Beyond heat baths II: Framework for generalized thermodynamic resource theories

Nicole Yunger Halpern\textsuperscript{1,2}

\textsuperscript{1}Institute for Quantum Information and Matter, Caltech, Pasadena, CA 91125, USA
\textsuperscript{2}Perimeter Institute for Theoretical Physics, 31 Caroline Street North, Waterloo, Ontario Canada N2L 2Y5

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Abstract

Cutting-edge experiments, which involve the nano- and quantum scales, have been united with thermodynamics, which describes macroscopic systems, via resource theories. Resource theories have modeled small-scale exchanges of heat and information. Recently, the models were extended to particle exchanges, and a family of thermodynamic resource theories was proposed to model diverse baths, interactions, and free energies. This paper motivates and details the family’s structure and prospective applications. How to model electrochemical, gravitational, magnetic, and other thermodynamic systems is explained. Szilárd’s engine and Landauer’s Principle are generalized, as resourcefulness is shown to be convertible not only between informational and gravitational-energy forms, but also among varied physical degrees of freedom in the thermodynamic limit. Quantum operators associated with extensive variables offer opportunities to explore nonclassical noncommutation. This generalization of thermodynamic resource theories invites the modeling of realistic systems that might be harnessed to test small-scale statistical mechanics experimentally.

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\textsuperscript{a} E-mail: nicoleyh@caltech.edu
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I. INTRODUCTION

Thermodynamics models diverse systems, from gases and ferromagnets to chemical reactions, soap bubbles, and electrochemical batteries. Such systems contain on the order of $10^{24}$ particles. But thermodynamic concepts such as heat, work, and entropy are relevant to small systems such as molecular motors and ratchets [1, 2], the unfolding of single DNA or RNA molecules [3–6], and nanoscale walkers [7]. How can the nano- and quantum scales, increasingly controllable in experiments, be reconciled with macroscopic thermodynamics? The resource-theory framework has described small-scale exchanges of heat [8–11]; information [12–14]; and, recently, particles [15]. These successes call for a generalization of thermodynamic resource theories to diverse realistic systems. This paper details the generalization proposed in [15].

This research program contributes to one-shot statistical mechanics. One-shot statistical mechanics blends conventional statistical mechanics with one-shot information theory to describe small scales (e.g., [16]). Shannon information theory concerns the efficiencies with which protocols such as data compression can be performed as the number $n$ of trials diverges. Infinitely many trials are never performed in reality. The efficiencies of finite-$n$ trials, and of protocols that might fail, follow from one-shot information theory [17]. One-shot information theory has been merged with statistical mechanics to describe small-scale heat, work, and entropy.

The information-theory tools applied to statistical mechanics include the resource-theory framework. A resource theory quantifies the value attributable to quantum states by an agent who can perform certain operations for free [18, 19]. Examples include the resource theories for pure bipartite entanglement (which will be called entanglement theory) [20], asymmetry [21–23] and quantum computation [24]. Each resource theory features an agent who can perform certain operations, called free operations, at zero cost. The free operations in the entanglement theory, for example, are local operations and classical communications (LOCC). Free operations include the creation of free states, such as product states in the entanglement theory. States that are not free, e.g., entangled states, are resources. Resources have value because they, with free operations, can simulate nonfree operations. Combined with LOCC, for example, a Bell pair can simulate quantum teleportation.

In the presence of a temperature-$T$ heat bath, nonequilibrium states have value because work can be extracted from them. Resource theories have quantified this value (e.g., [8–10, 25]: a fuller survey appears in Sec. III). Work quantities derived in these resource theories converge to the Helmholtz free energy $F := E - TS$ in the thermodynamic limit. Hence the theories will be called Helmholtz theories here. Each Helmholtz theory is equivalent to the other Helmholtz theories and is distinguished by the value $\beta$ of the bath’s inverse temperature. A Helmholtz theory in which all Hamiltonians are trivial ($H = 0$) has been portrayed as a resource theory for information [12, 26]. This theory has been called the resource theory of nonuniformity elsewhere [13]. Here, the theory will be called the resource theory for entropy, or the entropy theory, after the thermodynamic potential that quantifies resourcefulness.

Recently, Helmholtz theories were generalized [15]. Just as the Helmholtz free energy can be transformed into work, so can the grand potential, the Gibbs free energy, and other thermodynamic potentials. Systems exchange not only heat with baths, but also particles,
volume, and angular momentum \[27, 28\]. Helmholtz theories’ successes merit the generaliza-
tion of resource theories to the rest of thermodynamics. A generalization was proposed and
was illustrated with grand-potential theories, which model exchanges of energy and particles
with heat-and-particle baths, in [13].

This paper motivates and details the extended family of thermodynamic resource theories.
Potential applications are also highlighted. How to model gravitational, electrochemical, and
other thermodynamic systems is explained. Resourcefulness is shown to be convertible, in
the thermodynamic limit, amongst varied physical degrees of freedom. Such conversions
generalize Szilárd’s engine and Landauer erasure, which transform resourcefulness between
informational and gravitational-energy forms. The newly introduced forms of resourcefulness
are modeled by quantum operators that may fail to commute. This noncommutation may
be viewed as nonclassicality absent from Helmholtz theories.

The paper is organized as follows. Section II introduces notation and background. Gen-
eralized thermodynamic resource theories are defined in Sec. III and systems and states,
in Sec. IV Free equilibrating operations, which conserve quantities such as heat, particle
number, and volume, are defined in Sec. V. From free operations, the equilibrium form of
free-state density operators is derived in Sec. VI. Section VII demonstrates the equivalence
between the quasorder induced by free operations and \( d \)-majorization relative to equilibrium
states. In Sec. VIII, the storage of work in diverse forms, such as chemical energy, grav-
itational energy, and electrical energy, is explored. The work \( W_{\text{gain}}^\varepsilon(R) \) extractable from,
and the work \( W_{\text{cost}}^\varepsilon(R) \) required to create, one copy of a state \( R \) with a faulty protocol is
quantified in Sec. IX.

\( W_{\text{gain}}^\varepsilon(R) \) and \( W_{\text{cost}}^\varepsilon(R) \) converge, in the thermodynamic limit in Sec. X, to whichever free
energy lends its name to the resource theory under consideration. In the thermodynamic
limit, all states can be converted into each other reversibly. This convertibility general-
izes Szilárd’s engine and Landauer erasure. Section XI concerns open problems, such as
noncommutation of quantum operators that model extensive variables. This paper’s gen-
eralization of thermodynamic resource theories opens varied, realistic systems to modeling
by one-shot statistical mechanics. The generalization is intended to facilitate experimental
tests of one-shot theory.

II. THERMODYNAMIC BACKGROUND AND NOTATION

Conventional thermodynamics will guide our generalization of thermodynamic resource
theories. Intensive and extensive variables, the Fundamental Relation of Thermodynamics,
the energy and entropy representations, thermodynamic potentials, Legendre transforms,
natural variables, and Massieu functions will be reviewed. For details, readers are referred
to [27]. Though readers may know much of this material, topics such as Massieu functions
may be unfamiliar, and notation (most adopted from Callen [27]) is introduced.

A. Intensive and extensive variables

Every thermodynamic system \( \mathcal{S} \) has thermodynamic variables: properties, some con-
trolled by the experimenter, that characterize \( \mathcal{S} \) as a whole. Example thermodynamic vari-
ables appear in Table I.

\( \text{Intensive variables} \) remain constant as the system’s size changes. Examples include the
| Type of work       | Intensive variables | Extensive variables |
|-------------------|---------------------|---------------------|
| Mechanical (pressure-vol.) | $-p$               | $V$                 |
| Chemical          | $\mu_1^\alpha$     | $N_1^\alpha$        |
| Gravitational     | $\phi = gh$        | $m$                 |
| Electrochemical   | $\bar{\mu}_1^\alpha$ | $N_1^\alpha$       |
| Magnetic          | $B$                | $m$                 |
| Electrical        | $E$                | $p$                 |

**TABLE I:** Example energy intensive variables, extensive variables, and types of thermodynamic work: Pressure-volume work involves the negative $-p$ of pressure, as well as the volume $V$. Chemical work involves the standard chemical potential $\mu_1^\alpha$ of phase $\alpha$ of species $i$, as well as the number $N_1^\alpha$ of phase-$\alpha$ species-$i$ particles. Gravitational work involves the gravitational potential $\phi = gh$ and the mass $m$ (alternatively, as explained in Sec. VIII, the gravitational chemical potential $\bar{\mu}_1^\alpha$ and the number $N_1^\alpha$ of species-$i$ particles at height $\alpha$). Electrochemical work involves the electrochemical potential $\bar{\mu}_1^\alpha$; magnetic work, the magnetic moment $m$ and the external magnetic field $B$; and electrical work, the polarization $p$ and the external electric field $E$.

---

**B. Fundamental Relation; energy and entropy representations**

The Fundamental Relation of Thermodynamics “contains all thermodynamic information about the system” [27]. One can calculate from the relation, for example, conditions under which $S$ is in equilibrium. The relation’s energy representation is

$$ E = E(S, X_1, X_2, \ldots, X_k); $$

(1)

its equivalent entropy representation is

$$ S = S(X_0, X_1, X_2, \ldots, X_k). $$

(2)

If $E$ depends only on $V$, on the $N_1^\alpha$, and on $S$, $S$ is a simple system.

The energy intensive variable $p_i$ conjugate to $X_i$ is a partial derivative of $E$:

$$ p_0 := \left( \frac{\partial E}{\partial S} \right)_{X_m} = T \quad \text{and} \quad p_i := \left( \frac{\partial E}{\partial X_i} \right)_{S, X_m \neq i}, $$

(3)
wherein \( X_m \) remains constant for all \( m = 1, 2, \ldots, k \neq i \). For example, the pressure \( p \) is the negative of the energy intensive variable conjugate to volume:

\[
p = -\left( \frac{\partial E}{\partial V} \right)_{S, X_m \neq V}.
\]  

Equation (4) follows, for a simple single-species, single-phase system, from \( E = TS - pV + \mu N \). The entropy intensive variables \( F_i \) are partial derivatives of \( S \):

\[
F_i := \left( \frac{\partial S}{\partial X_i} \right)_{X_m \neq i}.
\]  

Entropy intensive variables vary with energy intensive variables as

\[
F_0 = \frac{1}{T} \quad \text{and} \quad F_i = -\frac{p_i}{T} \quad \forall i = 1, 2, \ldots, k.
\]  

Much of thermodynamics can be cast equivalently in the energy and entropy representations. Most generalized thermodynamic resource theories are cast in the energy representation. The resource theory for entropy (which models closed isolated systems) features the entropy representation for historical reasons.

C. Thermodynamic potentials, Legendre transforms, and natural variables

Thermodynamic potentials, or free energies, resemble a spring’s potential energy: The ability to perform work can be stored in, and drawn from, thermodynamic potentials. One thermodynamic potential is \( E \); the others result from Legendre transforming \( E \). Which variables are transformed depends on which properties of \( S \) an experimenter can control, or which properties remain constant. The Legendre-transform formalism will be introduced, then illustrated with four examples.

