Analytical Thermodynamics

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Abstract
This paper proposes a theory that bridges classical analytical mechanics and nonequilibrium thermodynamics. Its intent is to derive the evolution equations of a system from a stationarity principle for a suitably augmented Lagrangian action. This aim is attained for homogeneous systems, described by a finite number of state variables depending on time only. In particular, it is shown that away from equilibrium free energy and entropy are independent constitutive functions.

Keywords
Nonequilibrium thermodynamics \cdot Analytical mechanics \cdot Homogeneous systems

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1 Introduction

We find it appropriate to begin by putting briefly our theory into historical perspective; this we do in Sect. 1.1 here below. Next, in Sect. 1.2, we consider some variational formulations of thermodynamics. Finally, in Sect. 1.3, we introduce the stationarity principle of our choice and summarize the contents of our paper.

1.1 Primordial Variational Principles

Variational principles have a long, fascinating history. Perhaps, the first variational principle was put forward more than 2000 years ago by Hero of Alexandria, who postulated that a light
ray bouncing on a flat mirror follows the shortest path connecting two fixed points above the mirror. The law of reflection, stating that incoming and outgoing rays make the same angle with the normal to the mirror, then follows as a consequence.\(^1\) If light propagates at constant speed in a medium, then Hero’s principle easily converts into the principle of least time, formulated by Fermat in 1662. Elaborating on this, Fermat was able to derive Snell’s law of refraction. Such an achievement, however, did not suffice to make Fermat’s variational principle universally accepted. There were rival hypotheses, advanced by Descartes, Newton and Leibniz, all equally capable of accounting for Snell’s law, as narrated in Chap. 1 of Lemons’ book [42]. It was not just a matter of rivalry between opposing hypotheses (and schools): there were perplexing counterexamples too. In particular, Descartes’ followers showed that light impinging on a curved mirror may well follow the longest path joining two given points (see, p. 8 of [42]), instead of the shortest one.\(^2\) This incident simply teaches us that variational principles significant to physics should prudently be formulated as stationarity principles, thus renouncing any teleological implications with which they have too often been impregnated. As Lemons wittily puts it, “Apparently, nature is extravagant, as well as economical” [42, p. 8].

### 1.2 Thermodynamic Variational Principles

Thermodynamics has not been exempt from variational formulations, especially in its branch concerned with the evolution of states, often called nonequilibrium thermodynamics. Here, coherently with the true stance of Fermat’s principle, we shall mainly interpret these principles as stationarity requirements.

As appropriately summarized in [26], there are different types of variational principles for nonequilibrium thermodynamics. There are principles governing the rate of entropy production, with the intent of describing solely the evolution of the irreversible processes involved. The principle of least dissipation of energy, formulated by Onsager in a series of papers [47, 51–53], introduced a functional whose minimum determines the transition probability for the system from one state to another. This theory allowed to compute the probability density of thermodynamic variables, but it was confined to linear irreversible processes and Gaussian fluctuations. An extension to nonlinear processes can be found in [60].

More recently, Onsager’s principle has been the object of further reinterpretation and extension to soft matter systems in the work of Doi [13–17] (see also [75] for an application to active soft matter). In the same vein could be placed Gyarmati’s principle, from which, building on earlier works of Verházs and Vojta, one can derive the canonical equations of thermodynamics (see, in particular, Sect. VI.8 of [32]).\(^3\)

In the vast landscape of variational thermodynamic theories, a special role is played by the work of Biot [3–5]. What is relevant to our developments is Biot’s use of a d’Alembertian principle, which may also be described as a principle of minimal reduced dissipation, as proposed in [61] (see, in particular, Sect. 2.2.3), where it is used to derive the dynamical equations for dissipative ordered fluids. Specifically, the dissipation is delivered by a

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\(^1\)At first sight, this start might not seem related to the matter at hand, but the reader will soon discover that it really is.

\(^2\)The same counterexample shows that in a degenerate case the path of light may neither be the shortest nor the longest.

\(^3\)The reader could also profit from consulting the review [37] on this subject.
Rayleighian function $\tilde{R}$ and the quantity to be minimized is $\tilde{R} := R - \mathcal{W}$, where $\mathcal{W}$ is the total working.\(^4\)

There are also principles governing the whole thermodynamic evolution away from equilibrium,\(^5\) with the intent of describing all processes involved, reversible and irreversible alike.

Although not strictly variational in nature, the formalism of dissipative Poisson brackets, as expounded in general terms for example in [2, 30, 54],\(^6\) comes closer to the theme of our paper, which is concerned with deriving the equations that govern the thermodynamic evolution away from equilibrium with the methods of classical analytical dynamics.\(^7\)

### 1.3 Our Approach

The natural antecedent of our work is that of Gay-Balmaz and Yoshimura [23–25] (see, in particular, the review [26]). In this theoretical approach, a Hamilton’s action functional is required to be stationary under a nonholonomic constraint for the thermal variables of the system.\(^8\) Such a constraint, which is linear in the generalized velocities, incorporates the entropy production. The demand of stationarity for the Hamiltonian functional is phrased in a fashion akin to the Lagrange-d’Alembert principle, that is, by requiring stationarity of the action under the linear variational constraint generated by replacing the generalized velocity with variations of the generalized variables.\(^9\)

Our approach to analytical thermodynamics is different. We seek compatibility between the evolution equations of a system with a finite number of state variables and the laws of thermodynamics as formulated within Truesdell’s theoretical framework [69]. In our view, this represents a novel approach to nonequilibrium thermodynamics, in which the evolution out of equilibrium of a system is governed within a consistent Lagrangian formalism. The case of homogeneous systems is illustrated in Sect. 5. Thermal variables (here, for simplicity, a single one) are envisaged as cyclic, in accord with Helmholtz’s mechanical interpretation of thermodynamics summarized in Sect. 4. Their time derivatives enter the Lagrangian as a macroscopic manifestation of microscopic motions too fast to be detected. Section 3 is devoted to illustrate the role played by Rayleighian potentials in extending Hamilton’s functional to dissipative systems. Section 2 is a summary of elementary analytical mechanics.

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\(^4\)Equivalently, as in Biot’s original works, $\mathcal{R}$ could be minimized under the constraint that both generalized forces and total working are kept fixed (see [61, p. 119]). In such a formulation, this principle is also known as the principle of minimum constrained dissipation.

\(^5\)Or towards equilibrium, in the absence of external agencies.

\(^6\)Going backwards in time, these papers were preceded, essentially in the same line of thought, by [29], while the origin of the method can be retraced in an early paper by Kaufman and Morrison [39], framed in the context of the quasilinear equations of plasma physics. This paper was later followed by [38, 48, 49]. More recent applications of the method can be found in the specific fields of multiphase fluids [18] and dissipative magnetohydrodynamics [11].

\(^7\)A similar objective was recently pursued in [9], but without accounting for the second law of thermodynamics.

\(^8\)Despite the novelty of this approach, studies on the Lagrange-Hamilton formalism for nonequilibrium thermodynamics had appeared before in the literature: we mention, for example, [22] and refer the reader to the discussion in [73].

\(^9\)As remarked in [1, p. 44], the equations of motion generated by this principle differ from those (also called vakonomic) that are generated by requiring stationarity of the action under the nonholonomic constraint meant to restrict accessibility in phase space. Vakonomic dynamics was developed by V. V. Kozlov in a series of six papers published in the 1980’s (referenced as [329] in [1, p. 490]).
which serves the dual purpose of making our exposition self-contained and fixing our notation. At its opposite end, our paper is closed by Sect. 6, where we outline our conclusions.

2 A Modicum of Analytical Mechanics

Lagrange was first to see a serious limitation of Newton’s motion laws, namely, to be expressed in terms of the current positional coordinates of the mass points in a finite system, as observed against a fixed spacetime background. He was able to formulate the evolution laws of any system with finite degrees of freedom in terms of a stationarity condition for a system-specific action functional depending on the generalised coordinates of the objects in the system and on the time rates of those coordinates.

