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ABSTRACT

The classical Gibbs–Duhem relation is restricted to quasistatic thermodynamic processes and does not include kinetic energy contributions. Consequently, its connection to fluid mechanics remains indirect. Here, we derive a kinetic Gibbs–Duhem relation that consistently incorporates kinetic effects, thereby linking thermodynamic and mechanical descriptions of fluid motion. On this basis, we formulate a density evolution equation for inhomogeneous fluids. The proposed equation recovers, as limiting cases, the classical relations for the speed of sound, Bernoulli’s equation, and the van der Waals equation of state.

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I. INTRODUCTION

Classical continuum mechanics describes fluid motion through Newton’s second law,¹

$$\rho \frac{D\mathbf{u}}{Dt} = \rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p, \quad (1)$$

where ρ is the mass density, $\mathbf{u}$ is the velocity field, and p is the pressure. Newton’s law is formulated in the Lagrangian framework and has been remarkably successful in describing a wide range of continuum flows. However, inhomogeneous fluids involve strong coupling among mechanics, mass transport, and thermodynamics, motivating formulations that consistently account for these coupled effects.

A central thermodynamic relation is the Gibbs–Duhem equation constraining the mechanical and entropy forces as²

$$Dp + \phi D\mu + s_\tau D\tau = 0, \quad (2)$$

where μ is the chemical potential, ϕ is the volume fraction, τ is the absolute temperature, and s_τ is the thermal entropy density. The classical Gibbs–Duhem relation has been extended in the literature to nonequilibrium processes,^{3,4} in which thermodynamic variables such as the chemical potential μ , temperature T , or pressure p may deviate from their equilibrium values. In particular, the term “nonequilibrium” in Refs. 3 and 4 refers to deviations of these thermodynamic variables, p , τ , and μ from their equilibrium states. However, the kinetic free energy associated with the fluid motion, $\rho \mathbf{u}^2$, has not been

explicitly incorporated into these formulations. Consequently, the resulting thermodynamic framework does not explicitly account for the contribution of fluid motion to the thermodynamic description, and its connection to fluid mechanics remains indirect. In this work, we derive a generalized Gibbs–Duhem relation that explicitly incorporates the kinetic energy contribution associated with fluid motion. This extension provides a thermodynamic framework that directly couples thermodynamic variables to fluid motion and establishes a thermodynamically consistent basis for connecting nonequilibrium thermodynamics with fluid mechanics.

A second issue concerns the evolution of mass density. Equation (1) governs the acceleration of a material element but does not itself provide an evolution equation for the density. In many continuum formulations, this issue is circumvented by adopting the incompressibility constraint,^{5,6}

$$\frac{D\rho}{Dt} = \frac{\partial \rho}{\partial t} + \mathbf{u} \cdot \nabla \rho = 0, \quad (3)$$

which is well justified for many single-phase liquids and solids. In inhomogeneous fluids, however, diffusion, mixing, and excess-volume effects generally produce local density variations, making an explicit density evolution equation desirable.

A third consideration concerns the kinematic description of transport theory. In the classical Navier–Stokes model, an arbitrary control volume $\Omega \subset V$ inside the whole domain V is considered to derive the momentum evolution and density evolution based on the

Gauss's theorem in the Eulerian description. In this description, a velocity field $\mathbf{v}$ is prescribed at the boundary of the control volume, and the convective momentum-flux tensor across the boundary of the control volume is assumed to be written as⁷ $\mathbf{J}_v = \rho \mathbf{v} \otimes \mathbf{v}$. In the absence of external body forces acting on Ω , the local momentum conservation in the Eulerian description is expressed as

$$\frac{d(\rho \mathbf{v})}{dt} = \frac{\partial(\rho \mathbf{v})}{\partial t} + \nabla \cdot \mathbf{J}_v = \mathbf{0}. \quad (4)$$

Equivalently,

$$\frac{d(\rho \mathbf{v})}{dt} = \frac{\partial(\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) = \mathbf{0}. \quad (5)$$