\( E \) is a function of the independent variables \( S \) and \( X_{i=1,2,\ldots,k} \). Suppose that the experimenter cannot control all these variables but controls the intensive variables \( (T), p_1, p_2, \ldots, p_j \). The parentheses should be interpreted as follows: If an experimenter can hold \( T \) constant in a particular thermodynamic problem, \( T \) should be included in the list. If the experimenter cannot, \( T \) should be excluded. This notation enables us to treat \( T \) similarly to other independent variables in Legendre transforms while distinguishing \( T \) as required below.

A Legendre transform substitutes these intensive variables for the corresponding extensive variables in the set of independent variables:

\[
E[(T), p_1, p_2, \ldots, p_j] := E - \left( \frac{\partial E}{\partial S} \right)_{X_i} S - \sum_{i=1}^j \left( \frac{\partial E}{\partial X_i} \right)_{(S), X_m \neq i} X_i
\]  

\[
= E - (TS) - \sum_{i=1}^j p_i X_i.
\]  

A particular Legendre transform contains the symbols enclosed in extra parentheses (the \( T \) in Eq. (7), the second term on the RHS of Eq. (7), the subscript \( S \), and the \( TS \)) if and only if \( T \) replaces \( S \) in the Legendre transform. In Callen’s notation, \( E[p_1, \ldots, p_j] \) is
a function of \( p_1, \ldots, p_j, X_{j+1}, \ldots, X_k \). The subscript \( X_i \) denotes the constancy of \( X_i \) for all \( i = 1, 2, \ldots, k \); and \( X_{m \neq i} \) denotes the constancy of \( X_m \) for all \( m = 1, 2, \ldots, k \neq i \). The independent variables \((S), p_1, \ldots, p_j, X_{j+1}, \ldots, X_k \) are called natural variables. The most work that \( S \) can perform, or the most heat that \( S \) can release, on average while these natural variables remain constant equals the change in \( E[(S), p_1, p_2, \ldots, p_j] \). \( S \) reaches equilibrium when \( E[(T), p_1, p_2, \ldots, p_j] \) minimizes.

Example 1. Suppose the experimenter can control \( T \) but not \( S \). More useful than \( E \) is the Helmholtz free energy

\[
E[T] := E - TS =: F. \tag{9}
\]

If \( S \) is simple and consists of one species and one phase, \( F = F(T,V,N) \). The Helmholtz free energy characterizes systems that exchange heat with heat baths. The average work extractable from \( S \) during any constant-(\( T, V, N \)) process satisfies \( W \leq \Delta F \). \( S \) reaches equilibrium when the probability distribution over the possible microstates \( i \) becomes the canonical ensemble \( P_i = e^{-\beta E_i}/Z \), wherein \( \beta = 1/(k_BT) \) and \( Z \) normalizes the distribution.

Replacing not only \( S \) with \( T \), but also \( N \) with \( \mu \) yields the grand potential. If \( S \) consists of one species and one phase,

\[
E[T,\mu] := E - TS - \mu N =: \Phi(T,\mu,V). \tag{10}
\]

\( \Phi \) governs exchanges of heat and particles. If \( T, \mu, \) and \( V \) remain constant, \( S \) reaches equilibrium when microstates’ probabilities reach the grand canonical ensemble \( P_i = e^{-\beta(E_i-\mu N)}/Z \). Many chemicals react at room temperature and atmospheric pressure. Constant-\( T \), constant-\( p \) processes are described by the Gibbs free energy,

\[
E[T,p] := E - TS + pV =: G(T,p,N). \tag{11}
\]

(In lists of natural variables, \( p \) will sometimes take the place of the energy intensive variable \(-p\).) \( S \) reaches equilibrium when microstates’ probabilities reach the isothermal-isobaric ensemble \( P_i = e^{-\beta(E_i+p\mu)}/Z \). A variation on \( G \) suits a system characterized by a magnetic moment \( \mathbf{m} \) and subject to an external magnetic field \( \mathbf{B} \). If \( T \) and \( \mathbf{B} \) remain constant, the average work extractable remains below the change in the magnetic Gibbs potential,

\[
E[T,\mathbf{B}] := E - TS - \mathbf{B} \cdot \mathbf{m}. \tag{12}
\]

D. Massieu functions

Massieu functions are the entropy representations of thermodynamic potentials. Massieu functions include, and result from Legendre-transforming, the entropy:

\[
S[(F_0), F_1, F_2, \ldots, F_j] := S - \left( \frac{\partial S}{\partial X_0} \right)_{X_0 \neq 0, X_i \neq 0} X_0 - \sum_{i=1}^{j} \left( \frac{\partial S}{\partial X_i} \right)_{X_m \neq i} X_i. \tag{13}
\]

If \( (F_0), F_1, F_2, \ldots, F_j \) remain constant, \( S \) attains equilibrium when \( S[(F_0), F_1, F_2, \ldots, F_j] \) maximizes. Physical significances of Massieu functions are not as simple as the free energies’ interpretations as work and heat.

\footnote{Legendre-transforming all the extensive variables yields the trivial Fundamental Relation \( E = 0 \).}
TABLE II: Commonly used thermodynamic potentials, and characterizations of the corresponding resource theories: Sections [III][IV] explain Columns 4-6. Each Z denotes the partition function that normalizes the relevant state.

**III. HOW TO DEFINE THERMODYNAMIC RESOURCE THEORIES**

Different families of thermodynamic resource theories correspond to exchanges of different quantities by systems and baths. Equivalently, different families correspond to different sets of natural variables, to different free energies (as shown in Sec. [X]), and to different types of baths or external fields. The rest of this paper concerns systems whose natural variables include \( T \), as well as closed isolated systems (whose natural variables do not). Each parenthesized \( T \) should be interpreted as follows: If a closed isolated system is being modeled, the natural variables are extensive, so the \( T \) and the \( p_i \)'s should be ignored. Otherwise, the \( T \) and (depending on the system) perhaps some \( p_i \)'s should be regarded as present.

Below, how to specify a thermodynamic resource theory will be explained. The explanation will be illustrated with Helmholtz theories, grand-potential theories, and entropy theory. Table II summarizes the examples.

Suppose we wish to model interactions between a system \( S \) and a bath, using a thermodynamic resource theory. Suppose that the variables \( ((T),p_1,p_2,...,p_j,X_{j+1},X_{j+2},...,X_k) \) remain constant. The intensive variables \( (T),p_1,...,p_j \) characterize the bath to which the resource-theory agent has access. Each list of values of \( (T),p_1,...,p_j \) specifies one thermodynamic resource theory \( T^{(\beta,p_1,...,p_j)} \) for the thermodynamic potential \( E[T,p_1,...,p_j] \). (The inverse temperature is denoted by \( \beta = \frac{1}{k_B T} \).) All the resource theories characterized by the same intensive variables are mathematically equivalent and form a family. The bath exchanges with \( S \) the physical quantities represented by \( (X_0),X_1,...,X_j \).

The intensive natural variables \( p_i \) that specify \( T^{\beta,p_1,...,p_j} \) should be consistent with the Gibbs-Duhem Relation. The Gibbs-Duhem Relation interrelates a system’s intensive vari-
ables and can be expressed as
\[ \sum_{i=0}^{k} X_i dp_i = 0 \]  
(14)

[27]. Specifying sufficiently many variations \( dp_i \) specifies the rest of the \( dp_j \). The Gibbs-Duhem Relation leads to the Gibbs Phase Rule, which governs the number \( f \) of independent intensive variables [27, 29]. Attempts to independently specify more than \( f \) intensive variables yield the trivial Fundamental Relation \( E = 0 \). For an example, see Footnote[1]. Usually, the Gibbs-Duhem Relation will not worry us, and we can specify independently all the natural \( p_i \)'s desired. For example, the intensive variables of a simple single-species, single-phase system are \( (p_1, p_2, p_3) = (T, p, \mu) \). Two of these \( p_i \)'s can be specified independently. Each Helmholtz theory is defined by one \( p_i \) (\( \beta \)); and each grand-potential theory, by two \( p_i \)'s (\( \beta \) and \( \mu \)).

Example 2. The best-known family of thermodynamic resource theories consists of Helmholtz theories. Introduced without resource-theory language in [8], Helmholtz theories have been studied in [10, 23, 22, 33] and in one-shot settings in [9, 14, 18]. Quantum properties have been emphasized in [34, 35], and models similar to Helmholtz theories appear in [14, 23, 30]. Each Helmholtz theory models exchanges of energy with a heat bath characterized by an inverse temperature \( \beta \). Free operations preserve energy, and canonical ensembles \( e^{-\beta H}/Z \) specify free states. Central results include the work \( W_{\text{gain}}^\varepsilon(R) \) extractable from one copy of a quasiclassical state \( R \), and the work \( W_{\text{cost}}^\varepsilon(R) \) required to create one copy of \( R \), via faulty protocols [9]. \( W_{\text{gain}}^\varepsilon(R) \) and \( W_{\text{cost}}^\varepsilon(R) \) are one-shot analogs of the Helmholtz free energy \( F \).

Example 3. Grand-potential theories model exchanges of energy and particles with heat- and-particle reservoirs. These theories were introduced in [15] to illustrate the generalization, detailed fully in this paper, of thermodynamic resource theories beyond Helmholtz theories. To specify a grand-potential theory, one specifies values of the bath’s \( \beta \) and \( \mu \) (or, if particles of \( m \) species in \( \zeta \) phases are exchanged, one specifies \( \mu^\alpha_i \) for all \( i = 1, 2, \ldots, m \) and for all \( \alpha = 1, 2, \ldots, \zeta \)). Free operations conserve energy and particle number, and grand canonical ensembles are free. \( W_{\text{gain}}^\varepsilon(R) \) equals a one-shot analog of the grand potential \( \Phi \), and another one-shot analog bounds \( W_{\text{cost}}^\varepsilon(R) \).

Example 4. The entropy theory models closed isolated systems. This theory was introduced in [12, 20], which concern asymptotic contexts; was discussed in [11]; and was reviewed exhaustively in [13], which spotlights one-shot contexts. In [13] the entropy theory is called the resource theory of nonuniformity. Free states are microcanonical ensembles \( \left( \frac{1}{d}, \frac{1}{d}, \ldots, \frac{1}{d} \right) \) [12].

The nonuniformity theory is equivalent to a Helmholtz theory in which all Hamiltonians are trivial: \( H = 0 \) [12, 13]. Yet we shall see that the entropy theory models systems whose natural entropy-representation variables are \( (E, V, N) \) (if each systems is simple and consists of one species and one phase). \( (E, V, N) \) are the natural variables of closed isolated systems. Because the variables natural to the entropy theory are not natural to Helmholtz theories, the entropy theory can be viewed as distinct from any Helmholtz theory.

The family of entropy theories differs from the other families in two ways. First, the entropy family (that models simple single-species, single-phase systems) contains only one theory. The family has no intensive natural variables whose different possible values would
define different theories. Such an intensive variable would characterize a bath. Closed isolated systems do not interact with baths; so of course the entropy family lacks intensive natural variables. Second, the entropy theory is cast in the entropy representation. Central results—the amount of “information” extractable from, or needed to create, one copy of a state $\rho$—are entropies, rather than work quantities.