Hamilton quickly followed up with an even more general formulation, in which an orderly list of kinetic momenta replaces for the list of Lagrange’s rates of generalised coordinates. Analytical Mechanics (AM) as we reckon it today is in Hamiltonian form; its general purpose is to describe the deterministic and nondissipative evolution of a system with a finite number of degrees of freedom.

2.1 Lagrangians

Classically, a Lagrangian function—briefly, a Lagrangian—is a mapping

\[ L = L(q_1, q_2, \ldots, q_n, \dot{q}_1, \dot{q}_2, \ldots, \dot{q}_n; t) \]  

(2.1)

depending on a finite list of configuration parameters \( q_i \), the Lagrangian coordinates, their time derivatives \( \dot{q}_i \), and time \( t \).

The Lagrangian equations of motion of the mechanical system described by \( L \) are

\[ \frac{\partial L}{\partial q_i} - \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_i} \right) = 0 \quad (i = 1, 2, \ldots, n); \]  

(2.2)

they express the stationarity conditions of the Lagrangian action functional

\[ A_L[q] = \int_{t_1}^{t_2} L(q_1, q_2, \ldots, q_n; \dot{q}_1, \dot{q}_2, \ldots, \dot{q}_n; t) \, dt \]  

(2.3)

at a system’s path

\[ t \mapsto q(t) = (q_1(t), q_2(t), \ldots, q_n(t)), \]  

(2.4)

for whatever variation \( \delta q \) keeping the path ends \( q(t_1) \) and \( q(t_2) \) fixed. Precisely, equations (2.2) are arrived at by putting to null

\[ \frac{d}{d\varepsilon} (A_L[q + \varepsilon \delta q]) \]  

at \( \varepsilon = 0 \) and exploiting the quantification with respect to admissible variations. Equations (2.2) integrate a second-order system of \( n \) ODEs for \( q(\cdot) \). Under the standard assumption that

\[ \det[L_{ij}] \neq 0, \quad L_{ij} := \frac{\partial^2 L}{\partial \dot{q}_i \partial \dot{q}_j}, \]  

(2.5)
identifying nondegenerate Lagrangians, this system may be put in the normal form
\[ \ddot{q}_i = f_i(q, \dot{q}, t) \quad (i = 1, 2, \ldots, n), \] (2.6)
and solved uniquely for given initial conditions
\[ q(t_0) = q_0, \quad \dot{q}(t_0) = \dot{q}_0. \] (2.7)

The (total) energy associated with a Lagrangian \( L \) is
\[ E(q, \dot{q}, t) := \partial_{\dot{q}} L(q, \dot{q}, t) \cdot \dot{q} - L(q, \dot{q}, t), \] where \[ \partial_{\dot{q}} L \cdot \dot{q} = \sum_{i=1}^{n} \frac{\partial L}{\partial \dot{q}_i} \dot{q}_i, \] (2.8)
a definition valid irrespective of the validity of (2.5). This terminology is justified by thinking of the case that we call dynamical, that is, the familiar instance when a given Lagrangian is split as follows:10
\[ L = K - U \] (2.9)
into kinetic energy
\[ K = K(q, \dot{q}, t), \quad \text{with} \quad 2K = \partial_{\dot{q}} K \cdot \dot{q}, \] (2.10)
and potential energy
\[ U = U(q, t). \] (2.11)
In that case,
\[ E = \partial_{\dot{q}} K(q, \dot{q}, t) \cdot \dot{q} - K(q, \dot{q}, t) + U(q, t) = K(q, \dot{q}, t) + U(q, t), \] (2.12)
and kinetic plus potential energies make up the total energy. Note that (2.9) and (2.11) imply that
\[ L_{ij} = \frac{\partial^2 K}{\partial \dot{q}_i \partial \dot{q}_j} =: a_{ij}; \] (2.13)
moreover, it follows from (2.10)2 that \( \partial_{\dot{q}_i} K = a_{ij} \dot{q}_j \), and hence that the kinetic energy is a quadratic form, ruled by the symmetric matrix \( a_{ij} \):
\[ K = \frac{1}{2} \sum_{i,j=1}^{n} a_{ij} \dot{q}_i \dot{q}_j; \] (2.14)
the standard assumption that the kinetic energy be positive is more than enough to guarantee that (2.5)1 hold.

10Calling this case dynamical is typical of the Italian School of Mechanics (see, for example, [43, p. 247]). Along similar lines, in the British tradition, (see, for example, [77, p. 57]), the word natural is used when the Lagrangian contains only terms of degree 2 or 0 in the velocities.
Interestingly, if a Lagrangian function does not depend explicitly on time, then the associated energy is a motion constant (and conversely). In fact, from definition (2.8) we have that

\[
\frac{dE}{dt} = \frac{d}{dt} \left( \partial_q L \cdot \dot{q} + \partial_q L \cdot \ddot{q} - \partial_q L \cdot \dot{q} - \partial_q L \cdot \ddot{q} - \partial_t L \right) = \left( \frac{d}{dt} \left( \partial_q L \right) - \partial_q L \right) \cdot \dot{q} - \partial_t L,
\]

whence

\[
\frac{dE}{dt} = -\partial_t L
\]

(2.15)

along all solutions of (2.2); the announced result follows directly from this motion identity.

### 2.2 Hamiltonians

Hamilton proposed to encode all the properties of a mechanical system in a Hamiltonian function

\[
H = H(q_1, q_2, \ldots, q_n; p_1, p_2, \ldots, p_n; t),
\]

(2.16)

a mapping generally depending, in addition to time and a finite list \(q\) of configurational parameters, not on the time rates of the latter but on a list \(p = (p_1, p_2, \ldots, p_n)\) of kinetic momenta.\(^{11}\) He wrote the system’s Hamiltonian equations of motion as follows:

\[
\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad (i = 1, 2, \ldots, n),
\]

(2.17)

a first-order system of \(2n\) ODEs for the pair of functions of time \((q(\cdot), p(\cdot))\) delivering the time evolution of the Hamiltonian coordinates \((q, p)\) of the mechanical system at hand. Just as the Lagrangian equations for the action functional (2.3), the Hamiltonian equations of motion (2.17) can be shown to be the stationarity conditions at a path \(t \mapsto (q(t), p(t))\) of the Hamiltonian action functional

\[
\mathcal{A}_H\{q, p\} = \int_{t_1}^{t_2} (p \cdot \dot{q} - H(q, p, t)) \, dt, \quad p \cdot \dot{q} = \sum_{i=1}^{n} p_i \dot{q}_i,
\]

(2.18)

for all path variations keeping \(q(t_1)\) and \(q(t_2)\) fixed.\(^{12}\)

**Remark 1** Both Lagrange’s and Hamilton’s stationarity principles are formulated under identical restrictions on admissible path variations at the boundaries of the considered time interval. Consequently, *stricto sensu* both Lagrangian and Hamiltonian equations of motions (2.2) and (2.17) may solve a boundary-value problem in time for assigned values of \(q(t_1)\) and \(q(t_2)\); they are, however, commonly used to formulate time-evolution problems for given initial data (see also [21]).

\(^{11}\)Kinetic momenta, as they are called in the Italian tradition (see, for example, [43, p. 246]), were introduced by Hamilton, who called them *canonical*, an adjective which is used in more than one sense in the literature.

\(^{12}\)The functional \(\mathcal{A}_H\) is also called the *phase space action* (see, for example, [1, p. 37]).
2.3 Lagrangians vs. Hamiltonians

A question comes to mind: given a mechanical system, are its Lagrangian and Hamiltonian descriptions interchangeable? With a view toward answering, we develop a couple of preparatory considerations.

Firstly, for \( L \) a Lagrangian function as in (2.1) we introduce the kinetic momenta conjugated with the time rates of the Lagrangian coordinates, namely,

\[
p_i := \frac{\partial L}{\partial \dot{q}_i} \quad (i = 1, 2, \ldots, n). \tag{2.19}
\]

With this notion at hand, the Lagrangian equations of motion (2.2) can be written as follows:

\[
\dot{p}_i = \frac{\partial L}{\partial q_i} \quad (i = 1, 2, \ldots, n). \tag{2.20}
\]

We see that (2.2), a second-order system of \( n \) equations, is transformed into the first-order system of \( 2n \) equations consisting of (2.19) and (2.20).

