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Dual structure of thermodynamics

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Based on the properties of exponential distribution families we analyze the Fisher information of the Gibbs canonical ensemble to construct a new state function for simple systems with no mechanical work. This function possesses nice symmetry properties with respect to Legendre transform and provides a connection with previous alternative formulations of thermodynamics, most notably the work by Biot, Serrin, and Frieden and collaborators. Logical extensions to systems with mechanical work may similarly consider generalized Gibbs ensembles.

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I. INTRODUCTION

The theory of classical thermodynamics elegantly links energy and matter states in macroscopic systems in thermodynamic equilibrium [1,2]. It also allows us to rigorously describe the overall effect of transformations between different states of equilibrium, although it does not provide information about their actual dynamics. While historically thermodynamics developed from the intuitive notions of heat and temperature, subsequently the existence of more abstract, fundamental quantities such as internal energy, entropy, and their corresponding Legendre transforms became apparent; these are now considered primitive concepts in axiomatic and postulational theories of thermodynamics. Considerable effort has also been devoted to rigorously reformulating thermodynamics starting from temperature and heat as primitive quantities. We refer, in particular, to the work by Serrin and Silhavy [3–6], who derived the internal energy and entropy starting from an analytical formulation of the integral for cyclic processes based on temperature and a newly defined heat accumulation function. Related theories were also proposed in [7,8].

The inability of classical thermodynamics to describe nonequilibrium dynamics also spurred the search for more general theories. In particular, Onsager's theory [1], based on local equilibrium and a variational principle for a dissipation function (proportional to entropy production), helped explain the coupling among processes for small deviations from thermodynamic equilibrium. However, as has been repeatedly pointed out [1,9–12], a variational formulation based on entropy production extremization does not lead to the observed linear phenomenological laws commonly used in applications (e.g., Fourier's law of heat conduction has a constant conductivity, while entropy production maximization leads to a heat conductance which is inversely proportional to the square of the temperature). Several attempts were thus pursued to find alternative variational formulations. The work of Biot [13,14], in particular, showed that a variational formulation based on a quadratic function of temperature, obtained from a suitable linearization of thermodynamic availability for constant heat capacity, provides the familiar Fourier's heat conduction law. The theoretical bases of Biot's function were not completely clarified, however, and the extension to compressible media has remained elusive. More recently, Guo and coworkers [12,15] resumed Biot's function and used a similar quantity, called entransy and justified on the bases of a formal analogy between heat and electrical currents, to optimize engineering design in heat transfer (see also [16]).

Independently, a series of remarkable contributions by Frieden and collaborators [17–21] showed that variational formulations based on Fisher information may serve as a powerful means to obtain several physical laws, at the same time providing a reason for the ubiquitous presence of squares of gradients in such laws. Within this context, the additivity property of the Fisher information and its ability to measure "disorder" [20] are particularly appealing features from a thermodynamic point of view. More importantly, Frieden *et al.* [20,21] showed that Fisher information is endowed with a Legendre-transform structure which mirrors that of classical thermodynamics. This contribution was largely formal and the link with the usual thermodynamic variables remained somewhat unexplored. In an interesting step in this direction [22], much like Biot's function, Fisher information too was found to be a quadratic function of temperature for the case of constant heat capacity, with a proportionality coefficient containing a reference temperature which was left unspecified.

The three main lines of research described above developed independently and have remained disconnected. In what follows we discuss how they are related and show how a dual structure of thermodynamics emerges from the the formalism of exponential families (to which Gibbs equilibrium distributions belong) and their link to Legendre and cumulant transforms [23–25]. With specific reference to a simple system with constant volume and mass, we show how the correspondence between thermodynamic potentials, in either the entropy or the energy representation [1], is mirrored by an equivalent, dual representation based on Fisher information, with an interesting symmetry of the Legendre transformation. As pointed out by Biot [14] and Frieden and coworkers [20], this dual structure may be useful in variational formulations of nonequilibrium field theories of thermodynamics and continuum media.