IV. HOW TO SPECIFY SYSTEMS AND STATES

A model for thermodynamic systems is introduced, and a model for states is generalized from Helmholtz and entropy theories. These theories are shown to obey what is introduced as the fixed-eigensubspace condition.

A. Systems

Recall that the extensive variables $X_0, X_1, \ldots, X_k$, and $S$ characterize the thermodynamic system $S$. With each $X_i$, we will associate an operator. Jaynes proposed such an association in [28]. A Hamiltonian $H$ corresponds to $X_0 = E$, for example, and the number operator corresponds to $N$. Each variable and the corresponding operator (apart from $E$ and $H$) will be represented by the same symbol. Context will clarify whether $X_i$ represents a variable or an operator. For a discussion about the volume operator, see Appendix A.

Definition 1 (System). Each system $S$ in the thermodynamic resource theory $T^{(β),p_1,\ldots,p_j}$ is specified by a Hilbert space $\mathcal{H}$ and by the system operators $(H, X_1, \ldots, X_k)$. The system operators are Hermitian operators defined on $\mathcal{H}$.

For simplicity, we will often assume that the $X_i$ commute with each other and have discrete spectra.

B. States

Recall that (in non-entropy thermodynamic resource theories) $(T, p_1, p_2, \ldots, p_j, X_{j+1}, X_{j+2}, \ldots, X_k)$ are the natural variables of $S$. The extensive-variable operators $X_1, \ldots, X_j$ conjugate to $p_1, \ldots, p_j$ will be called state operators. To specify a state in a thermodynamic resource theory, one specifies state operators and a density operator.

Definition 2 (State). Let $S$ denote a system, associated with the Hilbert space $\mathcal{H}$, in the thermodynamic resource theory $T^{(β),p_1,\ldots,p_j}$. Each possible state of $S$ is specified by a $(j+2)$-tuple

$$R := (\rho, (H), X_1, \ldots, X_j),$$

wherein the density operator $\rho$ is a positive linear operator defined on $\mathcal{H}$.

More precisely, the family of entropy theories associated with each set $\{X_0, X_1, \ldots, X_k\}$ of natural variables contains only one theory. One entropy theory models simple single-species, single-phase systems, whose natural variables are $(E, V, N)$; one entropy theory models simple two-species, one-phase systems, whose natural variables are $(E, V, N_1, N_2)$; etc.

The entropy theory has been thought to be a Helmholtz theory associated with a zero-temperature or infinite-temperature bath. But equating $β = \infty$, 0 fails to reduce Helmholtz theories’ free operations to the entropy theory’s free operations. Details appear in Sec. [V].
Hence the resourcefulness of a quasiclassical $\rho$ and $R$, we will often focus on state operators and state operators that commute with each other and that have discrete spectra. If the state operators commute, we will call $R$ and $\rho$ quasiclassical. Free operations can diagonalize a quasiclassical $\rho$, according to Sec. V. Hence the resourcefulness of a quasiclassical $\rho$ is encapsulated in a vector $r = (r_1, r_2, \ldots, r_d)$ of the eigenvalues of $\rho$. A quasiclassical state, therefore, will often be represented by $R = (r, (H), X_1, \ldots, X_j)$.

**Example 5.** Helmholtz theories that model simple single-species, single-phase systems have the natural variables $(p_0, X_1, X_2) = (T, V, N)$. The only intensive natural variable is $p_0$, which is conjugate to $E$, which corresponds to the operator $H$. Hence each state is defined by $(\rho, H)$, as in [8, 9, 12, 15]. A grand-potential theory that models simple single-species, single-phase systems has the natural variables $(p_0, p_1, X_2) = (T, \mu, V)$. The $T$ and $\mu$ are conjugate to $E$ and $N$, so a state is specified by $(\rho, H, N)$, as in [13]. The entropy theory’s natural variables are extensive: $(X_1, X_2, X_3) = (E, V, N)$. To specify a state, one specifies only $\rho$, as in [12, 13, 26].

Let us introduce two more notations for states. First, recall that agents in resource theories can create free states at zero cost. With each quasiclassical state $R := (\rho, (H), X_1, \ldots, X_j)$ is associated a free state $G_R := (\gamma_R, (H), X_1, \ldots, X_j)$, wherein $\gamma_R$ has the form detailed in Sec. VI. In quasiclassical notation, $G_R = (g_R, (H), X_1, \ldots, X_j)$. Second, a composition of states $R : (\rho, (X_0r), \ldots, X_{jr})$ and $S : (\sigma, (X_0s), \ldots, X_{js})$ will be denoted by

$$R + S = (\rho \otimes \sigma, (X_{0r} + X_{0s}), X_{1r} + X_{1s}, \ldots, X_{jr} + X_{js}),$$

wherein $X_{1r} + X_{1s} = X_{is} \otimes 1 + 1 \otimes X_{is}$.

**C. Fixed-eigensubspace condition**

The system operators $X_{j+1}, \ldots, X_k$ do not specify states. In Helmholtz theories, for example, $V$ and $N$ do not characterize any state $(\rho, H)$. To understand the role played by non-state system operators in thermodynamic resource theories, we return to conventional thermodynamics. Recall from Sec. III that the change in a free energy bounds the work extractable (e.g., $W \leq \Delta F$) during a constant-$\rho$ (p_1, \ldots, p_j, X_{j+1}, \ldots, X_k) process. This constancy of the $X_{j+1}, \ldots, X_k$ suggests that the “action” in each thermodynamic resource theory occurs in one eigensubspace shared by $X_{j+1}, \ldots, X_k$.

**Proposition 1** (Fixed-eigensubspace condition). Suppose that $R := (\rho, (H), X_1, \ldots, X_j)$ denotes the state of any system $S$ specified by $H$, and by $(H), X_1, \ldots, X_k$ in $T^{(p_1, \ldots, p_j)}$. The support $\text{supp}(\rho)$ is in an eigenspace $H_0$ of $X_{j+1}$ that coincides with an eigenspace of $X_{j+2}$ and with an eigenspace of $X_{j+3}$ and so on for all $X_{i=j+1, \ldots, k}$:

$$\text{supp}(\rho) \subseteq H_0.$$  \hspace{1cm} (16)

All free unitaries $U$ (defined in Sec. V) preserve $H_0$: $|\psi\rangle \in H_0 \Rightarrow U|\psi\rangle \in H_0$.

The fixed-eigensubspace condition has previously been mentioned in a specialized context. The resource theory for entropy has been portrayed as a Helmholtz theory in which all Hamiltonians are trivial: $H = 0$. This portrayal was generalized: According to [15],

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the entropy theory is equivalent to a Helmholtz theory in which (i) every \( \text{supp}(\rho) \) is in one energy eigensubspace \( \mathcal{H}_0 \) and (ii) \( \mathcal{H}_0 \) is the only subspace transformed nontrivially by free unitaries. The fixed-eigensubspace condition generalizes and sharpens the claims in [11–13, 15]: The entropy theory (having the natural variables \( E, V, \) and \( N \)) is equivalent to a Helmholtz theory in which (i) every state’s \( \text{supp}(\rho) \) is one eigensubspace \( \mathcal{H}_0 \) shared by the state’s \( H, V, \) and \( N \) and (ii) \( \mathcal{H}_0 \) is the only subspace transformed nontrivially by any free unitary. The entropy theory models physical transformations that conserve the total energy, volume, and particle number.

Not only the entropy theory, but also every other thermodynamic resource theory, can be viewed as having “behind-the-scenes” \( X_i \)’s. Every Helmholtz-theory system corresponds to a \( V \) and an \( N \) that share an eigensubspace \( \mathcal{H}_0 \) in which \( \text{supp}(\rho) \) remains. “All the action takes place” in \( \mathcal{H}_0 \). Generalizing thermodynamic resource theories brings these \( X_i \) to light.

The fixed-eigensubspace \( X_i \) do not directly affect previously established results. Yet these \( X_i \) matter for four reasons: (1) These \( X_i \) clarify the relationship between the much-used Helmholtz and entropy theories. (2) As explained in Sec. XI.B, the \( N \)’s in Helmholtz theories invite a reconsideration of the meaning of “one-shot statistical mechanics.” (3) The existence of these \( X_i \) can be viewed as an assumption implicit in thermodynamic resource theories, and identifying one’s assumptions is advisable. (4) These \( X_i \) must exist for resource theories to model thermodynamics in all its natural-variable-containing glory.

V. FREE (EQUILIBRATING) OPERATIONS

In each resource theory, an agent can perform certain operations for free, without expending resources. The free operations in general thermodynamic resource theories are here termed equilibrating operations, as in [15].

**Definition 3** (Equilibrating operations). Each equilibrating operation \( \mathcal{E} \) on any state \( R := (\rho, (H_R), X_{1R}, \ldots, X_{jR}) \) consists of three steps:

1. composition with any free state \( G := (\gamma, (H_G), X_{1G}, \ldots, X_{kG}) \),

2. the transformation of \( \rho \otimes \gamma \) by any unitary that commutes with \( X_{iR} + X_{iG} \) for all \( i = (0), 1, \ldots, j \) and that satisfies the fixed-eigensubspace condition, and

3. the discarding of any component system \( A \).

\( \mathcal{E} \) has the form

\[
R \overset{\text{equil.}}{\longrightarrow} \mathcal{E}(R) = \left( \text{Tr}_A(U[\rho \otimes \gamma]U^\dagger), \left( \text{Tr}_A(H_R + H_G) \right), \text{Tr}_A(X_{1R} + X_{1G}), \ldots, \text{Tr}_A(X_{jR} + X_{jG}) \right),
\]

wherein

\[
[U, X_{iR} + X_{iG}] = 0 \quad \forall i = (0), 1, \ldots, j
\]

and \( U \) obeys the fixed-eigensubspace condition. That is, if \( \text{supp}(\rho \otimes \gamma) \) is in an eigensubspace \( \mathcal{H}_0 \) shared by all the \( X_{iR} + X_{iG} \), then \( U \) preserves \( \mathcal{H}_0 \):

\[
|\psi\rangle \in \mathcal{H}_0 \quad \Rightarrow \quad U|\psi\rangle \in \mathcal{H}_0.
\]
Equation (18) distinguishes general thermodynamic resource theories from Helmholtz theories. As will become clearer in Sec. VI, \( T^{\beta,p_1,\ldots,p_j} \) might, \textit{prima facie}, appear equivalent to a Helmholtz theory whose Hamiltonians are replaced by the effective Hamiltonians \( \tilde{H} = H - \sum_{i=1}^{j} p_j X_j \). But free unitaries in Helmholtz theories preserve \( \hat{H} \), whereas free unitaries in \( T^{\beta,p_1,\ldots,p_j} \) preserve \( X_i \) for all \( i = 0, 1, \ldots, j \). Because \( [U, \hat{H}] = 0 \) does not imply \( [U, X_i] = 0 \), more unitaries are free in the Helmholtz theory than in \( T^{\beta,p_1,\ldots,p_j} \).