As a second preparatory step, we regard each of relations (2.19)–the \( i \)-th, say–as an implicit equation in the unknowns \((p_i, q, \dot{q}, t)\), an equation that, in view of assumption (2.5), can be solved for \( \dot{q}_i \):\(^{13}\)

\[
\dot{q}_i = g_i(q, p, t); \tag{2.21}
\]

for later convenience, we rewrite these \( n \) relations in the compact form

\[
\dot{q} = g(q, p, t). \tag{2.22}
\]

We are now ready to answer the question we posed in the affirmative.

From \( L \) to \( H \): The Hamiltonian function corresponding to a given Lagrangian \( L \) is constructed by setting

\[
H(q, p, t) := p \cdot \dot{q} - L(q, \dot{q}, t), \tag{2.23}
\]

so as to let the integrands of the associated Lagrangian and Hamiltonian action functionals take the same values along the same path.\(^{14}\) Combining (2.23) with (2.21) and (2.22), we

\[^{13}\text{More precisely, assumption (2.5) only guarantees the local invertibility of (2.19). As shown in [20, Sect. 3.11], for (2.21) to be valid in a whole neighborhood, we must strengthen (2.5) by assuming that the mapping}

\[
\dot{q} \mapsto \frac{\partial L}{\partial q}
\]

\[^{14}\text{be a diffeomorphism. In [20], Lagrangians with such a property are also called regular. Dirac considered in [12] a more general form of Hamiltonian dynamics which can also be applied when momenta are not independent functions of (generalized) velocities.}

\[^{14}\text{It is straightforward to check that such an } H \text{ does not depend on } \dot{q}. \text{ Indeed, due to definition (2.19),}

\[
\frac{\partial H}{\partial \dot{q}_i} = p_i - \frac{\partial L}{\partial q_i} = 0.
\]
have that
\[ H(q, p, t) = p \cdot g(q, p, t) - L(q, g(q, p, t), t). \] (2.24)

Now, by taking \( H \) as given by (2.23) in the Hamiltonian equations of motion (2.17), we quickly see that the first of (2.17) reduces to an identity, while the second takes the form (2.2). All in all, equations (2.17) may be regarded as the Hamiltonian form of the Lagrangian equations (2.2).

**From \( H \) to \( L \)**: The Lagrangian corresponding to a given Hamiltonian \( H \) obtains by postulating that the first of (2.17) delivers the time rates of the Lagrangian coordinates conjugated to the kinetic momenta, and by setting
\[ L(q, \dot{q}, t) := p \cdot \dot{q} - H(q, p, t). \] (2.25)

Such an \( L \) is independent of \( p \) by (2.17); moreover, by (2.19),
\[ p_i = h_i(q, \dot{q}, t), \quad \text{or rather} \quad p = h(q, \dot{q}, t), \] (2.26)

whence the following form for (2.25):
\[ L(q, \dot{q}, t) = h(q, \dot{q}, t) \cdot \dot{q} - H(q, h(q, \dot{q}, t), t). \] (2.27)

We observe that
\[ \dot{H} = \partial_q H \cdot \dot{q} + \partial_p H \cdot \dot{p} + \partial_t H = \partial_t H \] (2.28)
along any motion. Hence, system’s Hamiltonian is a motion constant iff it does not depend on time explicitly. Relations (2.23) and (2.25) show that either both a Hamiltonian and the corresponding Lagrangian depend on time explicitly or neither does.

We also observe that relations (2.24) and (2.27) demonstrate that, given a mechanical system, its Hamiltonian is the Legendre transform of its Lagrangian, and conversely. The involutory nature of the Legendre transform is made patent by either (2.23) or (2.25), both of which imply that
\[ L(q, \dot{q}, t) + H(q, p, t) = p \cdot \dot{q}. \]

### 2.4 Hamiltonian Handling of the Dynamical Case

We begin with showing that, in this case,
\[ H = K + U = E, \] (2.29)
a motion constant: in view of (2.9)-(2.11) and (2.19),
\[ K = \frac{1}{2} p \cdot \dot{q}; \]
with this, (2.29) follows from (2.23), again (2.9), and (2.12).

Moreover, on setting
\[ p_i = m_i \dot{q}_i \] (2.30)
with \( m_i \) a positive constant, the mass associated with the Lagrangian coordinate \( q_i \), we have that

\[
H(q, p) = K(p) + U(q), \quad \text{with} \quad K(p) = \frac{1}{2} \sum_{i=1}^{n} m_i^{-1} p_i p_i.
\] (2.31)

Accordingly, the first of Hamiltonian motion equations (2.17) becomes an identity, the second takes a familiar Newtonian form:

\[
m_i \ddot{q}_i = (\dot{p}_i = -\partial_{\dot{q}_i} H) = -\partial_{q_i} U =: f_i \quad (i = 1, 2, \ldots, n),
\] (2.32)

with \( f_i \) the force acting on the system whenever the value of its \( i \)-th Lagrangian coordinate changes. On expressing the kinetic energy as

\[
K = \frac{1}{2} \sum_{i=1}^{n} m_i \dot{q}_i \dot{q}_i,
\]

and on setting

\[
f_K := -\frac{d}{dt} (\partial_{\dot{q}} K) \quad \text{and} \quad f_U := -\partial_{q} U
\] (2.33)

for, respectively, the inertial force and the potential force,\(^{15}\) we can reformulate (2.32) under form of the force balance

\[
f_K + f_U = 0,
\] (2.34)

a relation which is quickly shown equivalent to

\[
\dot{H} = 0.
\] (2.35)

Finally, we let \( U_A := U(q_A), K_A := K(p_A) \) and call

\[
W_{AB} := U_B - U_A,
\] (2.36)

the work performed on the system when it evolves from the state \((q_A, p_A)\) to the state \((q_B, p_B)\). Then, the fact that the system’s Hamiltonian is a motion constant implies the so-called work-and-kinetic energy theorem

\[
W_{AB} = K_A - K_B
\] (2.37)

according to which an increase (decrease) in potential energy is accompanied by a decrease (increase) in kinetic energy.

### 3 Rayleigh-Lagrange Dynamics

The dynamical case is of special importance in classical Statistical Mechanics (SM), where the typical system consists of a large number of constant-mass points, whose positions in

\(^{15}\)When restricting attention to potential energies that do not depend explicitly on time, the standard qualifier for \( f_U \) is conservative.
space are the system’s Lagrangian coordinates, acted upon by conservative forces. That theory stops short from handling systems which are not Hamiltonian, because they are acted upon by forces that (like, e.g., frictional forces) cannot be derived from a potential function. However, the reach of SM can be so extended as to handle non-Hamiltonian systems whose evolution manifests energy dissipation (see [70–72]).

In AM, handling dissipative forces was first made possible in 1871, by a change of format due to Rayleigh [58, 62, 63].

Let us introduce Rayleigh’s dissipation potential \( R(q, \dot{q}) \), with \( R(q, \cdot) \) a positive semidefinite quadratic form for all \( q \), and the associated dissipative force

\[
    f_R := -\partial_{\dot{q}} R. \tag{3.1}
\]

The corresponding Rayleigh-Lagrange dynamics is ruled by a force balance that generalizes (2.34), namely,

\[
    f_K + f_U + f_R = 0. \tag{3.2}
\]

It is the matter of a simple computation to show that under the present circumstances (2.35) is replaced by

\[
    \dot{H} - D = 0, \tag{3.3}
\]

with

\[
    D(q, \dot{q}) := \dot{q} \cdot \partial_{\dot{q}} R. \tag{3.4}
\]

As suggested in [74], the roles of \( R \) and \( D \) may be reversed, in that relation (3.4) may be regarded as a partial differential equation to be solved for the Rayleigh’s potential \( R \) conveying the information about a system’s dissipative features embodied in a physically plausible choice of function \( D \). It is proposed in [74] that \( D(q, \cdot) \) be chosen positive semidefinite (but not necessarily quadratic, as instead is commonly done) and vanishing identically at \( \dot{q} = 0 \).

