}} \left\{ m_j n_j \sum_{k}^{x,y,z} \hat{\mathbf{k}}\hat{\mathbf{k}} \left[\left(\overline{\overline{v}}_{\mathrm{N}j}^{(k)} \right)^2 + \hat{\mathbf{k}} \cdot \overleftrightarrow{J}_{\Pi,j} \cdot \hat{\mathbf{k}} \right] \right\} . \tag{46}$$

The double bar accent indicates RMS value of mode diffusion velocities. Mechanical pressure, defined as $-\mathrm{Trace}\left[\boldsymbol{\sigma}\right]/3$, equals thermodynamic pressure in equilibrium. An ideal gas has no long range forces ($\overleftrightarrow{J}_{\Pi,j} = 0$) and so thermodynamic pressure reduces to

$$p = \sum_{j}^{\text{species}} n_j m_j \left(\overline{\overline{v}}_{\mathrm{N}j} \right)^2 = \sum_{j}^{\text{species}} n_j k_{\mathrm{B}} T , \tag{47}$$

by the equipartition theorem or by direct summation over modes.

Both terms in (35) involve the mode population and therefore may be separated into mean local property values and rate factor, similar to the treatment of reactions and particle flow, and extrapolated in terms of the independent parameters. Various thermal-mechanical effects, such as expansion, piezoelectricity, electrostriction and magnetostriction, are represented by the extrapolation coefficients.

VII. ENERGY FLOW

Energy also flows convectively, carried with particles, and conductively, through work done by field forces. Again, flow across a phase boundary requires evaluation of (49) and (54) in each phase. This discussion otherwise assumes the same material phase exists in both a and b.

Convective energy flow carried by the jth species through an interface from subsystem a to subsystem b is

$$\dot{E}_{\mathrm{conv},j}^{a\to b} = \sum_{i}^{\substack{a \\ \text{modes}}} \epsilon_{ji} N_{ji} \sum_{k}^{\substack{b \\ \text{modes}}} \Gamma_{j,ik} . \tag{48}$$

Employing the definitions stated before (26) and (28), convective energy flux may be expressed as

$$J_{\mathrm{Econv},j}^{a\to b} \equiv \frac{1}{A_z} \dot{E}_{\mathrm{conv},j}^{a\to b} = n_{aj} v_{\mathrm{N}j}^{a\to b} \left\langle \epsilon_j \right\rangle_{\mathrm{N}}^{a\to b} . \tag{49}$$

Net flux may be extrapolated from equilibrium as

$$\mathbf{J}_{\mathrm{Econv},j}^{\text{co-moving}(z)} \approx \left\langle \epsilon_j \right\rangle_{\mathrm{N}}^{(z)} \mathbf{J}_{\mathrm{N}j}^{\text{co-moving}(z)} - n_j \overline{v}_{\mathrm{N}j}^{(z)} L_z \partial_z \left\langle \epsilon_j \right\rangle_{\mathrm{N}}^{(z)} \hat{\mathbf{z}} , \tag{50}$$

presuming that the interface is oriented to the $\hat{\mathbf{z}}$ principal axis. Otherwise, when the interface coincides with a phase boundary, this process should be analyzed as a particle exchange transformation in Sec. V.

In an observer's frame, the interface sweeps over energy density $U/V = \partial_V U + \sum_j \varepsilon_j n_j$, with net flux of

$$\begin{aligned} \mathbf{J}_{\mathrm{Econv}}^{\text{boundary}} &\approx \left(\partial_V U\right)\left(\mathbf{v} - \mathbf{u}\right) + \sum_{j}^{\text{species}} \mathbf{J}_{\mathrm{Qconv},j}^{\text{boundary}} \\ &\quad + \left(\varepsilon_{0j} + \epsilon_j^{\text{macro}}\right) \mathbf{J}_{\mathrm{N}j}^{\text{boundary}} - n_j \overleftrightarrow{D}_{\mathrm{N}j} \cdot \nabla \epsilon_j^{\text{macro}} . \end{aligned} \tag{51}$$