For a viscous fluid, the momentum flux also includes the viscous stress tensor $\boldsymbol{\tau}$, which arises from irreversible momentum transport across the boundary $\partial\Omega$ of the control volume Ω and is associated with entropy production. The momentum evolution in the Navier–Stokes model therefore becomes⁷

$$\frac{d(\rho \mathbf{v})}{dt} = \frac{\partial(\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) = \nabla \cdot \boldsymbol{\tau}. \quad (6)$$

The viscous momentum transport gives rise to entropy production and, correspondingly, to the dissipation of kinetic free energy. Multiplying Eq. (6) by $\mathbf{v}$, integrating over the total volume V , and applying Gauss's theorem gives, under suitable no-flux boundary conditions on ∂V , lead to

$$\frac{d}{dt} \int_V \rho \mathbf{v}^2 \delta V = - \int_V \eta \nabla \mathbf{v} : \nabla \mathbf{v} \delta V \leq 0, \quad (7)$$

where we have used the viscous stress tensor $\boldsymbol{\tau} = \frac{1}{2} \eta \nabla \mathbf{v}$ as an example. The double-dot product operator means $\nabla \mathbf{v} : \nabla \mathbf{v} = \text{Tr}(\nabla \mathbf{v}^T \nabla \mathbf{v})$.

Note that the viscous force should not be interpreted directly as a mechanical force. Rather, the viscous contribution is associated with irreversible entropy production. The corresponding thermodynamic force must satisfy the Gibbs–Duhem relation, which imposes a constraint between the mechanical and viscous contributions to the force balance [Eq. (2)]. A related example can be found in Ref. 8, where the mechanical force is constrained by the Boltzmann mixing entropy associated with the chemical potential. This perspective provides a fundamentally different viewpoint from the conventional Navier–Stokes formulation, in which viscous effects are introduced directly through the viscous stress in the momentum equation as a mechanical force.

Mass conservation, on the contrast, follows from the conservation of the total number of molecules. Introducing the mass-flux vector $\mathbf{J}_c = \rho \mathbf{v}$ across the boundary $\partial\Omega$ of the control volume, the continuity equation in the Eulerian description is written as

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \nabla \cdot \mathbf{J}_c = \frac{\partial\rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0. \quad (8)$$

This continuity equation is likewise derived based on Gauss's theorem applying on the control volume Ω and the boundary $\partial\Omega$ with pointing-out normal vector $\mathbf{n}$,

$$\frac{\partial}{\partial t} \int_\Omega \rho \delta\Omega = - \int_{\partial\Omega} \mathbf{J}_c \cdot \mathbf{n} \delta(\partial\Omega) = - \int_\Omega \nabla \cdot \mathbf{J}_c \delta\Omega. \quad (9)$$

When the control volume changes with time during the transport process, the same results can be derived using the Reynolds transport theorem. Alternatively, the above-mentioned results can be obtained from the Boltzmann transport equation,⁹ which is formulated within the Eulerian framework, where the motion of individual fluid particles is not explicitly tracked.

The above-mentioned derivation within the Eulerian framework raises an important question: if the transport of momentum through the boundary of a control volume $\partial\Omega$ is associated with viscous dissipation and entropy production [Eq. (6)], why does the corresponding mass flux not itself necessarily produce entropy? Note that there is no entropy production in Eq. (8), as the right hand side of Eq. (8) is zero.

The total mass, or equivalently the total number of molecules, is conserved. However, the local density ρ is not generally conserved within a fixed control volume; it can change as mass enters or leaves the volume. In particular, mass diffusion can lead to local variations in the density, such that $d\rho/dt \neq 0$, and can be accompanied by entropy production associated with the diffusive transport.¹⁰ In particular, Eq. (6) describes the evolution of the momentum density $\rho \mathbf{v}$. However, within the Eulerian description alone, it is not immediately clear how the viscous dissipation should be interpreted in terms of the evolution of the density ρ , the velocity $\mathbf{v}$, or their product $\rho \mathbf{v}$. More specifically, although the total kinetic energy $\int_V \rho \mathbf{v}^2 \delta V$ is dissipated by viscous effects [Eq. (7)], the Eulerian formulation does not explicitly reveal whether this dissipation should be attributed to changes in the velocity field, changes in the density field, or their coupled evolution. Clarifying this point is essential for establishing a consistent connection between mass conservation, momentum conservation, and entropy production.