The so-called overdamped regime comes about when the inertial force is negligible with respect to the dissipative force and a system’s time evolution is such that

\[
    \dot{H} \simeq \dot{U}. \tag{3.5}
\]

If, in addition, it is assumed that

\[
    R(q, \dot{q}) = \frac{1}{2} Z(q) \cdot \dot{q} \otimes \dot{q} \geq 0, \quad Z = Z^T, \tag{3.6}
\]

then the force balance (3.3) reduces to the kinetic equation

\[
    \partial_{\dot{q}} U + Z \dot{q} = 0, \tag{3.7}
\]

a condition that is quickly seen to be necessary for the stationarity at any fixed \( q \) of the Rayleighian

\[
    \mathcal{R}(q, \dot{q}) := \partial_{\dot{q}} U \cdot \dot{q} + R(q, \dot{q}). \tag{3.8}
\]

\[\text{16} \]That is, such that \( D(q, \cdot) \geq 0 \) for all \( q \).
In case matrix $Z$ in (3.6) is taken invertible, the kinetic equation (3.7) can be written as

$$\dot{q} = -Z^{-1}\partial_q U;$$

(3.9) provided $U$ is interpreted as the system’s free energy, (3.9) may be regarded as the stationarity condition of an Onsager-like variational principle, in the wake of [51], as recently reinterpreted in much soft matter literature.17

**Remark 2** Rayleigh-Lagrange dynamics for dissipative systems have a different standing than ordinary Lagrangian dynamics. The latter can be given a variational formulation in the classical form of stationarity of the action functional in (2.3), while the former can be given a variational formulation only in a d’Alembert fashion by requiring the stationarity of an action augmented by the addition of the virtual work expended by dissipative forces. The form appropriate to our developments of the stationarity of such an augmented action will be written in (5.1).

## 4 Mechanical Interpretations of Thermodynamics

Helmholtz, who was working before Boltzmann’s creation of a statistical approach to physics, pursued a purely mechanical interpretation of the objects of thermodynamics and a consistent deduction of the basic laws of that discipline. Interestingly, Boltzmann himself continued along Helmholtz’s nonprobabilistic path in his own treatment of periodic Lagrangian systems.

The thermodynamical objects in need of purely mechanical definitions are temperature, heat, entropy, etc. With Helmholtz, we begin by temperature $\vartheta$, that he regarded as a velocity-like variable and accordingly introduced as the time derivative of another object, the thermal displacement

$$\dot{\alpha} = \vartheta,$$

(4.1)

whose physical interpretation was at the time rather mysterious.18 The formal role Helmholtz assigned to thermal displacement was that of a cyclic coordinate, that is, a coordinate appearing in the Lagrangian of a mechanical system only through its time derivative, whose momentum is hence a motion constant [33, 34] (see Lanczos [40], pp. 125 ff.). With L. de Broglie [6–8], we call it a ‘fast’ variable, implying that only its time derivative is observable at the macroscopic time scale and is therefore included in the list of Lagrangian coordinates. Accordingly, we call ‘slow’ the ordinary Lagrangian coordinates, which are observable and have observable time derivative.19

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17We read in [15]: “The Onsager principle is an extension of Rayleigh’s principle of the least energy dissipation in Stokesian hydrodynamics.”

18Perhaps, not anymore, see [56]. For a demonstration of the role of thermal displacement in a virtual-power formulation of thermomechanics, see [55] and [57]. The reader is also referred to [28] for a different theory building on this notion, and to [31], where the theory in [28] is to some extent anticipated.

19In [75], when “the general steps for applying OVP [Onsager Variational Principle] to the dynamics of active soft matter” are listed, the first step is “[t]o choose a set of coarse-grained slow variables . . . to describe the time evolution of the macroscopic state of the system.”
4.1 Helmholtz’s Monocyclic Systems

Consider a monocyclic mechanical system, that is, a mechanical system whose Lagrangian, perhaps modulo a reordering, does not depend on the $n$-th coordinate:

$$L = L(q_1, q_2, \ldots, q_{n-1}, \dot{q}_1, \dot{q}_2, \ldots, \dot{q}_n, t), \quad (4.2)$$

For such a system, on recalling (2.20), we have that:

$$\frac{\partial L}{\partial q_n} = 0 \Rightarrow \dot{p}_n = 0 \Leftrightarrow p_n = c_n,$$

a result that, on recalling (2.19), we write as

$$\frac{\partial L}{\partial \dot{q}_n} - c_n = 0, \quad (4.3)$$

which makes it clear how $c_n$ is indeed determined by the initial conditions imposed on the specific motion being studied. We regard (4.3) as an implicit relation among the variables from which $L$ depends and $c_n$, and assume that it can be cast in normal form:

$$\dot{q}_n = f(q_1, q_2, \ldots, q_{n-1}; \dot{q}_1, \dot{q}_2, \ldots, \dot{q}_{n-1}; c_n; t). \quad (4.4)$$

With the use of (4.4), the first $(n-1)$ motion equation (2.2) yield the time evolution of the slow coordinates; having this information, we can revert to (4.4), and obtain the time evolution of the fast coordinate $q_n$ by quadrature.

**Remark 3** A fast coordinate is not observable, its time rate is. Think of a rigid conductor: its slow Lagrangian coordinates are the six parameters needed to describe its macroscopic rigid-body motion; temperature $\vartheta$, a fast coordinate, is observable, but thermal displacement $\alpha$, the scalar variable defined in (4.1), is not. Just as temperature gives a macroscopic information that we interpret as an account of the velocity fluctuations of a representative collection of body’s molecules, the thermal displacement can be regarded as accounting for the nonobservable fluctuations of those molecules about their lattice positions.

**Remark 4** For another example, this time with many fast variables (a polycyclic mechanical system, in Helmholtz’s terminology), think of a gas, with the molecule coordinates as the fast variables and the macroscopic parameters that determine the state of the system (pressure, volume, or temperature) as the slow variables.

Now, following Lanczos [40, p. 126], we wonder whether we can eliminate the cyclic variable $q_n$ before solving the time evolution equations for the non-cyclic variable $q_1, \ldots, q_{n-1}$, by reformulating appropriately the parent variational principle. Our aim is to find a Lagrangian $\bar{L}$ depending only on the non-cyclic variables of $L$ (and their time derivatives) so that the stationarity of the action $A_{\bar{L}}$ delivers precisely the same evolution equations for the non-cyclic variables of $L$, once use is made in them of (4.4).

To this end, given a system whose Lagrangian has the form (4.2), we may require that the associated Lagrangian action

$$A_L = \int_{t_1}^{t_2} L(q_1, q_2, \ldots, q_{n-1}; \dot{q}_1, \dot{q}_2, \ldots, \dot{q}_n; t) \, dt \quad (4.5)$$
be varied under the constraint (4.4):
\[
\delta \int_{t_1}^{t_2} \left[ L(q_1, q_2, \ldots, q_{n-1}; \dot{q}_1, \dot{q}_2, \ldots, \dot{q}_n; t) + \lambda (\dot{q}_n - f(q_1, q_2, \ldots, q_{n-1}; \dot{q}_1, \dot{q}_2, \ldots, \dot{q}_{n-1}; c_n; t)) \right] dt = 0. \tag{4.6}
\]

However, (4.4), even if incorporated in (4.6) through the Lagrange multiplier \(\lambda\) (which at this stage is an unknown function of time), is in general incompatible with having \(\delta q_n\) vanishing at both \(t = t_1\) and \(t = t_2\). It follows from (4.4) by integration that
\[
\delta q_n(t_2) - \delta q_n(t_1) = \int_{t_1}^{t_2} \left[ \sum_{i=1}^{n-1} \frac{\partial f}{\partial q_i} - \frac{d}{dt} \left( \frac{\partial f}{\partial \dot{q}_i} \right) \right] \delta q_i dt, \tag{4.7}
\]
under the usual assumption that \(\delta q_i = 0\) at both \(t = t_1\) and \(t = t_2\) for all \(i = 1, \ldots, n - 1\).