Free operations tend to evolve states toward free states. The free states, as shown in Sec. VI, are equilibrium states. Hence the name \textit{equilibrating operations}. Free operations induce a quasiorder on states, as explained in Sec. VII.

Example 6. Definition 3 can be shown to reduce to the free operations defined previously for Helmholtz and entropy theories (except that the fixed-eigensubspace condition does not appear explicitly in earlier definitions). In Helmholtz theories, just one extensive-variable operator, \( H \), characterizes each state. By Definition 3, therefore, all free unitaries satisfy \( [U, H_R + H_G] = 0 \). This restriction characterizes earlier definitions of Helmholtz theories’ free operations, which have been called thermal operations [8, 10]. In the entropy theory, no extensive-variable operators characterize states, so Definition 3 does not restrict free unitaries. Neither do earlier definitions of entropy-theory free operations, which have been called noisy operations [26].

Definition 3 illustrates (the previously known reason) why the entropy theory is not a Helmholtz theory in which \( \beta = 0 \) or \( \infty \). Equation 18 constrains the \( U \)’s that are free in Helmholtz theories but not the \( U \)’s that are free in the entropy theory. Setting \( \beta = 0, \infty \) in a Helmholtz theory does not lift the constraint, i.e., does not reduce Helmholtz-theory equilibrating operations to entropy-theory equilibrating operations.

VI. FREE (EQUILIBRIUM) STATES

The definition of equilibrating operations refers to free states but not to the forms that free states can assume. Using Definition 3, we will show that the only density operators that can be free in nontrivial thermodynamic resource theories are canonical-type ensembles. A resource theory will be called \textit{trivial} if free operations alone can generate states that do not appear explicitly as free states in the definition of free operations. Recall from Eqs. (5) and (6) that \( F_i \) denotes the entropy intensive variable conjugate to \( X_i \).

Theorem 2. Consider a thermodynamic resource theory \( T^{(\beta),p_1,\ldots,p_j} \) in which all states are quasiclassical. Every free state has the form

\[
G := (g, (X_0), X_1, \ldots, X_j),
\]

wherein element \( \alpha \) of \( g \) has the form

\[
g_\alpha = e^{-\frac{1}{k_B} [F_0 x_{0,\alpha} + F_1 x_{1,\alpha} + \ldots + F_j x_{j,\alpha}]} / Z,
\]

\( x_{i,\alpha} \) denotes eigenvalue \( \alpha \) of operator \( X_i \), and the partition function \( Z \) normalizes \( g \). If any other state were free, \( T^{(\beta),p_1,\ldots,p_j} \) would be trivial.

The proof of Theorem 2 generalizes from [13] almost trivially and appears in Appendix B. As noted in [13], the proof offers an operational alternative to canonical-ensemble derivations.
that depend on assumptions such as the Fundamental Assumption of Statistical Mechanics. According to the Fundamental Assumption, microcanonical ensembles represent isolated systems’ equilibrium states. The microcanonical form of the free states in the entropy theory (discussed in Example 7) can be derived from the definition of free operations and from the theory’s nontriviality [12]. This operational derivation sidesteps the Fundamental Assumption that has generated criticism (e.g., [28]).

Example 7. If \( T^{(\beta), p_1, \ldots, p_j} = T \) denotes the entropy theory, the argument of the exponential in Eq. (21) vanishes. The free state \( g \) is the microcanonical ensemble \( \left( \frac{1}{d}, \ldots, \frac{1}{d} \right) \), as in [12].

In Helmholtz theories, free states’ density operators have the form \( e^{-\beta H}/\operatorname{Tr}(e^{-\beta H}) \); and in grand-potential theories, \( e^{-\beta(H-\mu N)}/\operatorname{Tr}(e^{-\beta(H-\mu N)}) \).

VII. QUASIORDER ON STATES

Equilibrating operations induce a quasiorder on states. The quasiorder on quasiclassical states is shown to be equivalent to \( d \)-majorization relative to equilibrium states, termed equimajorization. Rescaled Lorenz curves illustrate equimajorization. Much of this section immediately generalizes [15], which generalizes [8, 9].

A. Equivalence of two quasiorders

A quasiorder on a set \( \mathcal{S} \) is a binary operation \( \leq \) that satisfies reflexivity and transitivity: For all \( A, B, C \in \mathcal{S} \), \( A \leq A \); and if \( A \leq B \) and \( B \leq C \), then \( A \leq C \) [37]. Equilibrating operations define a quasiorder \( \rightarrow_{\text{equil}} \) on the states in each thermodynamic resource theory. If equilibrating operations can transform \( R \) into \( S \), then \( R \rightarrow_{\text{equil}} S \).

The quasiorder on quasiclassical states will be shown to be equivalent to \( d \)-majorization. A matrix \( M \) is called \( d \)-stochastic if it preserves some vector \( d \):

\[
Md = d, \quad \sum_i M_{ij} = 1 \quad \forall i
\]

[37]. A vector \( r \) \( d \)-majorizes a vector \( s \), \( r \succeq_d s \), if some \( d \)-stochastic matrix \( M \) maps \( r \) to \( s \): \( Mr = s \) [37]. The \( d \)'s relevant to \( T^{(\beta), p_1, \ldots, p_j} \), are the equilibrium state relative to \( (T), p_1, \ldots, p_j \). Matrices \( M \) that preserve such equilibrium states will be called equistochastic, as in [15]. \( d \)-majorization relative to the uniform distribution \( \left( \frac{1}{d}, \ldots, \frac{1}{d} \right) \) is majorization, the quasiorder in the resource theory for entropy [12, 13, 26].

Definition 4. Let \( T^{(\beta), p_1, \ldots, p_j} \) denote a thermodynamic resource theory in which the states \( R := (r, (H), X_1, \ldots, X_j) \) and \( S := (s, (H), X_1, \ldots, X_j) \) share their extensive-variable state operators. \( R \) equimajorizes \( S \), written \( R \succeq_{\text{equil}} S \), if some stochastic matrix \( M \) that preserves the equilibrium state \( G_R := (g_R, (H), X_1, \ldots, X_j) \) maps \( r \) to \( s \). That is, if

\[
Mr = s, \quad Mg_R = g_R, \quad \text{and} \quad \sum_i M_{ij} = 1,
\]

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then $R \succeq_{(β),p_1,...,p_j} S$.

Let $R' := (r', (H_R), X_{1R}, \ldots, X_{jR})$ and $S' := (s', (H_S), X_{1S}, \ldots, X_{jS})$ denote states that do not share all their extensive-variable state operators. $R'$ equimajorizes $S$ if some stochastic matrix $M$ that preserves the equilibrium state

$$G_R + G_S := (g_R \otimes g_S, (H_R + H_S), X_{1R} + X_{1S}, \ldots, X_{jR} + X_{jS})$$

maps $r' \otimes g_S$ to $g_R \otimes s'$:

$$M(r' \otimes g_S) = (g_R \otimes s'), \quad M(g_R \otimes g_S) = (g_R \otimes g_S), \quad \text{and} \quad \sum_i M_{ij} = 1$$

implies $R' \succeq_{(β),p_1,...,p_j} S'$.

The second definition invokes a technique used in [12, 13] to compare entropy-theory states $r'$ and $s'$ defined on Hilbert spaces that have different dimensions. $r'$ can be composed with the free state $g_S$; the composite $r' \otimes g_S$, compared to $g_R \otimes s'$; and the first subsystem, discarded. Having defined two quasiorders in $T^{(β),p_1,...,p_j}$, we state their equivalence.

**Theorem 3.** Let $R$ and $S$ denote any quasiclassical states in $T^{(β),p_1,...,p_j}$. An equilibrating operation that maps $R$ to $S$ exists if and only if $R$ equimajorizes $S$:

$$R \xrightarrow{\text{equiv}} S \iff R \succeq_{(β),p_1,...,p_j} S.$$  \hspace{1cm} (25)

**Proof.** The proof immediately generalizes the proof of [15, Theorem 2], which concerns grand-potential theories. The grand-potential proof generalizes the proof of [8, Theorem 5], which concerns Helmholtz theories. The Helmholtz-theory proof relies on (i) a free operation $π_n$ that conserves energy and (ii) the equality of the energies of pure states that share a characteristic denoted by the pair $(u, v)$ of vectors. In [8], $(u, v)$ is denoted by $(r, s)$.

In grand-potential theories, an analog of $π_n$ conserves energy and particle number, and pure states that have the same $(u, v)$ have the same energy and particle number [15]. By the same token, in $T^{(β),p_1,...,p_j}$, an analog of $π_n$ that conserves multiple extensive properties can be constructed. Pure states associated with the same $(u, v)$ have the same set of eigenvalues of $(H), X_1, \ldots, X_j$. Replacing two statements about energies, in the proof of [8, Theorem 5], with statements about multiple $X_i$’s yields a proof of Theorem 3. \hfill $\square$

**B. Rescaled Lorenz curves**

Rescaled Lorenz curves illustrate the quasiorder on states. The curves were introduced into Helmholtz theories in [9]; reappeared in Helmholtz theories in [11, 38]; and characterize the entropy theory [13] and grand-potential theories [15]. These resource-theory applications have roots in works by Ruch, Schranner, Seligman, and others (e.g., [39]). Extant results are generalized concisely below; for details, readers are referred to the aforementioned sources.

**Definition 5 (Rescaled Lorenz curve).** Let $R := (r, (H), X_1, \ldots, X_j)$ denote any quasiclassical state in $T^{(β),p_1,...,p_j}$. Let $G_R$ denote the corresponding equilibrium state; and $Z$, the partition function of $G_R$. Suppose that $X_i$, for each $i = (0), 1, \ldots, j$, has $d$ discrete, not necessarily distinct, eigenvalues $x_{i1}, \ldots, x_{id}$. Let $r = (r_1, \ldots, r_d)$ be ordered such that

$$r_1 e^{\frac{1}{k_B}[(F_0 x_{i1}) + F_1 x_{i2} + \ldots + F_j x_{ij}]} \geq \ldots \geq r_d e^{\frac{1}{k_B}[(F_0 x_{id}) + F_1 x_{id} + \ldots + F_j x_{jd}]}.$$  \hspace{1cm} (26)
FIG. 1: Rescaled Lorenz curve $L_R$: Visualization of a state $R := (r, H, X_1, \ldots, X_j)$ in a general thermodynamic resource theory. $x_{i\alpha}$ denotes eigenvalue $\alpha$ of the state operator $X_i$, and the $F_i$ denotes entropy intensive variable conjugate to $X_i$ [Eqs. (5) and (6)].

wherein $F_i$ denotes the entropy intensive variable conjugate to $X_i$.