II. CANONICAL ENSEMBLE AND ITS FISHER INFORMATION

Consider a simple system with fixed volume V and particle number N in thermal equilibrium with a reservoir at temperature $T = 1/\beta$ (to simplify notation, the temperature is in natural units so that the Boltzmann constant is equal

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to 1). For our purposes here, it is convenient to write the Gibbs canonical distribution for a single random variable representing the internal energy, $\hat{U}$, as

$$p_{\hat{U}}(\hat{U};\beta)=\frac{g(\hat{U})}{Z(\beta)}e^{-\beta\hat{U}}=e^{-\Phi(\beta)-\beta\hat{U}-h_{\hat{U}}(\hat{U})}, \tag{1}$$

where $Z(\beta)$ is the partition function, and $h_{\hat{U}}(\hat{U})=-\ln g(\hat{U})$, with $g(\hat{U})$ the density of states, a function linking the microstates to the internal energy [26]; the Massieu function is $\Phi(\beta)=\ln Z(\beta)=-F/T$, with F the Helmholtz free energy. The probability density function, (1), belongs to the exponential family [23–25], for which several interesting properties are known (see the Appendix). In particular, $-\Phi$ is related to the the cumulant transform [24] of the distribution, (1), in that its derivatives with respect to the parameter β readily give the cumulants of $\hat{U}$ (see the Appendix). As a consequence,

$$-\frac{d\Phi}{d\beta}=\langle\hat{U}\rangle=U. \tag{2}$$

More importantly, their second derivatives are both the Fisher information of the distribution with respect to the parameter β (see the Appendix) and the variance of $\hat{U}$,

$$\mathcal{F}_U=\frac{d^2\Phi}{d\beta^2}=\langle(\hat{U}-U)^2\rangle, \tag{3}$$

which is

$$\mathcal{F}_U=-\frac{dU}{d\beta}=\frac{C(\beta)}{\beta^2}=C(T)T^2, \tag{4}$$

where $C(T)=Nc_v(T)$, with c_v the specific molar heat capacity. This result is in agreement with the well-established theory of fluctuations (see [28] and, in particular, Eq. (19.6) in [27]).

III. DUAL STRUCTURE OF THERMODYNAMICS

It is well known that the couple S and Φ and the couple U and F are linked by Legendre transform in the entropy, $S=S(U)$, and energy, $U=U(S)$, representations, respectively [1,29]. A similar correspondence involving Fisher information can be found starting from the first equality in (4),

$$\mathcal{F}_U(\beta)=-\frac{dU}{d\beta}, \tag{5}$$

which implies ([1], p. 142) that $U(\beta)$ is related by Legendre transform to another function $\mathcal{F}_S$, where

$$\mathcal{F}_S=\beta\mathcal{F}_U+U. \tag{6}$$

Although the previous equation is in units of energy, it is formally analogous to $S=\beta U+\Phi$ in the familiar entropy representation of thermodynamics. Thus, the relationship $\mathcal{F}_S=\mathcal{F}_S(\mathcal{F}_U)$ may be used as the fundamental equation, as an alternative to $S(U)$, for systems with no reversible (volume) work and mass exchanges.

It is also natural to consider a dual version of the energy representation, by dividing the previous equation, (6), by β and re-expressing it in terms of T,

$$\mathcal{F}_U=T\mathcal{F}_S+\mathcal{F}_F, \tag{7}$$

where $\mathcal{F}_F=-UT$. This equation corresponds to the familiar expression $U=TS+F$ in the energy representation and implies that $\mathcal{F}_U$ and $\mathcal{F}_F$ are Legendre transforms in the dual version of the "energy" representation, $\mathcal{F}_U=\mathcal{F}_U(\mathcal{F}_S)$. The correspondence is summarized in Table I.

TABLE I. Correspondence among thermodynamic variables in the dual representation.