These discussions motivate a closer examination of the relationship between mass transport, momentum transport, and entropy production. In particular, the Eulerian formulation describes these quantities through local conservation laws and fluxes across the boundaries of a fixed control volume. To clarify their respective physical roles, we therefore employ a Lagrangian framework, in which the motion of individual fluid elements is explicitly tracked. This perspective provides a more direct interpretation of how momentum transport and viscous dissipation arise at the level of a moving fluid element.

Motivated by these considerations, we derive a generalized Gibbs–Duhem relation that incorporates the kinetic energy contribution of fluid motion and formulate a corresponding density evolution equation in inhomogeneous fluids. The resulting framework provides a thermodynamically consistent description of the coupled evolution of density, momentum, and interfacial transport. In appropriate limiting cases, the theory recovers the classical expressions for the speed of sound, Bernoulli's equation, and the van der Waals equation of state, thereby demonstrating its consistency with established principles of fluid mechanics and thermodynamics.

II. DEFINITION AND NOTATIONS IN THE LAGRANGIAN FRAMEWORK

We use the Lagrangian description for the scalar field: $\phi(\mathbf{r}(t), t)$, and for the velocity field: $\mathbf{u}(\mathbf{r}(t), t)$. In $n \in \mathbb{Z}$ dimensions, we define the space vector of the fluid particle as

$$\mathbf{r}(t) = (x_1(t), x_2(t), \dots, x_n(t)) = \sum_{i=1}^n x_i(t) \mathbf{e}_i, \quad (10)$$

where $\mathbf{e}_i$ is the unit vector in the i th dimension. The definition of the fluid convection velocity is

$$\mathbf{u} = \frac{D\mathbf{r}}{Dt} = \sum_i \dot{x}_i \mathbf{e}_i = \sum_i u_i \mathbf{e}_i. \quad (11)$$

Here, u_i is the velocity component in the i th dimension.

The total time derivative is defined as

$$\frac{D\phi}{Dt} = \frac{\partial\phi}{\partial t} + \mathbf{u} \cdot \nabla\phi, \quad (12)$$

$$\frac{D\mathbf{u}}{Dt} = \frac{\partial\mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla\mathbf{u}, \quad (13)$$

$$\frac{D(\rho\mathbf{u})}{Dt} = \frac{\partial(\rho\mathbf{u})}{\partial t} + \mathbf{u} \cdot \nabla(\rho\mathbf{u}). \quad (14)$$

These definitions differ from the Eulerian description for the scalar field: $\phi(\mathbf{r}, t)$, and for the velocity field: $\mathbf{v}(\mathbf{r}, t)$. In the Eulerian description, as space $\mathbf{r}$ and time t are independent arguments, the following definition

$$\mathbf{v} = \frac{d\mathbf{r}}{dt} \quad (15)$$

cannot be directly used to describe the velocity. Instead, the velocity in the Eulerian description has to be prescribed. In general, the velocity $\mathbf{v}$ in the Eulerian description is not the same as the velocity $\mathbf{u}$ in the Lagrangian description, i.e., $\mathbf{v} \neq \mathbf{u}$. The time derivative in the Eulerian description can be expanded as

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \mathbf{v} \cdot \nabla\rho + \rho\nabla \cdot \mathbf{v}. \quad (16)$$

The first two terms have the same mathematical form as the total derivative in the Lagrangian description. However, it should be noted that the convective term, $\mathbf{v} \cdot \nabla\rho$, in Eq. (16) arises from the prescribed mass flux $\rho\mathbf{v}$ across the boundary of the control volume under a prescribed velocity field. Its physical meaning therefore differs from that of the particle-tracing velocity $\mathbf{u}$ in the Lagrangian description.

Moreover, we emphasize the definition of incompressibility in the Lagrangian framework. In the absence of mass exchange, an incompressible fluid is characterized by the invariance of the volume of each transported material element,

$$\frac{D(\delta V)}{Dt} = 0. \quad (17)$$

Because the mass in the material element δV is constant in the case without mass exchange with neighboring cells, this condition is equivalent to

$$\frac{D\rho}{Dt} = 0. \quad (18)$$

When mass exchange between neighboring material elements is allowed, however, these two conditions are no longer equivalent. A material element may retain a constant volume while its density changes as a result of mass transport, including diffusion and other forms of mixing. This distinction motivates a revised definition of incompressibility in the presence of mass diffusion.