Define the point $P_0 := (0, 0)$ and the points

$$P_m := \left( \sum_{\alpha=1}^{m} e^{-\frac{1}{k_B} \left( F_0 x_{0\alpha} + F_1 x_{1\alpha} + \cdots + F_j x_{j\alpha} \right)} \sum_{\alpha=1}^{m} r_{\alpha} \right)$$

for all $m = 1, \ldots, d$. The Lorenz curve $L_R^{(\beta), p_1, \ldots, p_j}$ for $R$, rescaled relative to $G_R$, is the piecewise linear curve, defined on $x \in [0, Z]$, that consists of $P_{m=0,\ldots,d}$ and that interpolates between $P_m$ and $P_{m+1}$ for all $i = 0, \ldots, d - 1$.

For simplicity, we will sometimes denote $L_R^{(\beta), p_1, \ldots, p_j}$ by $L_R$. If $R$ denotes a state in the entropy theory, the argument of the exponential in Eq. (27) vanishes. An example curve appears in Fig. 1.

Rescaled Lorenz curves encapsulate states’ resourcefulness, in the sense detailed in [9,13]. The more $L_R$ bends outward from the straight line that represents the equilibrium state $G_R$, the more value $R$ has. The value of a state can be quantified by many functions, called monotones [11,13,15]. Monotones include the work needed to create, and the work extractable from, a state (Sec. IX).

**Theorem 4.** Let $R := (r, (H), X_1, \ldots, X_j)$ and $S := (s, (H), X_1, \ldots, X_j)$ denote quasiclassical states that share their extensive-variable state operators in the thermodynamic resource theory $T^{(\beta), p_1, \ldots, p_j}$. An equilibrating operation $\mathcal{E}$ that transforms $R$ into $S$ exists if and only if the Lorenz curve for $R$, rescaled relative to the corresponding equilibrium state $G$, fails to dip below the rescaled Lorenz curve for $S$:

$$\mathcal{E}(R) = S \iff L_R^{(\beta), p_1, \ldots, p_j}(x) \geq L_S^{(\beta), p_1, \ldots, p_j}(x) \quad \forall x \in [0, Z],$$

(28)
FIG. 2: The rescaled Lorenz curves $L_R$ and $L_S$ lie above the curve $L_G$. Equilibrating operations, therefore, can transform the states $R$ and $S$ into the free state $G$. Because $L_R$ lies partially below and partially above $L_S$, equilibrating operations can transform neither $R$ into $S$ nor $S$ into $R$.

wherein $Z$ denotes the partition function of $G$.

Let $R' := (r, (H_{R'}), X_{1_{R'}}, \ldots, X_{j_{R'}})$ and $S' := (s, (H_{S'}), X_{1_{S'}}, \ldots, X_{j_{S'}})$ denote quasiclassical states that do not share all their $X_i = (0), 1, \ldots, j$. Equilibrating operations can transform $R'$ into $S'$ if and only if the Lorenz curve for $R' + G_{S'}$, rescaled relative to $G_{R'} + S'$, fails to dip below the rescaled Lorenz curve for $G_{R'} + S'$:

$$E(R') = S' \iff L_{R'+G_{S'}}^{(\beta, p_1, \ldots, p_j)}(x) \geq L_{G_{R'} + S'}^{(\beta, p_1, \ldots, p_j)}(x) \forall x \in [0, Z'],$$

(29)

wherein $Z'$ denotes the partition function for $G_{R'} + G_{S'}$.

Proof. The proof immediately generalizes the proof of [15, Proposition 3]. That Proposition 3 contains the manifestation, in grand-potential theories, of Theorem 4. The grand-potential proof does not depend on extensive-variable operators ($X_0 = H$ or $X_1 = N$) directly. The $X_i$’s affect the proof only insofar as $g_R$ depends on them. Hence the proof of [15, Proposition 3] can be restated in $T^{(\beta, p_1, \ldots, p_j)}$ under the assumption that $g_R$ has the form of Eq. (21).

An illustration of Theorem 4 appears in Figure 2.

VIII. MODEL FOR WORK AND BATTERIES

To calculate the work transferred during a state conversion, we must define work in resource theories intended to model quantum systems. In classical statistical mechanics, work is defined as an integral along a path through phase space. How to define a quantum analog has been debated [40]. In thermodynamic resource theories, work has been defined in four ways. Two of the definitions will be recast in terms of generalized thermodynamic resource theories. We will focus on energy-representation resource theories, whose natural variables include $\beta$. 

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Batteries have been modeled in four ways in thermodynamic resource theories. A two-level work bit appears in \[9, 11\]. Calculating with the bit is simple. Yet the bit can be difficult to use in practice, if the precise amount of work to be transferred during some state conversion is not known while the bit is prepared \[25\]. Relatively robust quasiclassical batteries appear in \[15, 25\]. In \[25\], a weight whose height changes stores gravitational potential energy. In \[15\], a battery is any system whose energy levels are finely spaced and that occupies only pure states. Coherences have been addressed in \[41\]. For simplicity, this paper focuses on quasiclassical batteries generalized from \[15, 25\]. The generalization will be illustrated when the weight in \[25\] is modeled with gravitational thermodynamic resource theories, which will be shown to be equivalent to grand-potential theories.

Consider a quasiclassical battery \(B \in T_{\beta, p_1, \ldots, p_j}\). The battery stores resourcefulness insofar as the battery’s density operator differs from the corresponding equilibrium state’s density operator. For simplicity, we assume that \(B\) occupies only energy eigenstates:

\[
B_E := (|E\rangle\langle E|, H, X_1, \ldots, X_j).
\]

(30)

In general thermodynamic resource theories, little distinguishes the energy operator \(H\) from the other \(X_i\)’s. Each \(X_i\) represents some physical degree of freedom (DOF). Resourcefulness can be stored in particle number, electric polarization, gravitational mass, and other DOFs. This diversification of the DOFs that can store resourcefulness resembles the generalization of Landauer erasure and Szilár’s engine in Sec. X.

If \(W\) denotes a positive number, then storing work in \(B\) maps \(B_E\) to \(B_E + W\), and withdrawing work maps \(B_E + W\) to \(B_E\). States’ work yields and work costs are defined as in \[15\]:

The maximum work \(W_{\text{gain}}(R)\) extractable from a state \(R\) is the greatest value of \(W\) for which \(R + B_E \xrightarrow{\text{equiv.}} B_{E+W}\). The minimum work cost \(W_{\text{cost}}(R)\) of creating \(R\) is the least value of \(W\) for which \(B_{E+W} \xrightarrow{\text{equiv.}} R + B_E\).

Example 8 (Weights in gravitational resource theories). Batteries can manifest as weights modeled by thermodynamic resource theories that model gravitational potential energy. Such theories, we shall see, are equivalent to grand-potential theories.

Gravitational fields are modeled as follows in conventional thermodynamics \[29, 42, 43\]. Consider a massive particle at a height \(h\) in a uniform gravitational field sourced by external masses. The particle’s mass \(m\) serves as an extensive variable. The gravitational potential \(\phi = gh\) serves as an intensive variable.

More generally, consider a system that contains \(q\) chemical species. Let \(m_i\) denote the mass of one species-i particle. Each particle sits at some height. The set \(\{h_0, h_1, \ldots, h_\zeta\}\) of possible heights will be approximated as discrete, similarly to the set in \[25\]. The ground is labeled as \(h_0\), and species-i particles at different heights are viewed as being in different phases \[29, 42, 43\]. The number of species-i particles at height \(h_\alpha\) is denoted by \(N_\alpha^i\). The system has the gravitational potential energy

\[
g \sum_{\alpha=1}^{\zeta} \sum_{i=1}^{q} m_i N_\alpha^i h_\alpha.
\]

(31)

Gravitational potential energy can be cast as a contribution to chemical energy \[29, 42, 43\]. The chemical potential \(\mu_\alpha^i\) that characterizes the phase \(\alpha\) of species \(i\) in the absence of gravitational and electric fields is called the standard chemical potential. Combining \(\mu_\alpha^i\)
with a gravitational term yields the chemical potential $\tilde{\mu}_i^\alpha$:

$$E \propto \sum_{\alpha=1}^\zeta \sum_{i=1}^q \mu_i^\alpha N_i^\alpha + g \sum_{\alpha=1}^\zeta m_i N_i^\alpha \mu_i^\alpha$$

(32)

$$= \sum_{\alpha=1}^\zeta \sum_{i=1}^q (\mu_i^\alpha + m_i g h_\alpha) N_i^\alpha$$

(33)

$$= \sum_{\alpha=1}^\zeta \sum_{i=1}^q \tilde{\mu}_i^\alpha N_i^\alpha.$$  

(34)

In the resource-theory framework, gravitational energy can be modeled with grand-potential theories. Each possible state of $B$ has the form

$$B_E := (\rho, H, N_0^1, \ldots, N_0^\zeta, \ldots, N_q^1, \ldots, N_q^\zeta),$$

(35)

wherein $\rho$ specifies the values of the $N_i^\alpha$. By analogy with Eq. (34),

$$H \propto \sum_{\alpha=1}^\zeta \sum_{i=1}^q \tilde{\mu}_i^\alpha N_i^\alpha.$$  

(36)

An analogous formalism describes the electrochemical energy of charged particles in an electric field [29, 42, 43]. Grand-potential theories, featuring states specified by $\{N_i^\alpha\}$ as well as by $H$, model fully the weight used often as a battery [25, 44]. Using the theory suited to the battery’s free energy, rather than a Helmholtz theory, becomes important if the battery has nongravitational DOFs. Such DOFs would be represented by extra extensive-variable operators in Eq. (35). Free unitaries must separately conserve the operator associated with each DOF. This separate conservation appears in the general definition of equilibrating operations but not in the definition of Helmholtz theories’ free operations.

IX. ONE-SHOT WORK YIELD AND WORK COST

Recall that the most work extractable, on average, during a process in which $(T), p_1, \ldots, p_j, X_{j+1}, \ldots, X_k$ remain constant is $W = \Delta E[(T), p_1, \ldots, p_j]$. When work is extracted from few copies of a state $R$, knowing the optimal average work might prove less useful than knowing the amount $W_\varepsilon^{\text{gain}}(R)$ of work outputted by a realistically faulty implementation of an optimal protocol. $W_\varepsilon^{\text{gain}}(R)$ can be calculated, and the work $W_\varepsilon^{\text{cost}}(R)$ required to create one copy of an approximation to $R$ can be bounded, with the hypothesis-testing entropy $D_\varepsilon^H$. Below, $D_\varepsilon^H$ and the failure tolerance $\varepsilon$ are defined as in [15]. $W_\varepsilon^{\text{gain}}(R)$ and $W_\varepsilon^{\text{cost}}(R)$ are quantified by immediate generalizations from [15]. Most of this section concerns free energies and so not the entropy theory. States are assumed to be quasiclassical.