Thus, taking \(\delta q_n(t_1) = 0\), the appropriate stationary condition for \(A_L\) in (4.5) subject to (4.4) is that the variation in (4.6) be proportional through a constant Lagrange multiplier \(\mu\) to \(\delta q_n(t_2)\) as given by (4.7):
\[
\delta \int_{t_1}^{t_2} \left( L + \lambda (\dot{q}_n - f) \right) dt - \mu \int_{t_1}^{t_2} \left[ \sum_{i=1}^{n-1} \frac{\partial f}{\partial q_i} - \frac{d}{dt} \left( \frac{\partial f}{\partial \dot{q}_i} \right) \right] \delta q_i dt = 0. \tag{4.8}
\]

Standard computations transform (4.8) into the following condition
\[
\int_{t_1}^{t_2} \left\{ \sum_{i=1}^{n-1} \left[ \frac{\partial}{\partial q_i} \left( L - (\mu + \lambda) f \right) - \frac{d}{dt} \left( \frac{\partial}{\partial \dot{q}_i} \left( L - (\mu + \lambda) f \right) \right) \right] \delta q_i - \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_n} + \lambda \right) \delta q_n \right\} dt = 0. \tag{4.9}
\]

Since here all \(\delta q_i\), for \(i = 1, \ldots, n\), are independent, (4.9) requires that
\[
\frac{\partial L}{\partial \dot{q}_n} + \lambda = \text{constant}. \tag{4.10}
\]

Evaluating (4.10) on (4.3), which is the implicit version of the constraint (4.4), we conclude that also \(\lambda\) is constant and so (4.9) reduces to the stationarity of the action \(A_L\) associated with a Lagrangian \(\bar{L} := L - c_0 \dot{q}_n\), where \(c_0 = \mu + \lambda\) is an arbitrary constant. It is a simple matter to check that setting \(c_0 = c_n\) has the noticeable advantage of making \(\bar{L}\) a function independent of \(\dot{q}_n\) when evaluated on the constraint (4.4), as then
\[
\frac{\partial \bar{L}}{\partial \dot{q}_n} = \frac{\partial L}{\partial \dot{q}_n} - c_n = 0.
\]

Thus, if in the modified Lagrangian
\[
\bar{L} := L - c_n \dot{q}_n \tag{4.11}
\]
we make use of (4.4), we are guaranteed to obtain a function depending only on the non-cyclic coordinates (their derivatives and the parameter \(c_n\)), whose evolution is described by
the usual Lagrange equations for a system with $n - 1$ degrees of freedom. The complete
evolution of the parent system with $n$ degrees of freedom is then obtained by quadrature of
(4.4), once the evolution of the non-cyclic coordinates is known.

**Remark 5** The modified Lagrangian $\overline{L}$ was first introduced by Routh in his essay [59] (see, in
particular Sects. 20 and 21 of Chapt. IV), where he also comments about his method being
“equivalent to a partial use of Hamilton’s transformation of Lagrange’s equations.” We also
learn in Larmor’s obituary of Routh [41] that

Lord Kelvin’s general theory of “ignoration of co-ordinates,” first published in 1879
in the second edition of Thomson and Tait’s treatise [68] […] probably existed in
manuscript anterior to Routh’s essay. […] This form of the theory, though more expressively suggested by the needs of physical dynamics, was less complete in one respect
than Routh’s, in that it did not bring the matter into direct relation with a single char-
acteristic function (Lagrangian function of Routh, kinetic potential of Helmholtz), but
simply obtained and illustrated the equations of motion that arose from the elimina-
tion of the cyclic co-ordinates that could be thus ignored. Later still, Helmholtz, in his
studies on monocyclic and polycyclic kinetic systems, which began in 1884 [33], and
culminated in the important memoir on the physical meaning of the Principle of Least
Action in vol. c. (1886) of Crelle’s Journal [35], developed the same theory more in
Routh’s manner, and built round it an extensive discussion of physical phenomena, so
that on the Continent the whole subject is usually coupled with his name. Shortly be-
fore, the work of Routh and Kelvin had already been co-ordinated with the Principle
of Action by more than one writer in England.

After having illuminated the connection between Routh’s theory and the stationarity of
the action, we apply Routh’s method in a generic case. We split the Lagrangian (4.2) addi-
tively:

$$L = K - U,$$

with

$$K = \frac{1}{2} \sum_{i,k=1}^{n} a_{ik} \dot{q}_i \dot{q}_k \quad (a_{ik} = a_{ki})$$

the kinetic energy, as in (2.14), and

$$U = U(q_1, q_2, \ldots, q_{n-1}; t)$$

the potential energy.\(^{20}\) Note that (4.13) can be written in the form:

$$K = \frac{1}{2} \sum_{i,k=1}^{n-1} a_{ik} \dot{q}_i \dot{q}_k + \left( \sum_{i=1}^{n-1} a_{in} \dot{q}_i \right) \dot{q}_n + \frac{1}{2} a_{nn} \dot{q}_n^2.$$

Under the present circumstances, this further splitting implies that

$$c_n = p_n = \frac{\partial K}{\partial \dot{q}_n} = \sum_{i=1}^{n-1} a_{in} \dot{q}_i + a_{nn} \dot{q}_n \quad \Rightarrow \quad \dot{q}_n = a_{nn}^{-1} \left( c_n - \sum_{i=1}^{n-1} a_{in} \dot{q}_i \right).$$

\(^{20}\)The symmetric matrix whose entries we denoted by $a_{ik}$ is customarily taken positive definite, so that, in
particular, all diagonal entries are positive.
Consequently,

\[ K - c_n \dot{q}_n = \frac{1}{2} \sum_{i,k=1}^{n-1} a_{ik} \dot{q}_i \dot{q}_k - \frac{1}{2} a_{nn}^{-1} \left( c_n - \sum_{i=1}^{n-1} a_{in} \dot{q}_i \right)^2 \]

and, by analogy with (4.12), we are driven to set:

\[ L = K - U, \]

with

\[ \bar{K} := \frac{1}{2} \left( \sum_{i,k=1}^{n-1} a_{ik} \dot{q}_i \dot{q}_k - a_{nn}^{-1} \left( \sum_{i=1}^{n-1} a_{in} \dot{q}_i \right)^2 \right) + a_{nn}^{-1} c_n \sum_{i=1}^{n-1} a_{in} \dot{q}_i, \quad (4.14) \]

\[ \bar{U} := U + \frac{1}{2} a_{nn}^{-1} c_n^2. \quad (4.15) \]

**Remark 6** It is worth noting that a Lagrangian \( L \) with a cyclic coordinate that contains only terms quadratic in the velocities is modified in a Lagrangian \( \bar{L} \) that also contains linear terms. In Whittaker’s terminology (see footnote 10), we may say that a cyclic coordinate drives a natural system into a non-natural one with one degree of freedom less.

If the kinetic coefficient \( a_{in} \neq 0 \), the velocity \( \dot{q}_n \) of the fast ‘ghost’ coordinate and the velocity \( \dot{q}_i \) of the slow coordinate are said to be kinetically coupled: a so-called gyroscopic term \( a_{in} \dot{q}_i \) is found in the kinetic energy \( \bar{K} \), a term which is linear in the rate \( \dot{q}_i \) and does not have a definite sign (see [40], p. 129). Furthermore, in the potential energy \( \bar{U} \) a positive contribution of kinetic origin is found, which morally accounts for the variable \( q_n \); in case of no kinetic coupling, this is the only manifestation of a microscopically fast variable, a candidate to be interpreted as stored heat content in case \( q_n \) is interpreted as thermal displacement.

**Remark 7** The connection between cyclic coordinates and hidden motions goes far beyond Helmholtz’s works. As lucidly explained by Lützen in his book [46] (see, in particular, Chap. 18), cyclic coordinates have an interesting history that, as already recalled in Remark 5, starts with Routh’s method [59] and has far reaching consequences. In particular, this method was used by J.J. Thompson in his papers [65, 66] and book [67] to interpret cyclic coordinates as manifestations of a hidden motion, in accord with Helmholtz. Thompson considered a dynamical system whose energy was only kinetic and consisted of two parts, both quadratic, the one in non-cyclic and the other in cyclic coordinates only; he proved that the cyclic kinetic energy can be converted through Routh’s method into an effective potential in the non-cyclic coordinates, thus showing that an ordinary potential energy can in principle be regarded as arising from a hidden motion. Liouville [45] went somehow the opposite way: he proved that any classical Lagrangian system, with kinetic and potential energies, can be converted into an equivalent one with only kinetic energy and a single added cyclic coordinate.