Entropy	Fisher information
S	$\mathcal{F}_S$
U	$\mathcal{F}_U$
Φ	U
$F=-T\Phi$	$\mathcal{F}_F=-TU$
$S=S(U)$	$\mathcal{F}_S=\mathcal{F}_S(\mathcal{F}_U)$
$U=U(S)$	$\mathcal{F}_U=\mathcal{F}_U(\mathcal{F}_S)$
$S=\beta U+\Phi$	$\mathcal{F}_S=\beta\mathcal{F}_U+U$
$U=TS+F$	$\mathcal{F}_U=T\mathcal{F}_S+\mathcal{F}_F$
$\beta=\frac{dS}{dU}$	$\beta=\frac{d\mathcal{F}_S}{d\mathcal{F}_U}$
$T=\frac{dU}{dS}$	$T=\frac{d\mathcal{F}_U}{d\mathcal{F}_S}$
$-U=\frac{d\Phi}{d\beta}$	$-\mathcal{F}_U=\frac{dU}{d\beta}$
$-S=\frac{dF}{dT}$	$-\mathcal{F}_S=\frac{d\mathcal{F}_F}{dT}$

Note that (6), because of (4), can also be written as

$$\mathcal{F}_S=CT+U. \tag{8}$$

This underlies another Legendre transform,

$$T=\frac{\mathcal{F}_S}{C}+F_T, \tag{9}$$

with $F_T=-U/C$, and of course also means that

$$C=\frac{\mathcal{F}_S}{T}+\frac{\int_0^T C(T')dT'}{T}, \tag{10}$$

which corresponds to Eq. (4) in [30].

IV. PARAMETER FLUCTUATIONS

For the system at constant V and N, $\mathcal{F}_U$ may be related to the ability to measure the inverse temperature β of the reservoir by observing the state of the internal energy of the system. This ability increases with the size of the system, N, because the fluctuations get smaller with N. It also increases with T^2 proportionally to the heat capacity at that temperature, $c_v(T)$, because larger heat capacities buffer temperature fluctuations, which would otherwise impair the estimate [see Eq. (4)]. This idea of using the system as a temperature measurement device can be traced back to [31,32] and is rooted in the theory of statistical inference [24,25].

For the exponential family, the maximized log-likelihood function is also the Legendre transform of the cumulant transform (see the Appendix); in our case of Eq. (1), the maximized log-likelihood function is $-S(U)$, which is also the Legendre transform of the cumulant transform $-\Phi(\beta)$. It thus follows that

$$\frac{dS}{dU}=\beta \tag{11}$$

and

$$\frac{d^2S}{dU^2} = -\frac{\beta^2}{Nc_v} = -\frac{1}{Nc_vT^2}, \tag{12}$$

as well as

$$-\frac{d^2S}{dU^2} = -\frac{d\beta}{dU} = \langle(\hat{\beta}-\beta)^2\rangle = \mathcal{F}_U^{-1}. \tag{13}$$

On the one hand, this allows us to make immediate contact with the stability theory of equilibrium conditions (see, e.g., Eq. (8.7) in [1]) and with the Riemanninan representation of thermodynamics [33,34]. In this context, Eq. (12) has been used as a measure of the curvature of the thermodynamic space and has been linked to the availability (i.e., the free energy difference with respect to equilibrium) lost, as, when starting from small perturbations, an isolated system irreversibly goes back to equilibrium [35] (a version of the Gouy-Stodola theorem [2]).

On the other hand, returning to the statistical inference interpretation, the maximum likelihood estimate $\hat{\beta}$ is known to have mean β and variance $(n\mathcal{F}_U)^{-1}$, where n is the number of independent observations of the internal energy of the system. The analogy of the foregoing expressions with those in Sec. II suggests the existence of a distribution of $\hat{\beta}$, with corresponding Fisher information and Legendre transform structure. In a Bayesian context this would correspond to the posterior distribution attributed to the uncertainty in the parameter β, of the type

$$p_{\hat{\beta}}(\hat{\beta};U) = e^{S(U)-U\hat{\beta}-h_{\hat{\beta}}(\hat{\beta})}, \tag{14}$$

so that $S(U)$ is related to its cumulant transform and

$$-\frac{d^2S}{dU^2} = \mathcal{I}_\beta = \frac{1}{\mathcal{F}_U} \tag{15}$$

is its Fisher information with respect to the parameter U. A Legendre structure for $\mathcal{I}_\beta$ can be constructed similarly to what was done for $\mathcal{F}_U$ in Sec. III, although it does not appear to be of immediate interest here.