A. Background

Consider a protocol for creating one copy of a target state $R := (r, (H), X_1, \ldots, X_j)$. A realistic trial generates an actual output $\hat{R} := (\tilde{r}, (H), X_1, \ldots, X_j)$ that might differ from
For simplicity, $R$ and $\tilde{R}$ are assumed to differ only due to their state vectors. The $L^1$ distance $\frac{1}{2}||r - \tilde{r}||_1$ quantifies the discrepancy. If the $L^1$ distance falls below the tolerance $\varepsilon \in [0, 1]$, the trial succeeds,

$$\frac{1}{2}||r - \tilde{r}||_1, \leq \varepsilon.$$  

(37)

and $\tilde{R}$ is said to be $\varepsilon$-close to $R$: $R \approx_\varepsilon R$. The existence of a free operation that maps $R$ to a state $\tilde{S} \approx_\varepsilon S$ is denoted by $R \succ_\varepsilon (\beta),p_1,\ldots,p_j S$. The work $W^\varepsilon_{\text{gain}}(R)$ that is $\varepsilon$-extractable from $R$ is the greatest $W$ that satisfies $R + B^+_E \succ_\varepsilon (\beta),p_1,\ldots,p_j B_{E+W}$ for any $E > 0$. The $\varepsilon$-work cost $W^\varepsilon_{\text{cost}}(R)$ is the least $W$ that satisfies $B_{E+W} \succ_\varepsilon (\beta),p_1,\ldots,p_j R + B_E$.

*Hypothesis testing* has been formulated in quantum-information contexts as follows [45]. Imagine being handed a quantum state and being told that the state is $\rho$ or $\gamma$. Knowing the forms of $\rho$ and $\gamma$, we wish to ascertain which state we were handed. We perform a positive operator-valued measurement (POVM) $\{Q, 1 - Q\}$. If the measurement yields outcome $Q$, the state is probably $\rho$; if $1 - Q$, then $\gamma$.

Errors of two types can occur. We commit a Type I error if we are given $\rho$ but $1 - Q$ obtains so we guess the state is $\gamma$. The Type I error probability equals $\text{Tr}((1 - Q)\rho)$. A Type II error occurs if we are given $\gamma$ but $Q$ obtains, so we guess the state is $\rho$. The Type II error probability $\text{Tr}(Q\gamma)$ can be constrained by $\varepsilon$ and $Q$. Consider choosing $Q$ such that the Type I error probability is at most $\varepsilon$: $\text{Tr}((1 - Q)\rho) \leq \varepsilon$. The *optimal* $Q$ minimizes the probability that a Type II error occurs. The hypothesis-testing entropy $D^\varepsilon_H$ is defined in terms of the optimal Type II error probability $b_\varepsilon(\rho||\gamma)$.

**Definition 6.** Let $\rho$ and $\gamma$ denote density operators defined on $\mathcal{H}$. Consider distinguishing between $\rho$ and $\gamma$ by hypothesis test. The optimal Type II error probability associated with any hypothesis test that has a Type I error probability of at most $\varepsilon$ is

$$b_\varepsilon(\rho||\gamma) := \min_{\text{Tr}(Q\rho) \geq 1 - \varepsilon, 0 \leq Q \leq 1} \text{Tr}(Q\gamma).$$  

(38)

The hypothesis-testing relative entropy is defined as

$$D^\varepsilon_H(\rho||\gamma) := -\ln b_\varepsilon(\rho||\gamma)$$  

(39)

or, equivalently, by $b_\varepsilon(\rho||\gamma) = e^{-D^\varepsilon_H(\rho||\gamma)}$.

For further details, see [15, 45].

**B. Quantification of one-shot work quantities**

$W^\varepsilon_{\text{gain}}$ can be calculated, and $W^\varepsilon_{\text{cost}}$ can be bounded, in terms of $D^\varepsilon_H$.

**Theorem 5.** Let $R := (r, H, X_1, \ldots, X_j)$ denote any quasiclassical state in any thermodynamic resource theory $\mathcal{T}^{(\beta),p_1,\ldots,p_j}$, and let $G_R := (g_R, H, X_1, \ldots, X_j)$ denote the corresponding equilibrium state. The most work $W^\varepsilon_{\text{gain}}(R)$ extractable from any $\tilde{R} \approx_\varepsilon R$ is

$$W^\varepsilon_{\text{gain}}(R) = \frac{1}{\beta} D^\varepsilon_H(r||g_R)$$  

(40)
for all \( \varepsilon \in [0, 1] \). The least work needed to form any \( \tilde{R} \approx \varepsilon R \) satisfies

\[
\max_{\delta \in [0, 1-\varepsilon]} \left[ \frac{1}{\beta} D_{H}^{1-\varepsilon-\delta}(r||g_{R}) - \frac{1}{\beta} \log \left( \frac{1}{\delta} \right) \right] \leq W_{\text{cost}}^{\varepsilon}(R) \leq \frac{1}{\beta} D_{H}^{1-\varepsilon}(r||g_{R}) - \frac{1}{\beta} \log \left( \frac{1-\varepsilon}{\varepsilon} \right)
\]

for all \( \varepsilon \in [0, 1] \).

Proof. The proof immediately generalizes the proof of [15, Theorem 5]. The latter theorem is the manifestation, in grand-potential theories, of Theorem 5 above. The grand-potential proof relies on equimajorization and on hypothesis tests between \( r \) and \( g_{R} \), which are well-defined in \( \mathcal{T}^{\beta,p_{1},...,p_{j}} \). Extensive-variable operators (\( X_{0} = H \) and \( X_{1} = N \)) do not appear in the grand-potential proof directly. The \( X_{i} \)'s affect the proof insofar as \( g_{R} \) depends on them. Hence the proof of [15, Theorem 5] can be restated in \( \mathcal{T}^{\beta,p_{1},...,p_{j}} \) under the assumption that \( g_{R} \) has the form in Eq. (21).

X. RECOVERY OF THE THERMODYNAMIC LIMIT; GENERALIZATION OF SZILÁRD'S ENGINE AND LANDAUER ERASURE

Consider distilling work from, or creating, many copies of a quasiclassical state \( R \) in any thermodynamic resource theory \( \mathcal{T}^{\beta,p_{1},...,p_{j}} \) other than the entropy theory:

\[
R^{\otimes n} := \left( r_{\otimes n}, \sum_{\alpha=1}^{n} H_{\alpha}, \sum_{\alpha=1}^{n} X_{1_{\alpha}}, \ldots, \sum_{\alpha=1}^{n} X_{j_{\alpha}} \right).
\]

As \( n \to \infty \), the thermodynamic limit (or asymptotic limit) is approached. As we shall see, \( W_{\text{gain}}^{\varepsilon}(R^{\otimes n}) \) and \( W_{\text{cost}}^{\varepsilon}(R^{\otimes n}) \) converge to thermodynamic free energies as \( n \to \infty \). The energy representation in most thermodynamic resource theories will be contrasted with the entropy representation in the entropy theory; the optimal asymptotic rate of interconversion between states will be derived; and asymptotic interconvertibility will be shown to generalize Szilárd work extraction and Landauer erasure. Finally, that \( W_{\text{gain}}^{\varepsilon}(R^{\otimes n}) \) can differ from \( W_{\text{cost}}^{\varepsilon}(R^{\otimes n}) \) will be generalized from [15].

The thermodynamic limit follows from the Asymptotic Equipartition Theorem (AEP) [45]

\[
\lim_{n \to \infty} \frac{1}{n} D_{H}^{\varepsilon}(r^{\otimes n}||g_{R}^{\otimes n}) = D(r||g_{R}) \quad \forall \varepsilon \in (0, 1),
\]

wherein the relative entropy is \( D(r||g_{R}) := \sum_{\alpha} \log r_{\alpha} - \log g_{\alpha} \). AEPs have been used to derive the thermodynamic limits of Helmholtz theories [9], the entropy theory [1], and grand-potential theories [15]. Applying Eq. (42) to Eq. (41) and to Ineqs. (41) yields

\[
\lim_{n \to \infty} W_{\text{gain}}^{\varepsilon}(R^{\otimes n}) = \lim_{n \to \infty} W_{\text{cost}}^{\varepsilon}(R^{\otimes n}) = \frac{1}{\beta} D(r||g_{R}) \quad \forall \varepsilon \in (0, 1).
\]

Let us substitute in the definition of \( D \). We will define logarithms as base-\( e \), denote eigen-
value $\alpha$ of $X_i$ by $x_{i\alpha}$, and denote the partition function by $Z$:

$$
\frac{1}{\beta} D(r||g_R) = \frac{1}{\beta} \sum_{\alpha} r_\alpha \left[ \log(r_\alpha) - \log \left( \frac{e^{-\beta(E_\alpha - p_1 x_{1\alpha} - \ldots - p_j x_{j\alpha})}}{Z} \right) \right]
$$

$$
= \frac{1}{\beta} \sum_{\alpha} r_\alpha \log(r_\alpha) + \sum_{\alpha} r_\alpha (E_\alpha - p_1 x_{1\alpha} - \ldots - p_j x_{j\alpha}) + \frac{1}{\beta} \log Z \quad (44)
$$

$$
= \langle H \rangle_r - T k_B S(r) - p_1 \langle X_1 \rangle_r - \ldots - p_j \langle X_j \rangle_r + k_B T \log Z. \quad (45)
$$

The dimensional factor $k_B$ converts the Shannon entropy $S(r) := -\sum_i r_i \log(r_i)$ into thermodynamic entropy [31], and $\langle \ldots \rangle_r$ denotes an expectation value relative to the distribution $r$. The operators’ expectation values may be interpreted as thermodynamic extensive variables.

Equation (46) has the same form as Eq. (8). In the thermodynamic limit, the average work extractable from one copy of $R$, and the average work needed to create one copy, with a faulty protocol approach the free energy that lends its name to $T^{p_1,\ldots,p_j}$. In Helmholtz theories, Eq. (46) evaluates to $F := E - TS$; in grand-potential theories, to $\Phi := E - TS - \mu N$.

Resource-theory results converge to known thermodynamic results while shedding new light on single instances of states.

That Eq. (46) contains an energy contrasts with the analogous result in the entropy theory. The resource in the entropy theory has been called information [12, 26] and nonuniformity [13]. The average resourcefulness extractable from, and the average resourcefulness needed to create, one copy of $R$ has been shown to equal

$$
D(r||g_R) = \log d - S(r) \quad (47)
$$

in the asymptotic limit [12, 26]. $d$ denotes the number of elements in $r$, and $g_R = (\frac{1}{d}, \ldots, \frac{1}{d})$ denotes a microcanonical ensemble. Equation (46) has dimensions of energy, whereas Eq. (47) is dimensionless like entropy. The entropy-theory Eq. (47) is in the entropy representation, whereas the Eq. (46) that characterizes other thermodynamic resource theories is in the energy representation.

Equation (46) implies the optimal asymptotic rate of conversion. Let $m_n$ denote the greatest number of copies of $S$ that equilibrating operations can generate from $n$ copies of $R$. The optimal rate of conversion from $n$ copies is

$$
\mathcal{R}_n(R \xrightarrow{\text{equil.}} S) = \frac{m_n}{n}. \quad (48)
$$

In the asymptotic limit, $\mathcal{R}_n$ approaches the optimal asymptotic conversion rate:

$$
\lim_{n \to \infty} \mathcal{R}_n(R \xrightarrow{\text{equil.}} S) = \mathcal{R}_\infty(R \xrightarrow{\text{equil.}} S). \quad (49)
$$

In $T^{p_1,\ldots,p_j}$,

$$
\mathcal{R}_\infty(R \xrightarrow{\text{equil.}} S) = \frac{D(r||g_R)}{D(s||g_S)}. \quad (48)
$$

During the optimal conversion protocol, $D(r||g_R)$ units of work are extracted per copy of $R$, and one copy of $S$ is generated per $D(s||g_S)$ units of work. Equation (48) has been
derived for Helmholtz theories [9, 10], grand-potential theories [15], and the nonuniformity theory [12, 13, 26].