Convective heat flux is distinguished by subtracting the mode independent formation and macroscopic $\epsilon_j^{\text{macro}}$ components of mode energy:

$$\begin{aligned} \mathbf{J}_{\mathrm{Qconv},j}^{\text{boundary}} \equiv \sum_{k}^{x,y,z} \Bigg\{ & \left(\left\langle \epsilon_j \right\rangle_{\mathrm{N}}^{(k)} - \varepsilon_{0j} - \epsilon_j^{\text{macro}} \right) \mathbf{J}_{\mathrm{N}j}^{\text{boundary}(k)} \\ & + \Big[\left(\varepsilon_j - \left\langle \epsilon_j \right\rangle_{\mathrm{N}}^{(k)} \right) n_j \, \hat{\mathbf{k}} \cdot \left(\mathbf{v} - \mathbf{u} \right) \\ & - n_j \overline{v}_{\mathrm{N}j}^{(k)} L_k \partial_k \left(\left\langle \epsilon_j \right\rangle_{\mathrm{N}}^{(k)} - \epsilon_j^{\text{macro}} \right) \Big] \hat{\mathbf{k}} \Bigg\} . \end{aligned} \tag{52}$$

Conductive energy flow $\dot{E}_{\mathrm{cond}}^{a\to b}$ from subsystem a to b may be expressed in the same form as (40) except that the difference in the mode energy $(\epsilon_{jk} - \epsilon_{ji})$ replaces the momentum change $\boldsymbol{\Pi}_{j,ik}$ between transition modes. Similarly separate the contribution from long range interaction from short range exchange proportional to interface area. It is convenient also to distinguish high frequency long range energy exchange as radiant emission and absorption. Work done by low frequency applied fields converts the field potential energy within the system boundary into particle motion. The short range contribution represents the conductive part of heat flux,

$$\sum_{j}^{\text{species}} J_{\mathrm{Qcond},j}^{a\to b} \equiv \left(1/A_z\right) \dot{E}_{\mathrm{cond}}^{a\to b}\Big|_{\text{contact}} , \tag{53}$$

because formation and macroscopic energy cancel in $\epsilon_{jk} - \epsilon_{ji}$, leaving only the microscopic energy difference.

Factor this flux into heat density and mean heat conduction velocity:

$$J^{a\to b}_{\mathrm{Qcond},j} = \frac{Q_a}{V} v^{a\to b}_{\mathrm{Q}j} \ . \tag{54}$$

Flux through an interface aligned with a principal axis is parallel to that axis due to symmetry in mode transitions, the same as for particle and momentum flux. Net flux, when the a–b interface aligns with principal axis $\hat{\mathbf{z}}$, may be extrapolated to first order from equilibrium, indicated by the single bar accent:

$$\begin{aligned}\mathbf{J}^{(z)}_{\mathrm{Qcond},j} &= \hat{\mathbf{z}}\left(J^{a\to b}_{\mathrm{Qcond},j} - J^{b\to a}_{\mathrm{Qcond},j}\right)\\ &\approx -\hat{\mathbf{z}}\left[\overline{v}^{(z)}_{\mathrm{Q}j} L_z \partial_z\left(\frac{Q}{V}\right) + \left(\frac{Q}{V}\right) L_z \partial_z \overline{v}^{(z)}_{\mathrm{Q}j}\right] .\end{aligned} \tag{55}$$

Define the rank two thermal diffusivity tensor analogous to the particle diffusivity tensor (29):

$$\overleftrightarrow{D}_{\mathrm{Q}j} \equiv \hat{\mathbf{x}}\hat{\mathbf{x}}\,\overline{v}^{(x)}_{\mathrm{Q}j} L_x + \hat{\mathbf{y}}\hat{\mathbf{y}}\,\overline{v}^{(y)}_{\mathrm{Q}j} L_y + \hat{\mathbf{z}}\hat{\mathbf{z}}\,\overline{v}^{(z)}_{\mathrm{Q}j} L_z \ . \tag{56}$$

Conductive heat flux along all three principal axes may then be expressed as

$$\begin{aligned}\mathbf{J}_{\mathrm{Qcond},j} &\approx -\overleftrightarrow{D}_{\mathrm{Q}j} \cdot \nabla\left(\frac{Q}{V}\right)\\ &- \left(\frac{Q}{V}\right)\left(\hat{\mathbf{x}} L_x \partial_x \overline{v}^{(x)}_{\mathrm{Q}j} + \hat{\mathbf{y}} L_y \partial_y \overline{v}^{(y)}_{\mathrm{Q}j} + \hat{\mathbf{z}} L_z \partial_z \overline{v}^{(z)}_{\mathrm{Q}j}\right) .\end{aligned} \tag{57}$$

The heat diffusion velocity tends to be relatively insensitive to system parameters so that flux is dominated by heat density gradient, which expands as

$$\begin{aligned}\nabla\left(\frac{Q}{V}\right) &= \left(\frac{C_{\mathrm{V}}}{V}\right)\nabla T + \sum_k \left(\varepsilon_k - \varepsilon_{0k}\right)\nabla n_k\\ &- \nabla\left(\frac{E^{\mathrm{macro}}}{V}\right) + \frac{1}{V}\left.\frac{\partial U}{\partial\varphi}\right|_V \nabla\varphi + \cdots \ .\end{aligned} \tag{58}$$

Equation (57) includes Fourier's law and all other first order effects related to conductive heat flow through a single material phase.