### 4.2 Hertzian Mechanics

We read in [40] (Chapter V, Sect. 4) that the fact that potential energy may include the kinetic contribution of a nonobservable coordinate, as shown for example in (4.15), induced Hertz [36] to dream of a forceless mechanics; a cursory account of his views follows.
It helps to premise a classification of forces, in spite of the somewhat obsolete terminology. Within a Lagrangian/Hamiltonian framework there are two types of forces: (1) monogenic, when their incremental working, defined as

$$dw^{(m)} = \sum_{i=1}^{n} F_i^{(m)} dq_i,$$

is deducible from a scalar work function $V(q_1, \ldots, q_n; \dot{q}_1, \ldots, \dot{q}_n; t)$:

$$dw^{(m)} = \sum_{i=1}^{n} \left( \frac{\partial V}{\partial q_i} - \frac{d}{dt} \left( \frac{\partial V}{\partial \dot{q}_i} \right) \right) dq_i \quad \Rightarrow \quad F_i^{(m)} := \frac{\partial V}{\partial q_i} - \frac{d}{dt} \left( \frac{\partial V}{\partial \dot{q}_i} \right);$$

The negative of the work function is identified with the potential energy: $U = -V$; monogenic forces are said conservative if their work function does not depend on $\dot{q}$ and $t$.

(2) polygenic, otherwise, that is, when no work function can be associated to their incremental working

$$dw^{(p)} = \sum_{i=1}^{n} F_i^{(p)} dq_i,$$ (4.16)

where the generalized forces $F_i^{(p)}$ are assumed to be functions of the $q_i$’s and (possibly) of the $\dot{q}_i$’s too.

Monogenic forces are associated with holonomic kinematic conditions, in the sense that contingent kinematic conditions on a system’s evolution are maintained by monogenic forces: on p. 114 of [40], we read: “...Hamilton’s principle holds for arbitrary mechanical systems which are characterized by monogenic forces and holonomic auxiliary conditions”; the same assertion holds when a Lagrangian formulation is adopted. Nonholonomic kinematic conditions call for polygenic forces; examples of the latter are inertia forces and friction forces. When a system is acted upon by noninertial polygenic forces, in addition to monogenic forces whose work function $V$ is absorbed in the usual way in the Lagrangian $L$, the equations of motion are

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_i} \right) - \frac{\partial L}{\partial q_i} = F_i^{(p)} \quad (i = 1, 2, \ldots, n)$$ (4.17)

(cf. equation (59.4), on p. 146 of [40]).

In [40], Lanczos credits Hertz with the idea that a typical mechanical system has many ‘hidden’ (≡ nonobservable) degrees of freedom, that is, degrees of freedom that are not conveyed into the system’s Lagrangian by a set of slow coordinates; and that there are two kinds of such hidden degrees of freedom, those associable with polygenic forces and those associable with fast Lagrangian variables, whose presence is reflected in the kinetic portion of the potential energy and, possibly, in the gyroscopic terms of the kinetic energy. Apparently, according to Lanczos, Hertz went so far as to propound a forceless Hamiltonian mechanics, in which all of potential energy, just as kinetic energy itself, has a kinetic origin, in that it is induced by fast Lagrangian variables.
4.3 Helmholtz’s Heat Theorem

This theorem establishes a representation for the mechanical analogue of entropy; it can be seen as a tool to explain on the basis of the microscopic laws of mechanics the statement of the Second Law of the XIX century’s thermodynamics of homogeneous systems to the effect that \textit{coldness}, the inverse of temperature, is the integrating factor needed to reconstruct entropy from heat exchange [10, 19]. We prove it in the simplest instance of a monocyclic Lagrangian system, whose coordinates are only two, one slow and one fast.

Let the relevant Lagrangian be

\[ L(q_s, \dot{q}_f; q_s, \dot{q}_f; t) = K(\dot{q}_f) - U(q_s) = \frac{1}{2} p_f \dot{q}_f - U(q_s), \quad \text{with} \quad p_f = m \dot{q}_f, \]

and let the total incremental working be

\[ dw = g_f dq_f, \]

where \( g_f \) appears to be a (generalized) force doing work against the fast variable \( q_f \) and which we may assume to depend on \( q_s \). Then, in view of (4.16) and (4.17), the motion equations are

\[ \frac{\partial L}{\partial q_s} = 0, \quad \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_f} \right) - g_f = 0 \quad \iff \quad \dot{p}_f - g_f = 0. \]

Next, the incremental heat exchange is equated to the incremental working performed on the system, and use is made of the motion equations [68]:

\[ dQ = g_f dq_f = \dot{p}_f \dot{q}_f dt = \dot{q}_f dp_f; \]

a division by \( p_f \dot{q}_f = 2K \) yields

\[ \frac{dQ}{2K} = d(\log p_f). \]

With this, on setting

\[ 2K =: \text{temperature} \quad \vartheta \quad \text{and} \quad \log p_f := \text{entropy} \quad S, \quad (4.18) \]

we have the desired conclusion:

\[ \frac{dQ}{\vartheta} = dS, \]

with \( \vartheta^{-1} \), the ‘coldness’, as the integrating factor. Note that this result does not depend on the form of the potential energy.

5 Analytical Thermodynamics of Homogeneous Systems

Here, building upon Helmholtz’s mechanistic interpretation, we introduce a formal analytic theory for the thermodynamics of \textit{homogeneous} systems. Our aim is to provide a theoretical setting for \textit{nonequilibrium} thermodynamics, within which the evolution out of equilibrium
can be derived from the Lagrangian/Hamiltonian formalism illustrated above. Our approach will be constructive: starting from the basic potentials of classical thermodynamics, namely, free energy, entropy, and dissipation (or entropy production), we seek Lagrangians (and Hamiltonians) that govern evolution out of equilibrium consistently with the law of thermodynamics.\textsuperscript{21}

Homogeneous systems have admissible thermodynamic states that can be described by \( n-1 \) variables, changing with time but uniform in space, the entries of a state vector \( q_s = (q_1, \ldots, q_{n-1}) \in \Omega \), where \( \Omega \subset \mathbb{R}^{n-1} \) is a given admissible set. In the language introduced in Sect. 4, the vector \( q_s \) consists of slow variables, whose time derivatives do not feature in the Lagrangian. We assume that a single fast variable, \( q_f \), of a microscopic origin and unobservable at the macroscopic scale, produces observable macroscopic effects through its time derivative \( \dot{q}_f \), which we phantom related to the temperature \( \vartheta \) of the system, in a manner that will be made precise. Thus, the Lagrangian \( L \) will be a function \( L = L(q_s; \dot{q}_f) \).

In Helmholtz’s terminology, the typical homogeneous system we envision is monocyclic, governed by a Lagrangian action principle which we extend both in a d’Alembert fashion—so as to incorporate nonconservative thermodynamic forces, depending only on the state vector \( q_s \) and collected in a vector \( Q_s = (Q_1, \ldots, Q_{n-1}) \)—and in a Rayleigh fashion—so as to incorporate also dissipative forces, depending on \( q_s \) and \( \dot{q}_f \) and derived from a potential \( R = R(q_s; \dot{q}_s, \dot{q}_f) \) which depends also on the rate of the fast coordinate \( q_f \). Precisely, we require the stationarity of action \( A_L \) augmented by the virtual work associated with all forces:

\[
\delta A_L + \int_{t_0}^{t_1} \left( Q_s \cdot \delta q_s - \frac{\partial R}{\partial \dot{q}_s} \cdot \delta q_s - \frac{\partial R}{\partial \dot{q}_f} \delta q_f \right) dt = 0.
\]

\textbf{Remark 8} We regard the generalized velocities \((\dot{q}_s, \dot{q}_f)\) as neutral to the variation indicated in (5.1) (as effectively said in [32, p. 167]) and hence we keep them constant during that variation (in tune with the way variational constraints are treated in [26]).