Equation (48) implies that, in the asymptotic limit, all states are reversibly interconvertible. From enough copies of any \( R \), equilibrating operations can generate copies of any \( S \). The optimal \( R \)-to-\( S \) rate equals the inverse of the \( S \)-to-\( R \) rate. This interconvertibility may surprise us. The resourcefulness of \( R \) might manifest in one form—as information, chemical energy, a magnetic moment, etc.—while the resourcefulness of \( S \) manifests in another. That thermodynamic resourcefulness of each sort can transform into thermodynamic resourcefulness of every other is not a priori obvious. After all, though LOCC can asymptotically interconvert all pure bipartite entangled states, LOCC cannot interconvert all pure tripartite entangled states [46–48]. Equation (48) implies that thermodynamic resourcefulness resembles bipartite, rather than tripartite, entanglement.

This transformability generalizes Szilárd’s engine and Landauer erasure. Szilárd’s engine converts information into work [44]. The classical engine consists of a particle known to occupy a box’s left-hand side. Consider sliding a partition through the box’s center, attaching a weight to the partition, and coupling the particle to a temperature-\( T \) heat bath. The particle, modeled by an expanding ideal gas, pushes the partition to the box’s right-hand side. The weight rises, its gravitational potential energy compensating for the loss of information about the particle’s location. Landauer erasure, resulting from reversing Szilárd’s engine, converts work into information [49]. In general thermodynamic resource theories, resourcefulness can be converted not only between informational and gravitational-potential-energy forms. Resourcefulness can be converted amongst all the physical DOFs represented by state operators. Value can be encoded in particle number, magnetic moments, etc.

Though the large-\( n \) limit of \( W_{\text{gain}}^{\varepsilon}(R^\otimes n) \) equals that of \( W_{\text{cost}}^{\varepsilon}(R^\otimes n) \), the rates at which these quantities approach the limit differ. Information theory has been used to show that, in grand-potential theories,

\[
W_{\text{gain}}^{\varepsilon}(R^\otimes n) \approx \frac{1}{\beta} \left[ n \, D(r||g_R) - O(\sqrt{n}) \right]
\]

and

\[
W_{\text{cost}}^{\varepsilon}(R^\otimes n) \approx \frac{1}{\beta} \left[ n \, D(r||g_R) + O(\sqrt{n}) \right]
\]

as \( n \) grows large [15]. The proof does not depend on the extensive-variable state operators \( X_{i=0,1,...,j} \) explicitly. The proof depends on the \( X_i \)’s only implicitly, insofar as \( g_R \) depends on the \( X_i \). As in the proof of Theorem 3, the grand-potential proof can be restated in \( \mathcal{T}^{\beta,p_1,...,p_j} \), under the assumption that \( g_R \) has the form in Eq. (21).

XI. OPEN QUESTIONS

Having generalized thermodynamic resource theories, we present opportunities for further investigation. First, the generalization introduces nonclassicality via extensive-variable operators that can fail to commute and via the modeling of spins. Second, the number operator \( N \) enables one copy of a state \( R \) to manifest in a macroscopic number of particles, inviting a reconsideration of what “one-shot” means. The reconsideration might facilitate experimental tests of one-shot theory, as might the equivalence between families of thermodynamic resource theories. Third, whether thermodynamic resource theories model “heat
potentials” as they model work potentials remains unknown. Also, the asymmetry between free-energy theories, which reflect the energy representation of thermodynamics, and the entropy theory, which reflects the entropy representation, might be eliminated.

The foregoing challenges may offer novel insights into thermodynamic resource theories. A more-straightforward task is to ensure that all Helmholtz-theory results generalize to arbitrary $T^{\beta,p_1,...,p_j}$. Theorems 2, 3, and 4 generalize theorems about Helmholtz and grand-potential theories. That other Helmholtz-theory results, including ones about catalysis [11] and about $[\rho, H] \neq 0$ [10, 34, 35], generalize may be checked.

A. Nonclassicality

The generalization of thermodynamic resource theories introduces quantum operators that model extensive variables that may fail to commute. Also, the generalization expands thermodynamic resource theories’ ability to model spins.

1. Noncommutation

Many Helmholtz-theory results concern states whose density operators $\rho$ commute with their Hamiltonians $H$ [8, 9, 15]. Noncommutation of $\rho$ and $H$ has been explored recently in [10, 34, 35]. $\rho$ and $H$ are the only operators that can fail to commute, because they alone define states in Helmholtz theories. In $T^{\beta,p_1,...,p_j}$, more operators can fail to commute: $\rho, H,$ and $X_i$ for all $i = 1, \ldots, j$. Jaynes considers noncommutation of such extensive-variable operators, including failure by operators $X_i \neq 0$ to commute with $H$ [28]. Noncommutation impacts free states, free operations, and interpretations of thermodynamic resource theories.

Let $R := (\rho, H, X_1, \ldots, X_j)$ denote a state whose $[H, X_1] \neq 0$. Consider attempting to associate $R$ with a free state $G_R$. The density operator $\gamma_R$ of $G_R$ could not be derived as in Appendix E $\gamma_R$ is shown, under the assumption that the $X_i$ commute, to depend on $X_i$ as $e^{-F_i X_i}$:

\[ \gamma_R \propto \prod_{i=0}^{j} e^{-\frac{1}{k_B} F_i X_i} = e^{-\frac{1}{k_B} \sum_{i=0}^{j} F_i X_i} \]

[Eq. 21]. If the $X_i$ fail to commute, the Baker-Campbell-Hausdorff Formula prevents any possible $\gamma_R$ from having the canonical form of Eq. (51).

Unlike in Helmholtz theories, noncommutation can restrict the unitaries that can evolve $R$ for free. In a Helmholtz theory $T^\beta$, nontrivial functions $U = f(H)$ of $H$ can evolve states $R := (\rho, H)$. Free time evolution, for example, manifests as $U(t) = e^{-\frac{i}{\hbar} H t}$ if $H$ remains constant. In a non-Helmholtz theory $T^{\beta,p_1,...,p_j}$, noncommutation of $X_i$’s can prevent states from being able to evolve for free under all nontrivial $U = f(H)$. In extreme situations, free unitaries may be restricted to $U(\phi) = e^{i\phi} \mathbb{1}$ for $\phi \in \mathbb{R}$.

For example, let $R := (\rho, H, X_1, X_2)$ denote a state whose $[X_1, X_2] \neq 0$ in $T^{\beta,p_1,p_2}$. A simple Hamiltonian might have the form $H = p_1 X_1 + p_2 X_2$ \footnote{This form of $H$ is inspired by Fundamental Relations such as the $E = B \cdot m$ of a system whose magnetization is $m$ and that occupies an external magnetic field $B$.} As $H$ does not commute
with $X_1$ or $X_2$, neither does $U(t) = e^{-i\frac{H}{\hbar}t}$. Time evolution does not manifest as a free unitary. To understand the physical significance of this surprising mathematical conclusion, one might apply insights from quantum mechanical SO coupling, in which the orbital angular momentum $L$ and the spin angular momentum $S$ are not conserved separately.

2. Spin magnetic systems

Generalizing thermodynamic resource theories expands our ability to model spins. Spins appear in many quantum-information and condensed-matter applications. Many applications have been probed experimentally, as in nuclear magnetic resonance. These experiments might guide the exploration of quantumness in, and possible tests of, thermodynamic resource theories.

Spins have magnetic moments that be modeled as follows in thermodynamic resource theories. Let $\mathcal{S}$ denote a magnetic system that has a total magnetic dipole moment $\mathbf{m}$ and that occupies an external magnetic field $\mathbf{B}$. The field serves as an intensive variable; and $\mathbf{m}$, as an extensive variable [27]. If $\mathcal{S}$ contains just one species and one phase, its Fundamental Relation has the energy representation

$$E = TS - pV + \mu N + \mathbf{B} \cdot \mathbf{m}$$

[27, 42, 43]. If $E$, $V$, $N$, and $\mathbf{m}$ remain constant, $\mathcal{S}$ invites modeling by the entropy theory. If $T$ and $\mathbf{B}$ remain constant, $\mathcal{S}$ invites modeling by resource theories for the Gibbs magnetic potential

$$E[T, \mathbf{B}] := E - TS - \mathbf{B} \cdot \mathbf{m}.$$  

Generalizing thermodynamic resource theories beyond Helmholtz theories is necessary, for two reasons, to model magnetic systems. First, $(E, V, N, \mathbf{m})$ are the natural variables of entropy. Casting constant-$(E, V, N, \mathbf{m})$ problems in terms of the Helmholtz free energy would complicate calculations. Second, suppose a magnetic system has a DOF other than $\mathbf{m}$. Free unitaries must conserve the DOFs separately. This conservation appears in the definition of general equilibrating operations but not in the definition of Helmholtz theories’ free operations.

B. Meaning of “one-shot”; experimental tests

The entropy, Helmholtz, and grand-potential theories have been portrayed as alternatives to traditional thermodynamics, which describes on the order of $10^{24}$ particles [9, 11, 15, 35]. In these theories (more generally, in one-shot statistical mechanics), one-shot information theory is applied to single copies of a state. The work extractable from, and the work cost of creating, $n$ copies of a state converge to thermodynamic potentials as $n \to \infty$.

The significance of $n$ merits reevaluation in the light of $N$. $N$ has been shown to belong in thermodynamic resource theories because $N$ resembles $E$ in conventional thermodynamics. The $\mathbf{B} \cdot \mathbf{m}$ in Eq. (53) has been derived under the assumption that $\mathcal{S}$ has a homogeneous magnetic moment [27]. A homogeneous magnetic moment characterizes the bulk of a spatially large system. If few spins are modeled with a thermodynamic resource theory in the spirit of one-shot statistical mechanics, any use of Eq. (53) must be justified without any large-system assumption. Any description of a small polarizable system whose $E \propto \mathbf{p} \cdot \mathbf{E}$ would require similar justification [39].
and $E$ manifests in resource theories (as $H$) $N$ can have arbitrarily large eigenvalues. In Helmholtz theories, $N$ remains “behind the scenes” due to the fixed-eigensubspace condition. Still, supp($\rho$) can be in an eigensubspace of $N$ associated with a large particle number. One copy of a state $R := (\rho, H)$ can correspond to $10^{24}$ particles, to a conventional thermodynamic system. Yet one copy of $R$ has been called “one-shot” and has been contrasted with conventional thermodynamics.