Many applications, such as continuous chemical processing, plumbing, electronics and airfoil design, involve net flow in a non-equilibrium steady state. In this case, no parameters change in time for any single-phase subsystem. For example, in an isotropic material, (7) becomes

$$\begin{aligned}0 &= \partial_t Q_{\mathrm{outside}} + \partial_t E^{\mathrm{inflow}}_{\mathrm{macro}} + \sum_j \varepsilon_{0j}\,\Delta N^{\mathrm{outside}}_j\\ &\approx \partial_t Q_{\mathrm{cond}} - V\nabla\cdot\sum_j \langle\epsilon_j\rangle_{\mathrm{N}} \mathbf{J}^{\mathrm{boundary}}_{\mathrm{N}j} \ .\end{aligned} \tag{59}$$

Therefore, conductive heat outflow must balance net inflow of particle energy. No heat is generated or absorbed by a steady flow of particles unless the mean energy of the flowing particles changes. Such change might be due to a temperature gradient, known as the Thomson effect, or other parameter gradients, or due to flow from one phase to another, known as the Peltier effect when the particle flow is electric current.

To analyze the latter case, define a system enclosing a junction between two phases a and b of conductive material surrounded by a heat reservoir. Let flow be uniaxial, for simple description, and A be the system cross-section. Steady state conductive heat flow from the reservoir is

$$\partial_t Q_{\mathrm{cond}} \approx A \sum_j \left(\langle\epsilon_{bj}\rangle_{\mathrm{N}} - \langle\epsilon_{aj}\rangle_{\mathrm{N}}\right)\mathbf{J}^{\mathrm{boundary}}_{\mathrm{N}j} \ . \tag{60}$$

This result obscures that flow occurs in three stages: (1) Flow into the system a boundary contributes excess heat to the system equal to $A\sum_j\left(\langle\epsilon_{aj}\rangle_{\mathrm{N}} - \varepsilon_{aj}\right)J_{\mathrm{N}j}$ as the incoming particles thermalize. (2) Flow across the junction is a particle transformation contributing excess latent energy $A\sum_j\left(\varepsilon_{bj} - \varepsilon_{aj}\right)J_{\mathrm{N}j}$ as particles from a thermalize in b. (3) Flow out of b leaves excess energy of $A\sum_j\left(\varepsilon_{bj} - \langle\epsilon_{bj}\rangle_{\mathrm{N}}\right)J_{\mathrm{N}j}$. Assuming that all flow is electric current $I_j = Aq_jJ_{\mathrm{N}j}$ driven by a constant applied field, heat flow from the reservoir may be expressed as

$$\partial_t Q_{\mathrm{cond}} \approx \sum_j^{\mathrm{species}}\left(\Pi_{bj} + \frac{\varepsilon_{bj} - \varepsilon_{aj}}{q_j} - \Pi_{aj}\right) I_j \ , \tag{61}$$

The first and third stages are characteristic of each phase. Define the Peltier coefficient as $\Pi_j \equiv \left(\langle\epsilon_j\rangle_{\mathrm{N}} - \varepsilon_j\right)/q_j$.

Note that state energy $E_s \approx E_s^{(\varphi=0)} + N_jq_j\varphi$ when the electric field driving the particle flow is weak. There is a thermoelectric reciprocal relation between Peltier and Seebeck effects in this weak field limit:

$$S_j = \frac{\varepsilon_j - \langle\epsilon_j\rangle_{\mathrm{N}}}{k_{\mathrm{B}}T^2\,\partial_\varphi\eta_j|_V} \approx \frac{\langle\epsilon_j\rangle_{\mathrm{N}} - \varepsilon_j}{q_jT} = \frac{\Pi_j}{T} \ . \tag{62}$$

The Thomson coefficient $\mathcal{K}_j = \partial_T\Pi_j - S_j\partial_\varphi\Pi_j$ is related to these two effects when a temperature gradient also induces an electric potential gradient.