By the special form of \( L \), in (5.1)

\[
\delta A_L = \int_{t_0}^{t_1} \left\{ - \left( \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_f} \right) \delta q_f + \frac{\partial L}{\partial q_s} \cdot \delta q_s \right\} dt;
\]

in accord with our discussion in Sect. 4, \( \delta q_f \) is a kind of virtual thermal displacement. Moreover, \( Q_s \) has a purely mechanical origin and we think of it as a function of \( q_s \) only: there is no force performing virtual work against a thermal displacement.

The evolution (dynamical) equations associated with the variational principle stated in (5.1) are obtained by requiring that stationarity is achieved there for arbitrary variations \((\delta q_s, \delta q_f)\); these equations read as

\[
\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_f} + \frac{\partial R}{\partial \dot{q}_f} = 0,
\]

\[
\frac{\partial L}{\partial q_s} - \frac{\partial R}{\partial \dot{q}_s} + Q_s = 0.
\]

\textsuperscript{21}This approach characterizes the meaning that we properly attach to analytical thermodynamics; it differs from that implied by Li in the title of his book [44], where analytical is meant to evoke the solid, theoretical structure provided to thermodynamics since the pioneering, elegant work of Gibbs [27] (see p. v of [44]).
In (5.1), as in [74] and unlike what is customary, we do not assume that \( R(q_s; \cdot, \cdot) \) is a quadratic form for all \( q_s \);\(^{22}\) we want only to interpret it as a dissipation potential, characterized by the property

\[
\dot{q}_s \cdot \frac{\partial R}{\partial \dot{q}_s} + \dot{q}_f \frac{\partial R}{\partial \dot{q}_f} = \mathcal{D}(q_s; \dot{q}_s, \dot{q}_f),
\]

where \( \mathcal{D} \), the dissipation, is an assigned function, positive semidefinite in \( (\dot{q}_s, \dot{q}_f) \).\(^{23}\) As pointed out in [74], the Rayleigh potential \( R \) can then be easily retried through the formula

\[
R(q_s, \dot{q}_s, \dot{q}_f) = \int \mathcal{D}(q_s; e^s \dot{q}_s, e^s \dot{q}_f) \, ds \bigg|_{s=0},
\]

whenever \( \mathcal{D} \) is a homogeneous function of degree \( d \) in \( (\dot{q}_s, \dot{q}_f) \) (an assumption which is not needed here), relation (5.5) delivers

\[
R = \frac{1}{d} \mathcal{D}.
\]

The role of \( \mathcal{D} \) is fully appreciated within a thermodynamic framework, such as the one expounded by Truesdell [69, pp. 9-10] (see also [61, p. 126]). In one of the many ways to formulate the Second Law of thermodynamics, we may say that \( \mathcal{D} \) fills the gap between the heating \( \mathcal{Q} \) provided to the system and the rate of entropy growth \( \dot{\mathcal{S}} \), as

\[
\vartheta \dot{\mathcal{S}} - \mathcal{Q} = \mathcal{D} \geq 0,
\]

where \( \vartheta \) is the absolute temperature.\(^{24}\) The First Law of thermodynamics is formulated as

\[
\dot{U} = \mathcal{W} + \mathcal{Q},
\]

where the rate of internal energy \( \dot{U} \) is balanced by the mechanical power expended by all nondissipative agencies \( \mathcal{W} \) and the thermal power \( \mathcal{Q} \). Letting

\[
\mathcal{F} := \dot{U} - \vartheta \dot{\mathcal{S}}
\]

denote Helmholtz’s free energy, and making use of (5.8), we rewrite (5.7) in the form

\[
\mathcal{W} - \dot{\mathcal{F}} - \vartheta \dot{\mathcal{S}} = \mathcal{D} \geq 0.
\]

To lay the basis of our analytical thermodynamics governed by (5.3a), (5.3b), we need to establish a relation with classical thermodynamics that goes beyond the natural identification in (5.5). We need to link \( L \) to \( \mathcal{F} \) and \( \mathcal{S} \), for which we assume the following constitutive relations

\[
\mathcal{F} = \mathcal{F}(\vartheta; q_s) \quad \text{and} \quad \mathcal{S} = \mathcal{S}(\vartheta; q_s),
\]

\(^{22}\)This assumption would guarantee that (5.3b) could be reduced to normal form, which is not explicitly contemplated in our theory.

\(^{23}\)As customary, by this we simply mean that \( \mathcal{D}(q_s; \cdot, \cdot) \geq 0 \) for all choices of \( q_s \).

\(^{24}\)In Truesdell’s words [69, p. 9], “We assume the existence of a second kind of working, \( \mathcal{Q} \), called heating, which is not identified with anything from mechanics” (see also [61, p. 125]).
which are in tune with the classical view of considering both \( F \) and \( S \) as functions depending on temperature and thermodynamic state. We also need to link \( \dot{q}_f \) to \( \vartheta \); for the time being, we assume that

\[
\vartheta = f(\dot{q}_f), \tag{5.12}
\]

as most of the theory developed below will be independent of the specific choice of the function \( f \).

We readily obtain from (5.3a), (5.3b) and (5.4) that

\[
- \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_f} \right) \dot{q}_f = F - \frac{\partial L}{\partial q_s} \cdot \dot{q}_s - Q_s \cdot \dot{q}_s = -\dot{F} - \dot{\vartheta} S, \tag{5.13}
\]

where we have made use of (5.10) and identified \( \mathcal{W} \) as the working of all nondissipative thermodynamic forces (both conservative and non-conservative),

\[
\mathcal{W} = \left( \frac{\partial L}{\partial q_s} + Q_s \right) \cdot \dot{q}_s. \tag{5.14}
\]

By expanding the first and last terms in (5.13), with the aid of (5.11) and (5.12), we arrive at

\[
\frac{\partial^2 L}{\partial q^2} \ddot{q}_f + \frac{\partial}{\partial q_s} \left( \dot{q}_f \frac{\partial L}{\partial q_f} \dot{q}_s + f'(\dot{q}_f) \ddot{q}_f + \frac{\partial \mathcal{F}}{\partial q_s} \cdot \dot{q}_s \right) = \left( \frac{\partial F}{\partial \vartheta} + S f' \right) \ddot{q}_f + \frac{\partial F}{\partial q_f} \cdot \dot{q}_s. \tag{5.15}
\]

Requiring the linear forms in \((\ddot{q}_f, \dot{q}_s)\) on the two sides of this equation to be identical, we derive the equations

\[
\left( \frac{\partial \mathcal{F}}{\partial \vartheta} + \mathcal{F} \right) f' = \frac{\partial^2 L}{\partial q^2} \ddot{q}_f, \tag{5.16a}
\]

\[
\mathcal{F}(f(\dot{q}_f); q_s) = \dot{q}_f \frac{\partial L}{\partial q_f} + G(\dot{q}_f), \tag{5.16b}
\]

where \( G \) is an arbitrary function. Differentiating both sides of (5.16b) with respect to \( \dot{q}_f \) and using (5.16a), we conclude that

\[
\mathcal{F} f' = - \frac{\partial}{\partial q_f} (L + G), \tag{5.17}
\]

whence it follows that

\[
L(q_s; \dot{q}_f) = - \int_0^{\dot{q}_f} \mathcal{F}(\tau; q_s) d\tau - G(\dot{q}_f) - A(q_s), \tag{5.18}
\]

where \( A \) is an arbitrary function. To determine \( G \), we make use of (5.18) in (5.16a), obtaining that

\[
\dot{q}_f \frac{\partial G}{\partial q_f} = -\left( \frac{\partial \mathcal{F}}{\partial \vartheta} + \mathcal{F} \right) f' - \left( \frac{\partial \mathcal{F}}{\partial \vartheta} f'' + \mathcal{F} f'' \right) \dot{q}_f, \tag{5.19}
\]

which can be solved by quadrature for \( G \), provided that the following compatibility condition is obeyed:

\[
\frac{\partial}{\partial q_s} \left\{ f' \left( \frac{\partial \mathcal{F}}{\partial \vartheta} + \mathcal{F} \right) + f'' \dot{q}_f \frac{\partial \mathcal{F}}{\partial \vartheta} + f'' \dot{q}_f \mathcal{F} \right\} = 0. \tag{5.20}
\]
Remark 9 Condition (5.20) is rather intricate as it also involves the unknown function \( f \) expressing \( \vartheta \) as in (5.12). We can give it a more transparent expression by using the inverse function \( \phi \) of \( f \), defined by

\[
\dot{q}_f = \phi(\vartheta).
\]  