III. THEORY

A. A single fluid particle

As a starting point, we consider an idealized system consisting of a single fluid particle with mass m and volume δV . The mass density

ρ is defined as $\rho = m/\delta V$. This particle moves with a velocity of $\mathbf{u}$. We write the total energy of the system as

$$E = m\mathbf{u}^2 + p\delta V = (\rho\mathbf{u}^2 + p)\delta V = (e + p)\delta V, \quad (19)$$

where the kinetic free energy density e is defined as $e = \rho\mathbf{u}^2$. The pressure p is a Lagrange multiplier associated with the constant volume δV .^{11,12} We reformulate the kinetic energy density as $\rho\mathbf{u}^2 = \rho\mathbf{u} \cdot \mathbf{u}$. Thus, the total derivative of the system energy reads

$$DE = [\rho\mathbf{u} \cdot D\mathbf{u} + D(\rho\mathbf{u}) \cdot \mathbf{u} + Dp]\delta V + (e + p)D(\delta V). \quad (20)$$

For an incompressible particle that the volume is a constant in the transport process, i.e., $D(\delta V) = 0$, the last term in Eq. (20) vanishes. Applying the dissipation principle^{13,14} to the first term inside the bracket leads to the following diffusion equation for the velocity:

$$\boxed{\frac{D\mathbf{u}}{Dt} = \frac{\partial\mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla\mathbf{u} = \nabla \cdot D_u \nabla \mu_u}, \quad (21)$$

where the chemo-velocity potential is defined as

$$\mu_u = \frac{1}{2} \frac{\partial e}{\partial \mathbf{u}} = \rho\mathbf{u}. \quad (22)$$

The mobility D_u is related to the viscosity η as $D_u = \eta/\rho^2$. Here, our concept is that the viscous force is an entropic force, which is associated with the velocity entropy s_u as

$$\mu_u \cdot \frac{D\mathbf{u}}{Dt} = -\tau \frac{Ds_u}{Dt}. \quad (23)$$

The acceleration, $\mathbf{a} = D\mathbf{u}/Dt$, appearing in Newton's law is conventionally associated with a mechanical force. However, it has recently been proposed that acceleration may instead originate from an entropic force.^{15–17} Our formulation in Eqs. (21) and (23) is consistent with this entropic interpretation of acceleration, in which the temporal evolution of the velocity is directly related to velocity entropy. This concept is also compatible with the principle of special relativity, as discussed in the Appendix. Furthermore, by employing the Gibbs–Duhem relation to constrain the mechanical and entropic forces, the present formulation of velocity entropy provides a thermodynamic framework that recovers Newton's law, as demonstrated below.

In the classic thermodynamics,³ the standard Gibbs–Duhem relation is obtained by subtracting the dissipation term from the total derivative of the system energy. Adopting this spirit, the remaining terms in Eq. (20) is a Gibbs–Duhem like relation containing the mechanical and entropic forces as

$$\boxed{D(\rho\mathbf{u}) \cdot \mathbf{u} + Dp = 0}, \quad (24)$$

where the first term depicts the entropic force and the second term represents the mechanical force. Dividing by Dx_i in the above-mentioned equation and using the relation $\mathbf{u} = D\mathbf{r}/Dt$, we obtain n equations,

$$\frac{D(\rho\mathbf{u})}{Dt} \cdot \frac{D\mathbf{r}}{Dx_i} + \frac{Dp}{Dx_i} = 0, \quad i = 1, 2, \dots, n. \quad (25)$$

As $D\mathbf{r}/Dx_i = \mathbf{e}_i$ [Eq. (10)] and $D(\rho\mathbf{u}) \cdot \mathbf{e}_i = D(\rho u_i)$, Eq. (25) is rewritten as

$$\frac{D(\rho u_i)}{Dt} + \frac{Dp}{Dx_i} = 0, \quad i = 1, 2, \dots, n. \quad (26)$$

Equation (26) can also be expressed in the vector form,

$$\frac{D(\rho \mathbf{u})}{Dt} = \frac{\partial(\rho \mathbf{u})}{\partial t} + \mathbf{u} \cdot \nabla(\rho \mathbf{u}) = -\nabla p, \quad (27)$$

which is nothing but the momentum balance equation.