VIII. PHASE STABILITY

From the previous sections, diffusion is an inherently local phenomenon. Energy, momentum and particles diffuse continually. Macroscopic conditions in the thermodynamic limit stabilize when counter-propagating flows are equal, defining a stable material phase in equilibrium.

Transport equations (16), (31), (45), (51) and (57) all exhibit stabilizing influence on equilibrium states. Deviation of any independent parameter from the current equilibrium value produces flows toward recovering that state, countering the disruption. Le Chatelier's principle is one version of this general conclusion.

Diffusion is a response to all existing parameter gradients, which can produce uncommon results. For example, energy may flow with a temperature gradient in the presence of a strong applied field, contradicting Sadi Carnot's founding claim that heat always flows from hotter to colder regions. Instead, the statement "energy, momentum and particles diffuse toward a steady state" captures the essence of thermodynamics.

When two phases can coexist, a system typically evolves to the more stable phase. However, systems may be superheated or supercooled if prepared under unusually quiet conditions. Fluctuation in local energy density then can trigger rapid transition to a more stable state consistent with system parameters. Otherwise, fluctuations play no role in determining mean flows or an equilibrium state.

IX. CONCLUSIONS

General, yet concise, transport equations are derived here by recognizing all forms of stable particle as distinct species. This allows consistent quantum mechanical treatment of diffusion between species and regions without delving into specific particle interaction models. Doing so also answers key nagging questions posed in the introduction.

The condition of uncorrelated mode populations is sufficient to show that energy, momentum and particles always diffuse on average toward a steady equilibrium state. Net flows tend to disperse high mode concentration, often described as dissipation. Gradients in system parameters produce a variety of thermodynamic effects, sometimes at odds with common experience in extreme cases. We naturally infer forward progress from diffusion. This behavior appears spontaneous and irreversible to an observer unaware of microscopic activity.

The thermodynamic equation of motion is not invariant under Galilean transformations and therefore presents no contradiction between observers. Deterministic Lagrangian dynamics "emerge" when diffusion is insignificant. This is typically true in classical cases involving a few bodies with negligible friction and internal activity. Otherwise, diffusion can be suppressed in specially designed apparatus limiting all but a few mode transition rates, such as by reducing ambient interaction in a vacuum.

Observers moving fast relative to each other may be able to infer the equilibrium distribution with four temperature parameters and transition rates from the other through Lorentz transformation. Diffusion must still be evaluated in the observer's reference frame through the thermodynamic equation of motion (45).

Diffusion, with an apparent "arrow of time," occurs because there are more modes that a particle may transition into than those consistent with the prior state of the system. What we would recognize as "backwards" evolution becomes less likely as the system complexity increases. This conclusion holds true even if antiparticles do travel in the opposite direction of time [24]; they diffuse just as we expect for normal particles.

Diffusion depends only on local conditions. A global condition is not required to define equilibrium, and would conflict with local quantum mechanical transport. Furthermore, these transport equations describe behavior that transitions continuously, as complexity increases, from random walk in simple systems to diffusion in the thermodynamic limit. There is no distinction between chemical and biological function in modal analysis. Active agents are accounted for naturally in the mode spectrum. No additional assumption, reference to cyclic processes and ensembles, interpretation of probability, or quantity, such as entropy and information, is needed to explain what we observe.

Reciprocal relations exist between any two or more parameters when the corresponding flows share mutual diffusion velocities and the partition function is analytic. These relations hold, however, only in the limit of weak disruption and when the associated kinetic rate quotient is practically constant.

Fluctuations typically average out over a measurement and are inconsequential to thermodynamic properties and transport, apart from triggering phase transitions and causing random walk in particle trajectories. To first order, mean flows are driven by macroscopic mean property gradients.

The rate of transformation and flow equals the mode transition rate and population over the entire mode spectrum. Mode spectrum and transition rates are sensitive to local material structure. This sensitivity produces hysteresis and anomalous behavior, such as the Mpemba effect, in which the same system prepared differently evolves differently under similar macroscopic conditions.

This new approach also shifts our philosophical view of natural processes. Equilibrium is balance of flows. All systems evolve toward balance, not disorder, as the Second Law is usually interpreted. Balance can produce complicated structures. Evolution of life then is highly likely under suitable conditions.