(5.21)

The following identities are immediate consequences of (5.12) and (5.21),

\[
\phi' f' = 1 \quad \text{and} \quad \phi'' f'^2 + \phi' f'' = 0,
\]

where a prime ' denotes differentiation. Simple computations then show that (5.20) is equivalent to

\[
\frac{\phi'}{\phi} \left( \frac{\partial \mathcal{F}}{\partial \vartheta} + \mathcal{J} \right) + \frac{\partial \mathcal{J}}{\partial \vartheta} - \frac{\phi''}{\phi'} \mathcal{J} = \Sigma(\vartheta),
\]  

(5.22)

with \( \Sigma \) an arbitrary function. Given \( \mathcal{F} \) and \( \mathcal{J} \), (5.22) can be interpreted as an equation for \( \phi \).

Remark 10 It might be a bit disheartening to realize that there is no function \( \phi \) satisfying (5.22) for an ideal polyatomic gas. Indeed, by taking (to within inessential additive constants)

\[
\mathcal{J} = \frac{M}{m} k \ln(\vartheta^3 V) \quad \text{and} \quad \mathcal{U} = \frac{M}{m} 3k \vartheta,
\]  

(5.23)

where \( k \) is the Boltzmann constant, \( M \) is the total mass of the gas, \( m \) the mass of a gas molecule, and \( V \) the volume occupied by the system (see, for example, p. 9 of [50]), we easily see that (5.22) is violated for any \( \phi \), if \( V \) is to be interpreted as a \( q_s \) variable. We have no clear justification for such a disappointing result.

Combining equation (5.18) with (5.16b) to eliminate \( G \), and carrying out under the present circumstances the general developments in the first part of Sect. 2.3, we find the Hamiltonian \( H(p_f; q_s) \) conjugated with \( L \) in terms of \( \mathcal{F} \) and \( \mathcal{J} \),

\[
H(p_f; q_s) = \mathcal{F}(\vartheta; q_s) + \int_0^\vartheta \mathcal{J}(\tau; q_s) d\tau + A(q_s),
\]  

(5.24)

where \( \vartheta \) is now meant to be a positive function \( \tilde{f} \) of the kinetic momentum \( p_f \) conjugated with \( \dot{q}_f \) and possibly of \( q_s \).

Remark 11 According to (2.19), it follows from (5.18) that

\[
p_f = -\frac{\partial G}{\partial \dot{q}_f} - \mathcal{J}(f(\dot{q}_f); q_s) f'(\dot{q}_f).
\]  

(5.25)

Assuming that (5.25) can be inverted to deliver \( \dot{q}_f \), we see from (5.12) that \( \tilde{f} \) does in general depend on both \( p_f \) and \( q_s \).

Our task is thus accomplished: we have found in (5.18) a whole class of Lagrangians whose dynamical equations (5.3a), (5.3b) represent evolutions out of equilibrium consistent
with the basic laws of classical thermodynamics. It is perhaps remarkable that every compatible Lagrangian $L$ depends directly on the entropy $S$ and indirectly (via $G$ in (5.19)) on the free energy $\mathcal{F}$, while the associated Hamiltonian $H$ has a more transparent expression (5.24) featuring both $S$ and $\mathcal{F}$.

**Remark 12** In equilibrium thermodynamics, $S$ and $\mathcal{F}$ are related through the equation

$$ S = -\frac{\partial \mathcal{F}}{\partial \vartheta} \tag{5.26} $$

(see, for example, [64, p. 127]). Now, in equilibrium all dissipative forces cease to act and Rayleigh-Lagrange dynamics is not different from Hamiltonian dynamics. Thus, by applying (2.17) with $H$ as in (5.24), we readily recover (5.26) and add a further requirement,

$$ \frac{\partial \mathcal{F}}{\partial q_s} + \frac{\partial}{\partial q_s} \int_0^\beta S(\tau; q_s) d\tau + \frac{\partial A}{\partial q_s} = 0, \tag{5.27} $$

that is, an equation for the equilibrium state vector.

**Remark 13** It is perhaps worth noting that, were (5.26) adopted as a constitutive law for $S$, (5.24) would deliver a Hamiltonian $H_0$ independent of $p_f$,

$$ H_0(q_s) = \mathcal{F}(0; q_s) + A(q_s). \tag{5.28} $$

In such an instance, equation (5.27) reduces to the customary requirement of stationarity for the free energy, if we set $A \equiv \text{constant}$ and we regard it as a gauge function for the free energy.

**Remark 14** As a simple application of our method, we now recover the classical case considered by Onsager and Machlup [53] for the evolution of irreversible processes near equilibrium. We assume that (5.26) be satisfied near equilibrium as well, so that the Hamiltonian can be written as a function of the state vector $q_s$ only, as in (5.28). Specifically, we take

$$ H_0 = \frac{1}{2} \sum_{i,j=1}^{n-1} h_{ij} q_i q_j, \tag{5.29} $$

where $h_{ij}$ is a symmetric, positive definite matrix. If, as in [53], we write the Rayleigh potential as

$$ R = \frac{1}{2} \sum_{i,j=1}^{n-1} r_{ij} \dot{q}_i \dot{q}_j, \tag{5.30} $$

where $r_{ij}$ is another symmetric, positive definite matrix, independent of $q_s$, we readily see that equation (5.3a) is identically satisfied, while equation (5.3b) become

$$ \sum_{j=1}^{n-1} (r_{ij} \dot{q}_j + h_{ij} q_j) = 0, \quad i = 1, \ldots, n - 1, \tag{5.31} $$

which have the same form as the phenomenological laws (2-13) of [53], the only difference being that the matrix $h_{ij}$ is there replaced by the matrix $s_{ij}$ representing the quadratic approximation of the entropy near equilibrium (see also [60]).
6 Conclusion

We have proposed a thermodynamic theory that builds on the formalism of classical analytical mechanics.

We have adopted Helmholtz’s mechanical interpretation of thermodynamics with its typical distinction between slow and fast variables, the latter characterized as thermal. Truesdell’s thermodynamic theory, with its classical interpretation of entropy, has set the background, the connection with analytical mechanics being provided by Rayleigh’s dissipation potential, here extended beyond its native quadratic limitation.

Our major result was to derive a whole class of Hamiltonians (each defined to within an arbitrary state function), such that the associated evolution equations could be established in accord with constitutive laws for both free energy and entropy, which in our nonequilibrium setting are unrelated. As a first application of our method, we showed that near equilibrium it delivers Onsager’s linear laws for irreversible processes.

At least two issues remain unsettled. First, a certain degree of indeterminacy for both Lagrangian and Hamiltonian associated with a given constitutive choice of free energy and entropy. How is the evolution away from equilibrium described by (5.3a), (5.3b) affected by this?

Second, apart from a cursory incursion into Onsager and Machlup’s theory, we have not yet applied our proposed method to the evolution of some simple system, as are, for example, those considered in [9]. This should be done, although Remark 10 would suggest that such a task might require more ingenuity than expected.

More ambitiously, we also plan to apply our theory to cases relevant to the promising field of soft matter systems, where Onsager’s principle has recently seen a surge of renewed interest. A reliable guidance to these problems can be found in the recent review [76].

Finally, even a more futuristic avenue for further exploration could be foreseen. We treated only homogeneous systems, with a finite number of state variables depending only on time. An extension of the theory to continuous fields, which is presently lacking, would be desirable.

Author contributions Both authors contributed in identical measure

Declarations

Competing interests The authors declare no competing interests.

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