It is worth emphasizing that the momentum evolution equation is mathematically equivalent to the proposed generalized Gibbs–Duhem relation. In this sense, the generalized Gibbs–Duhem framework provides a direct connection between fluid mechanics and classical thermodynamics. Unlike the Navier–Stokes formulation, viscous effects are not introduced through the momentum evolution equation. Instead, they are incorporated in Eq. (21) through the velocity entropy, thereby embedding dissipation within the thermodynamic description rather than treating it as an explicit mechanical force. For the approximation of incompressible fluid particle that $D\rho/Dt = 0$, Eq. (27) replicates Newton's law,

$$\rho \frac{D\mathbf{u}}{Dt} = -\nabla p. \quad (28)$$

In the Eulerian framework, the pressure force enters the momentum balance through Newton's law of motion, as in the derivation of the Boltzmann transport equation. It is important to note, however, that Newton's law is fundamentally formulated in the Lagrangian framework, where one follows a material element of volume δV and introduces the pressure p as a Lagrange multiplier enforcing the relevant constraint on the transported material element. The present derivation therefore differs conceptually from conventional transport theories formulated directly within the Eulerian framework.

B. Density evolution equation of a many body system

We now consider a many body system for a constant volume element δV in the Lagrangian description. The volume element δV contains a number of fluid particles. The volume and density of each fluid particle are denoted by δV_i and ρ_i , respectively. In the volume element δV , the mass density is defined as

$$\rho = \frac{\sum \rho_i \delta V_i}{\delta V}. \quad (29)$$

In this case, the density can vary with time because, during the transport process, fluid particles can flow into and out of the constant volume element δV . The time evolution of the density is derived in this section.

For the many body system, the system energy is expressed by the following integration:

$$E = \int_V (e + p) \delta V = \int_V (\rho \mathbf{u}^2 + p) \delta V. \quad (30)$$

Repeating the same derivation as in Sec. III A, we obtain the momentum balance equation [Eq. (27)] and the velocity dissipation equation [Eq. (21)]. Multiplying both sides of Eq. (21) by $\rho \mathbf{u}$, we obtain the dissipation law as

$$\frac{D}{Dt} \int_V \rho \mathbf{u}^2 \delta V = - \int_V \frac{\eta}{\rho} \nabla \mu_u : \nabla \mu_u \delta V \leq 0. \quad (31)$$

When the density is uniform in space, the above-mentioned dissipation law is equivalent to that of the Navier–Stokes model [Eq. (7)],

$$\frac{D}{Dt} \int_V \rho \mathbf{u}^2 \delta V = - \int_V \eta \nabla \mathbf{u} : \nabla \mathbf{u} \delta V \leq 0. \quad (32)$$

The momentum balance equation [Eq. (27)] minus the velocity dissipation equation [Eq. (21)] multiplying by ρ leads to a density evolution equation,

$$\mathbf{u} \frac{D\rho}{Dt} = -\nabla p - \rho \nabla \cdot D_u \nabla \mu_u. \quad (33)$$

The validity of this density evolution equation is demonstrated as follows.

Under isentropic condition, the density evolution equation reduces to

$$\boxed{\mathbf{u} \frac{D\rho}{Dt} = -\nabla p.} \quad (34)$$

In an isotropic case, we replicate the classic definition of sound speed,¹

$$u = \sqrt{\frac{D\mathcal{P}}{D\rho}}; \quad \mathcal{P} = -p. \quad (35)$$

Here, the negative sign denotes a different norm vector direction of the fluid particle. When the norm vector is pointing out, the Lagrange multiplier term for the pressure is $+p\delta V = -\mathcal{P}\delta V$. When the norm vector is pointing inside, the Lagrange multiplier term for the pressure is $-p\delta V$.