We conclude this section by noting that (15) also corresponds to a relation between variances of $\hat{U}$ and $\hat{\beta}$,

$$\langle(\hat{U}-U)^2\rangle\langle(\hat{\beta}-\beta)^2\rangle = 1, \tag{16}$$

which is formally analogous to an uncertainty relationship. While the interpretation of such a relationship in the context of statistical inference is quite clear, its physical interpretation is more controversial and its discussion is outside the scope of the present work; we refer to the quite extensive literature (e.g., [36–40] and references therein) for this issue.

V. CONSTANT HEAT CAPACITY

The case of a constant heat capacity, $C = Nc$, is particularly simple and in this case the Legendre transforms acquire nice symmetry properties. Microscopically such a condition results from energy equipartition ([1], pp. 291, 376), which implies that the internal energy has a quadratic dependence on the (micro)states of the $\nu = 2C$ degrees of freedom. The resulting canonical distribution, (1), is a Γ distribution with scale parameter β, shape parameter C, mean C/β, and variance C/β^2:

$$\begin{aligned} p_{\hat{U}}(\hat{U};\beta) &= \frac{\beta^C}{\Gamma(C)}\hat{U}^{C-1}e^{-\beta\hat{U}} \\ &= e^{C\ln\beta-\ln\Gamma(C)-\beta\hat{U}-(1-C)\ln(\hat{U})}. \end{aligned} \tag{17}$$

TABLE II. Expressions of the thermodynamic variables for the case of a constant heat capacity, C. Note that S_0, U_0, and T_0 are assumed equal to 0.

Entropy	Fisher information
$S(U) = C\ln U$	$\mathcal{F}_S(\mathcal{F}_U) = 2\sqrt{C\mathcal{F}_U}$
$U(S) = e^{S/C}$	$\mathcal{F}_U(\mathcal{F}_S) = \frac{1}{4C}\mathcal{F}_S^2$
$\Phi(\beta) = C(1-\ln(\beta/C))$	$U(\beta) = C/\beta$
$F(T) = CT(1-\ln(CT))$	$\mathcal{F}_F(T) = \frac{1}{C}U^2$

The fundamental relations and the resulting thermodynamic potentials are reported in Table II and illustrated graphically in Fig. 1. The symmetries of the Legendre transformations, $S(U)$ and $\Phi(\beta)$ as well as $\mathcal{F}_U(\mathcal{F}_S)$ and $\mathcal{F}_F(T)$, respectively, are clearly visible, in the first case being logarithmic functions and in the second case being quadratic functions (see Table II).

VI. CONNECTION TO PREVIOUS WORK

The above results are directly connected to the previous work by Friden, Soffer, Plastino, and collaborators [17–21] on the Fisher information and the Legendre structure, the novelty here being in the explicit expressions for various quantities related to the canonical ensemble and the connection with the properties of the exponential families of distributions and their Legendre transformation symmetries (especially evident in the case of a constant heat capacity). The connections to the Bayesian interpretations of statistical mechanics and thermodynamics and the related uncertainty relationships have also been mentioned in Sec. IV, but the link to the other lines of work mentioned in the introduction remains to be discussed.

We begin with the work of Biot [13,14] and Guo *et al.* [12,15]. For the case of a constant heat capacity, (4) gives a Fisher information $\mathcal{F}_U$ which is quadratic with temperature and corresponds to the function used by Biot [13,14] and Guo *et al.* [12,15] in their variational formulation of heat conduction, as well as to the quantity obtained in [22]. In the general case of $C(T)$, $\mathcal{F}_F$ is found to be equal to the negative of twice the entransy function of Guo *et al.* [12,15], obtained there following Biot and using a formal analogy with electrical capacitance.