Magnets illustrate this seeming contradiction. Consider a magnet that consists of about $10^{24}$ spins, whose total magnetic moment is $m$, and that occupies the state $R$. If $T$ and the external magnetic field $B$ remain constant, a resource theory for $E[T, B]$ models the distillation of work from $R$. By Eq. (40), the work extractable from one system of approximately $10^{24}$ spins is the one-shot quantity $W_{\text{gain}}(R)$.

The paradox might facilitate experimental tests of one-shot statistical mechanics. Whether supp($\rho$) is in the $N = 1$ eigensubspace or the $N = 10^{24}$ eigensubspace does not affect resource-theory calculations. $N = 1$ states interest one-shot theorists, whereas mathematically equivalent $N = 10^{24}$ states can be controlled more easily in laboratories. To test one-shot results such as Eqs. (40) and (41), one might use systems of $10^{24}$ particles. Ascertaining the form of a $\rho$ that characterizes a large system poses a practical challenge.

Like $N$, the mathematical equivalence of families of thermodynamic resource theories might facilitate experimental tests. Having been theoretically developed extensively, Helmholtz theories merit testing. Helmholtz theories are equivalent, up to a Legendre transform, to Gibbs-free-energy theories. Chemists apply the Gibbs free energy $G := E[T, p] := E - TS + pV$ often, as to room-temperature, atmospheric-pressure chemical reactions. Whether common experiments could test one-shot statistical mechanics remains to be explored. Polymers offer another possible platform. The mechanical force $f$ applied to a length-$L$ polymer appears in the Helmholtz free energy

$$F = -pV + \mu N + fL$$

This $F$ corresponds to a family of thermodynamic resource theories, and polymers have been strained to test fluctuation relations experimentally [6, 51, 52]. Generalizing thermodynamic resource theories expands the theories’ potential for modeling real physical systems. Such systems might serve as platforms for experimental tests of one-shot statistical mechanics.

C. Further generalization

Much as this paper has generalized thermodynamic resource theories, two further generalizations appear possible. First, each thermodynamic potential might be associated with both a family of energy-representation theories and a family of entropy-representation theories. Second, “heat potentials” such as the enthalpy might correspond to families of theories.

Recall from Sec. II that conventional thermodynamics can be formulated equivalently in energy and entropy representations. In most of the thermodynamic resource theories in this paper, resourcefulness manifests as work, and work yields and work costs converge to free energies in the thermodynamic limit. These theories reflect the energy representation.

---

6 Particle number resembles energy because both are represented by extensive variables. As Jaynes says, “the energy plays a preferred role among all dynamical quantities because it is conserved . . . however, . . . all measurable quantities may be treated on the same basis, subject to certain precautions” [50].
In the entropy theory, a \(d\)-dimensional state \(r\) represents a closed isolated system. The resourcefulness extractable from, and the resourcefulness cost of creating, \(r\) converge to the entropic quantity \(\log d - S(r)\) \[26\]. The entropy theory reflects the entropy representation.

That an energy-representation resource theory models closed isolated systems seems a reasonable expectation. That entropy-representation theories are equivalent to Helmholtz and grand-potential theories seems a reasonable expectation. Realizing or discounting those expectations may shed new light on general thermodynamic resource theories.

We have focused on thermodynamic potentials whose natural variables include \(T\) (and on the entropy \(S\)). \(T\) is not a natural variable of “heat potentials” such as the enthalpy \[27\]. The change in a system’s enthalpy \(E[p] := E + pV =: H\) equals the most heat extractable during a constant-\(p,V,N\) process. That resource theories correspond to heat potentials, just as resource theories correspond to work potentials, seems a reasonable guess. Which state vectors \(g\) would characterize free states remains unclear. Many thermodynamic texts remain silent about equilibrium ensembles associated with natural variables that exclude \(T\) (apart from the microcanonical ensemble). Other derivations of equilibrium ensembles do not apply to natural variables that exclude \(T\) \[31\], though Jaynes’s derivation suggests that \(g\) is an exponential \[50\]. The resource-theory framework may offer insights about the relationship between work potentials and heat potentials.

XII. CONCLUSIONS

This paper has motivated and detailed the generalization of thermodynamic resource theories beyond heat baths. Traditional thermodynamics led to a correspondence between one family of thermodynamic resource theories and each type of interaction (equivalently, each set of natural variables, thermodynamic potential, and type of bath or external field). Intensive natural variables were shown to specify thermodynamic resource theories; and extensive variables, to specify systems and states. From free equilibrating operations, the canonical-type form of free density operators was derived. Free operations were shown to induce a quasiorder equivalent to \(d\)-majorization relative to equilibrium states.

Batteries were shown to store resourcefulness in diverse physical forms, such as gravitational and electrochemical energy. One-shot work-quantities were calculated and bounded, and converged to thermodynamic potentials in the asymptotic limit. Resourcefulness was shown to be convertible not only between informational and gravitational-energy forms, but also among other DOFs in the thermodynamic limit. This interconvertibility generalized Szilárd’s engine and Landauer erasure.

Opportunities for exploration include noncommutation of quantum operators that model extensive variables, as well as applications to real physical systems. Whether the entropy theory can be cast in the energy representation, and Helmholtz theories in the entropy representation, remain open questions. Also of interest is whether resource theories correspond to heat potentials such as the enthalpy. Generalizing thermodynamic resource theories opens diverse realistic systems—possibly such as polymers, electrochemical batteries, and magnets—to modeling. This opening should facilitate experimental tests of one-shot statistical mechanics.
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XIV. APPENDICES

Appendix A VOLUME AS AN OPERATOR

In Sec. IV extensive thermodynamic variables are associated with operators. The volume $V$ is such a variable. Jaynes represents volume with an operator in [28]. But what is a volume operator? It might be understood similarly to the position operator $x$. The position operator is often explained in terms of a photon that scatters off a particle (whose position is to be measured) and into a detector. From this story, we extrapolate to the idea of a general position operator $x$. A similar story may be told about $V$.

Consider a gas in a box that consists of five rigid walls and one moveable partition. The partition’s position governs the gas’s volume. As the partition is a quantum object, its position fluctuates and merits modeling with an operator $x$. So, by extension, does the box’s volume.

Like $x$ and unlike $N$, $V$ has a continuous spectrum. A rigorous incorporation of this continuity into Sections IV-X is expected to follow from a discretization of space and a limit in which the discretization vanishes [53]. Space may simply be discretized for the purposes of this paper, as in [25].

Recall that the $X_i$ are Hermitian operators defined on a Hilbert space $H$. If the spectrum of $V$ approximates or achieves continuity, so do the degeneracies of the other $X_i$’s. Associating the number operator $N$ with a continuous variable may contradict intuition. But the possible numbers $n_i$ of particles can form a discrete set while each $n_i$ has a continuous set of degeneracies. In other words, the system $S$ can consist of one particle, or two particles, or three, and so on. One particle can occupy a volume of 1 $m^3$, or 1.001 $m^3$, or 1.002 $m^3$, and so on. So can two particles, and so can three. A similar combination of discrete and continuous spectra is modeled with rigged Hilbert spaces in [54].

Sufficiently large numbers $n_i$ of particles cannot fit in sufficiently small volumes (if $S$ is not a relativistic system such as a black hole). For example, the macroscopic $n_i = 10^{24}$ seems incompatible with the sub-Planck-scale $v_j = 10^{-105} m^3$. How can $N$ and $V$ share an eigenstate $|n_i, v_j\rangle = |10^{24}, 10^{-105} m^3\rangle$? This eigenstate must correspond to an energy so enormous that $S$ effectively cannot occupy $|n_i, v_j\rangle$. Systems are assumed not to occupy states associated with energies above some cutoff.
Appendix B  DERIVATION OF THE FORM OF FREE STATES

Let us prove Theorem 2 in Sec. VI.

**Theorem.** Consider a thermodynamic resource theory \( \mathcal{T}(\beta,p_1,\ldots,p_j) \) in which all states are quasiclassical. Every free state has the form

\[
G := (g, (X_0), X_1, \ldots, X_j),
\]

wherein element \( \alpha \) of \( g \) has the form

\[
g_\alpha = e^{-\frac{1}{k_B}[(F_0 x_{0\alpha}) + F_1 x_{1\alpha} + \ldots + F_j x_{j\alpha}]} / Z,
\]

\( x_{i\alpha} \) denotes eigenvalue \( \alpha \) of operator \( X_i \), and the partition function \( Z \) normalizes \( g \). If any other state were free, \( \mathcal{T}(\beta,p_1,\ldots,p_j) \) would be trivial.

**Proof.** Theorem 2 trivially generalizes [15, Theorem 1]. In [15], the grand-canonical form of the \( g \)'s in grand-potential theories was derived in three steps. Let us sketch these steps first.

First, the derivation of the microcanonical form \( \frac{1}{d}, \ldots, \frac{1}{d} \) of the entropy theory’s free states is reviewed. Horodecki et al. derive the form in [12] via a proof by contradiction. Suppose that some nonuniform state \( u_0 \) were free. An agent could generate a large number \( n \) of copies of \( u_0 \). Using free unitaries, the agent could Shannon compress the mixedness in \( (u_0)^\otimes n \), separating the mixedness from a state arbitrarily close to being pure. Able to create purity and mixedness, the agent could create states other than \( u_0 \) for free.

Second, the free states in Helmholtz theories are shown to be canonical ensembles: \( g_i = e^{-\beta E_i} / Z \). The weight of \( g \) on each energy subspace \( S_E \) is shown to be distributed uniformly across the energy levels that span \( S_E \) because of Step 1. Then, the ratio \( g(E + \Delta) / g(E) \) of two weights is shown to depend only on the gap \( \Delta \) between the levels. The ratio is shown to vary as \( e^{-\beta \Delta} \), and all gaps in all free states are shown to correspond to the same \( \beta \).

Finally, the free states \( G := (g, H, N) \) in grand-potential theories are shown to be grand canonical ensembles. If \( N \) is totally degenerate, \( G \) represents a bath whose particle number remains constant, like the free states in a Helmholtz theory. Hence \( g_i \) varies with \( E_i \) as \( e^{-\beta E_i} \). By an analogous argument, \( g_i \) varies with \( n_i \) as \( e^{\beta \mu n_i} \). Hence \( g_i = e^{-\beta(E_i - \mu n_i)} / Z \). The canonical-ensemble derivation generalizes immediately to \( \mathcal{T}(\beta,p_1,\ldots,p_j) \). The argument applied to \( N \) applies to each \( X_i \), so Eq. (57) follows from

\[
g_\alpha = e^{-\beta(E_\alpha - p_1 x_{1\alpha} - \ldots - p_j x_{j\alpha})} / Z \quad \text{(58)}
\]

\[
g_\alpha = e^{-\frac{1}{k_B}[(\frac{1}{T} x_{0\alpha}) + \frac{p_1}{T} x_{1\alpha} + \ldots + \frac{p_j}{T} x_{j\alpha}]} / Z \quad \text{(59)}
\]

\[
g_\alpha = e^{-\frac{1}{k_B}(F_0 x_{0\alpha} + \ldots + F_j x_{j\alpha})} / Z. \quad \text{(60)}
\]

\[\text{An alternative resource-theory derivation of the canonical ensemble appears in [11].}\]

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