By using the relation $D(\rho \mathbf{u}^2) = \mathbf{u}^2 D\rho + 2\rho \mathbf{u} \cdot D\mathbf{u}$ and the isentropic condition $D\mathbf{u}/Dt = \mathbf{0}$ (or $D\mathbf{u} = \mathbf{0}$), Eq. (34) is further simplified as

$$D(p + \rho \mathbf{u}^2) = 0. \quad (36)$$

This result is nothing but Bernoulli's equation.

Next, we demonstrate that the density evolution equation recovers the equation of state for an ideal gas. As discussed above, the velocity field is interpreted as containing the mean thermal velocity. In the absence of macroscopic motion, the velocity $\mathbf{u}$ therefore represents the mean thermal velocity of the molecules. At this mesoscopic length scale, the density is defined consistently with this velocity field. The corresponding kinetic energy density is then given by

$$\rho \mathbf{u}^2 = R_g \tau / v_m, \quad \text{or} \quad \mathbf{u}^2 = R_g \tau / M, \quad (37)$$

where R_g is the universal gas constant, M depicts the molar mass, and v_m is the molar volume. In the 1D steady state, the density evolution for inviscid fluids reduces to

$$\frac{R_g \tau}{M} D\rho = D\mathcal{P}. \quad (38)$$

Integrating Eq. (38) for a constant τ , we obtain the following equation:

$$\mathcal{P} = \frac{R_g \tau}{M} \rho + C, \quad (39)$$

where the integration constant C is zero as $\mathcal{P} \rightarrow 0$ as $\rho \rightarrow 0$. Therefore, Eq. (39) replicates the EOS of ideal gas,

$$\mathcal{P}v_m = R_g\tau. \quad (40)$$

C. Galilei invariance

A physical model is said to be Galilean invariant if it retains the same form under a Galilean transformation,

$$\mathbf{x}' = \mathbf{x} + \mathbf{u}_0 t, \quad (41)$$

$$t' = t + t_0, \quad (42)$$

where both $\mathbf{u}_0$ and t_0 are constants. For inviscid flow, the Boltzmann transport equation for the momentum evolution reads^{3,9}

$$\frac{\partial(\rho\mathbf{u})}{\partial t} + \nabla \cdot (\rho\mathbf{u} \otimes \mathbf{u}) = -\nabla p. \quad (43)$$

In this theory, the Galilei invariance is not satisfied.¹⁰ Expanding the second term by using the vector calculus $\nabla \cdot (\mathbf{a} \otimes \mathbf{b}) = (\nabla \cdot \mathbf{a})\mathbf{b} + \mathbf{a} \cdot \nabla \mathbf{b}$, the above-mentioned equation can be rewritten as^{7,10}

$$\rho \frac{D\mathbf{u}}{Dt} + \frac{d\rho}{dt}\mathbf{u} = -\nabla p. \quad (44)$$

It is clear that Eq. (44) does not satisfy Galilean invariance when $\frac{d\rho}{dt} \neq 0$, since the velocity is not Galilean invariant. Under a Galilean transformation, the velocity transforms according to $\mathbf{u}' = \mathbf{u} + \mathbf{u}_0$.

The present model is Galilei invariant for inviscid flow. Integrating the Gibbs–Duhem relation, Eq. (24), we obtain the pressure as

$$p = -\rho\mathbf{u}^2. \quad (45)$$

Substituting this expression for the pressure into the density equation, Eq. (34), it is readily seen that Galilean invariance is satisfied, as the non-Galilean-invariant velocity terms appear on both sides of the equation and cancel out,

$$-\dot{\mathbf{u}}|\mathbf{e}_u \frac{D\rho}{Dt} = \rho \dot{\mathbf{u}}|\mathbf{e}_u \cdot \nabla \mathbf{u} + \dot{\mathbf{u}}|\mathbf{e}_u \cdot \nabla(\rho\mathbf{u}) + \rho \dot{\mathbf{u}}|\mathbf{e}_u \times (\nabla \times \mathbf{u}) + \dot{\mathbf{u}}|\mathbf{e}_u \times \nabla \times (\rho\mathbf{u}). \quad (46)$$

Here, $\mathbf{e}_u$ is the unit vector. Moreover, the velocity diffusion equation is also Galilei invariant.