These transport equations match known empirical laws under specific conditions. Consequently, this work establishes a concrete foundation for all physical sciences without disrupting current applied theory based on these laws. This foundation assists further development of each field, particularly in areas between disciplines, by providing common principles, methods and language for analysis.

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[1] Clausius, R. *The Mechanical Theory of Heat* (MacMillan & Co., Walter R. Browne (transl), 1879).

[2] Gibbs, J. W. On the equilibrium of heterogenous substances. Transactions of the Connecticut Academy, 3 (1878): 103–246 and 343–524.

[3] Landi, G. T., and M. Paternostro. Irreversible entropy

production: From classical to quantum. Rev. Mod. Phys. 93 (2021): 035008.

[4] Farias, C., V. A. Pinto, and P. S. Moya. What Is the Temperature of a Moving Body. Sci. Rep. 7 (2017): 17657.

[5] Strunk, C. Quantum Transport of Particles and Entropy. Entropy 23 (2021): 1573. doi.org/10.3390/e23121573

[6] Uffink, J. Compendium of the foundations of classical statistical physics. J. Butterfield and J. Earman (eds), Philosophy of Physics, Amsterdam: North Holland (2007): 923-1047.

[7] Goldstein, H. *Classical Mechanics* (2^{nd} edition, Addison Wesley, 1980), Section 1–4.

[8] Onsager, L. Reciprocal Relations in Irreversible Processes I. Phys Rev 37 (1931): 405; Reciprocal Relations in Irreversible Processes II. Phys. Rev. 38 (1931): 2265.

[9] Brownell, J. H. Distinguishing flow from fluctuation in the fluctuation-dissipation theorem. doi.org/10.5281/zenodo.14009808 (2024).

[10] Uffink, J. Bluff your way in the second law of thermodynamics. Studies in History and Philosophy of Science Part B: Studies in History and Philosophy of Modern Physics 32.3 (2001): 387.

[11] Frigg, R., and C. Werndl. Entropy – a guide for the perplexed. *Probabilities in Physics*, edited by C. Beisbart & S. Hartmann (Oxford University Press, 2011): 115–42.

[12] Brownell, J. H. Entropy is not maximum in the equilibrium state of multi-phase and reactive systems. doi.org/10.5281/zenodo.14009800 (2024).

[13] Parrondo, J., J. Horowitz and T. Sagawa. Thermodynamics of information. Nature Phys. 11 (2015): 131–139.

[14] Strasberg, P., and A. Winter. First and Second Law of Quantum Thermodynamics: A Consistent Derivation Based on a Microscopic Definition of Entropy. PRX Quantum 2 (2021): 030202.

[15] Brownell, J. H. On the transition from quantum decoherence to thermal dynamics under natural conditions. arXiv:2409.12986 [physics.gen-ph] (2024).

[16] Planck, M. *Vorlesungen über Thermodynamik* (Leipzig: Veit & Comp. 1897): 113.

[17] Bridgman, P. W. Statistical mechanics and the second law of thermodynamics. Science 75.1947 (1932): 428.

[18] Marchetti, M. C., J.-F. Joanny, S. Ramaswamy, T. B. Liverpool, J. Prost, M. Rao and R. A. Simha. Hydrodynamics of Soft Active Matter. Rev. Mod. Phys. 85 (2013): 1143.

[19] Takatori, S. C., and J. F. Brady. Towards a Thermodynamics of Active Matter. Phys. Rev. E 91 (2015): 032117.

[20] Brownell, J. H. Negative internal entropy production. doi.org/10.5281/zenodo.14009793 (2024).

[21] Zhang, J., P. W. Hess, A. Kyprianidis, P. Becker, A. Lee, J. Smith, G. Pagano, I.-D. Potirniche, A. C. Potter, A. Vishwanath, N. Y. Yao and C. Monroe. Observation of a Discrete Time Crystal. Nature 543.7644 (2017): 217–220.

[22] Smits, J., L. Liao, H. T. C. Stoof and P. van der Straten. Observation of a space-time crystal in a superfluid quantum gas. Phys. Rev. Lett. **121** (2018): 185301.

[23] Kongkhambut, P., J. Skulte, L. Mathey, J. G. Cosme, A. Hemmerich and H. Keßler. Observation of a continuous time crystal. arXiv:2202.06980 (2022).

[24] Feynman, R. P. The theory of positrons. Physical Review 76 (1949): 749.