D. Stokes flow and Navier–Stokes model

For incompressible flow with uniform density, we have $D(\rho\mathbf{u}) = \rho D\mathbf{u}$ and the generalized Gibbs–Duhem relation reads

$$-D\mathcal{P} + \rho\mathbf{u} \cdot D\mathbf{u} = 0. \quad (47)$$

Dividing both sides by dx_k , $k = 1, 2, \dots, n$ and adopting the velocity dissipation equation, $D\mathbf{u}/Dt = D_u \nabla^2 \mathbf{u} = (\eta/\rho) \nabla^2 \mathbf{u}$ [Eq. (21)] for a uniform density, we recover Stokes's formulation for fluid dynamics,

$$-\nabla \mathcal{P} + \eta \nabla^2 \mathbf{u} = 0. \quad (48)$$

Introducing a time relaxation factor for the Stokes-flow model τ_s in the context of steepest descent method,¹⁸ we obtain

$$\frac{1}{\tau_s} \frac{D\mathbf{u}}{Dt} = -\nabla \mathcal{P} + \eta \nabla^2 \mathbf{u}. \quad (49)$$

Artificially defining $1/\tau_s = \rho$, the Navier–Stokes model for incompressible flow is replicated.

E. Multicomponent chemical system

For multicomponent chemical systems, the volume element δV cannot, in general, be represented as a simple sum of the volumes of all fluid particles contained within it, because excess space may exist between the particles. For example, consider a cubic volume element δV containing two spherical particles. In general, δV is not equal to the sum of the volumes of the two spherical particles, because additional space exists between them. We refer to this additional space as the excess volume.

Note that the excess-volume effect can also arise in single-component fluids, because the volume element may contain multiple fluid particles, even when all particles belong to the same component or phase. More generally, excess volume can arise from the spatial arrangement and interactions among fluid particles and is therefore not restricted to multicomponent systems or to mixing between different chemical species. In this sense, the excess-volume effect may be associated with mixing or, more generally, with the non-additivity of the volumes occupied by individual fluid particles.

If the excess volume is distributed among the fluid particles according to a prescribed rule, the volume associated with each fluid particle is modified from δV_i to $\delta V'_i = \delta V_i + \delta V_i^e$, where δV_i^e denotes the excess volume assigned to the i th fluid particle. In this way, we have the following equality:

$$\delta V = \sum_i \delta V'_i. \quad (50)$$

The mass density according to Eq. (29) is modified as

$$\rho = \frac{\sum_i \rho_i \delta V'_i}{\delta V} = \sum_i \rho_i \phi_i, \quad \phi_i = \frac{\delta V'_i}{\delta V}, \quad (51)$$

where we define the volume composition vector as $\boldsymbol{\phi} = (\phi_1, \phi_2, \dots, \phi_K)$; K denotes the number of chemical components in the system.

Considering the chemical composition effect, we write the free energy functional of the system as

$$E = \int_V [f(\boldsymbol{\phi}) + \rho\mathbf{u}^2 + p] \delta V = \int (e + p) \delta V. \quad (52)$$

The first part is the Helmholtz-type chemical free energy density, $f = \theta - \tau s$ (θ : internal energy excluding thermal kinetic energy, s : entropy); it depends on the chemical composition vector $\boldsymbol{\phi}$. The energy density is defined as $e = f(\boldsymbol{\phi}) + \rho\mathbf{u}^2$. We split the entropy into three parts: Boltzmann mixing entropy s_ϕ , thermal entropy s_τ , and velocity entropy s_u ,

$$s = s_\phi + s_\tau + s_u. \quad (53)$$

The evolution of these three entropies leads to the mass diffusion, heat diffusion, and velocity diffusion equations, respectively, as demonstrated by the following calculus.

Applying the standard thermodynamics based on Euler's homogeneous function theorem to the chemical free energy $f(\boldsymbol{\phi})$ and using the relation $D(\delta V) = 0$, the total derivative of the free energy functional E reads

$$DE = \int_V \left[\sum_i (\mu_i D\phi_i + \phi_i D\mu_i) + \mu_\tau D\tau + \tau D\mu_\tau + (\rho \mathbf{u}) \cdot D\mathbf{u} + \mathbf{u} \cdot D(\rho \mathbf{u}) + Dp \right] \delta V. \quad (54)$$

The discussion of the case in which the free-energy functional depends on the composition gradient is presented elsewhere.¹⁹ Applying the dissipation principle^{13,14} to $D\tau$ and $D\phi_i$ terms in Eq. (54), we obtain the heat and mass diffusion equations,

$$\frac{D\tau}{Dt} = \nabla \cdot D_\tau \nabla \mu_\tau, \quad (55)$$

$$\frac{D\phi_i}{Dt} = \nabla \cdot D_i \nabla \mu_i, \quad (56)$$

where D_τ and D_i are the mobilities associated with the heat and mass diffusivities. The respective thermal and chemical potentials are defined as

$$\mu_\tau = \frac{\partial e}{\partial \tau}; \quad (57)$$

$$\mu_i = \frac{\partial e}{\partial \phi_i}. \quad (58)$$

The $(\rho \mathbf{u}) \cdot D\mathbf{u}$ term in Eq. (54) results in the velocity diffusion equation, as already discussed in Sec. III A.

The time evolution of the temperature and composition is associated with the thermal and Boltzmann mixing entropy as

$$\mu_i \frac{D\phi_i}{Dt} = -\tau \frac{Ds_{\phi_i}}{Dt}, \quad (59)$$

$$\mu_\tau \frac{D\tau}{Dt} = -\tau \frac{Ds_\tau}{Dt}. \quad (60)$$

The rest terms in Eq. (54) are left into the Gibbs–Duhem relation

$$Dp + \sum_i \phi_i D\mu_i + \tau D\mu_\tau + \mathbf{u} \cdot D(\rho \mathbf{u}) = 0. \quad (61)$$

The first three terms are the standard Gibbs–Duhem relation in classic thermodynamics. The last term is the new contribution by considering the kinetic free energy. Dividing both sides by Dx_i , we obtain the momentum balance equation with chemical and thermal effects.

IV. CONCLUSION

We have proposed a generalized Gibbs–Duhem relation that explicitly incorporates kinetic energy,

$$Dp + \sum_i \phi_i D\mu_i + \tau Ds_\tau + \mathbf{u} \cdot D\mu_u = 0. \quad (62)$$

Remarkably, this generalized relation is mathematically equivalent to the corresponding momentum evolution equation. As a result, the proposed framework establishes a direct connection between Gibbsian thermodynamics and fluid mechanics, providing a unified description of nonequilibrium thermodynamics and mechanical processes.

Based on the modified Gibbs–Duhem relation, we have derived a density evolution equation for fluid dynamics,

$$\mathbf{u} \frac{D\rho}{Dt} = -\nabla p - \sum_i \phi_i \nabla \mu_i - \tau \nabla \mu_\tau - \rho \nabla \cdot D_u \nabla \mu_u. \quad (63)$$

The derived density evolution equation is validated by reproducing sound speed, Bernoulli's law, and equation of state for ideal gas, in limiting cases.

We anticipate that this work will provide new insights into the development of nonequilibrium thermodynamics and stimulate further advances in fluid dynamics.

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AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

Author Contributions

Fei Wang: Conceptualization (lead); Formal analysis (lead); Investigation (lead); Writing – original draft (lead).

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

APPENDIX: COMPATIBILITY OF THE VELOCITY ENTROPY WITH SPECIAL RELATIVITY

For electromagnetic field with effective mass density ρ , the kinetic free energy is expressed as $E_k = \int_V \rho \mathbf{c} \cdot \mathbf{c} \delta V$, where $\mathbf{c}$ denotes the transport speed of electromagnetic field, i.e., the light speed. The velocity entropy evolution is written as

$$\rho \mathbf{c} \cdot \frac{D\mathbf{c}}{Dt} = -\tau \frac{Ds_c}{Dt}, \quad (A1)$$

where s_c is the velocity entropy. As there is no entropy production for light transport, we obtain the following equality in the Lagrangian framework:

$$\frac{D\mathbf{c}}{Dt} = \mathbf{0}; \quad \frac{Ds_c}{Dt} = 0. \quad (A2)$$

The velocity entropy theory also enables us to derive the classic Maxwell equations; its comprehensive discussion has been presented elsewhere.¹⁹

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