Note also that for a constant heat capacity, because of (20), one has that, for both reversible and irreversible transformations between equilibrium states,

$$\Delta\ln\mathcal{F}_U = -\frac{\Delta S}{C}. \tag{18}$$

Thus, considering the classical process of heat flow between two bodies of equal mass and heat capacity, initially at equilibrium at different temperatures (e.g., [1], p. 101), heat conduction always increases both the entropy and $\mathcal{F}_U$ when approaching equilibrium.

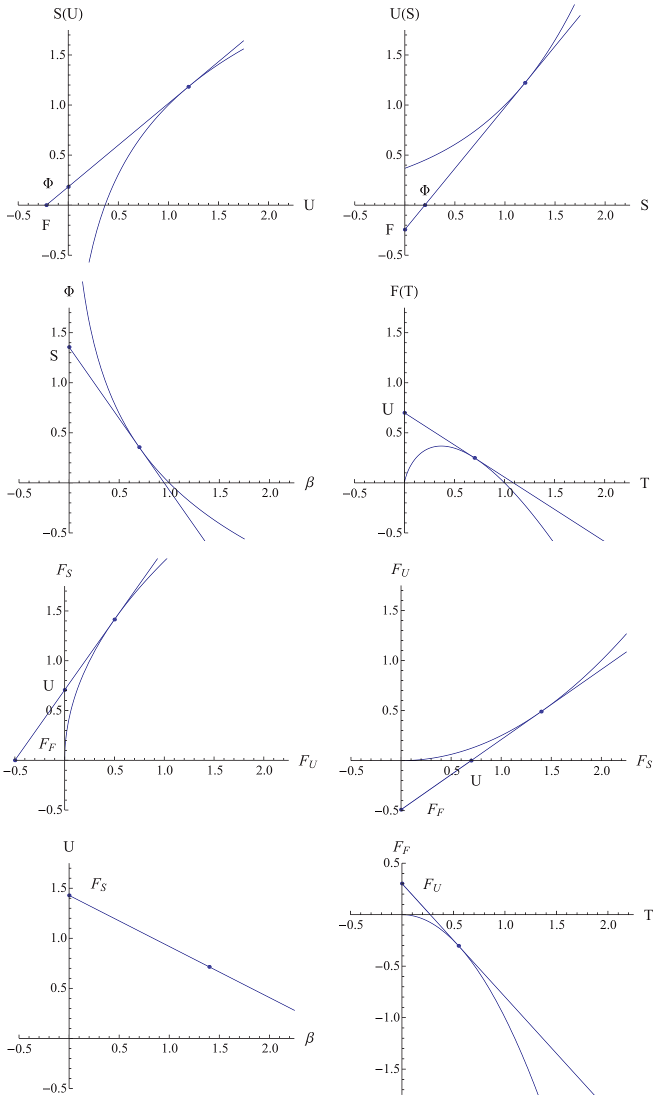

FIG. 1. (Color online) Sketch of the various thermodynamic functions and their Legendre transforms for the case of a constant heat capacity.

It should be noted, however, that, for the general case $C(T)$, Biot (see [14], p. 86) used a different function, defined as

$$\mathcal{F}_B = \int_0^U T(U')dU', \tag{19}$$

where $T(U)$ is the inverse function of $U(T) = \int_0^T C(T')dT'$. While $\mathcal{F}_B$ is proportional to $\mathcal{F}_U$ in Sec. II and is equal to the entransy for a constant heat capacity, i.e.,

$$\mathcal{F}_B = \tfrac{1}{2}\mathcal{F}_U = \tfrac{1}{2}CT^2, \tag{20}$$

it is not so in the general case. To find such a link, consider first that, using (5) and for reversible heat flow only,

$$-d\beta\mathcal{F}_U = dU = dQ^{\text{rev}} = TdS, \tag{21}$$

so that

$$\frac{\mathcal{F}_U}{T} = T^2\frac{dS}{dT}. \tag{22}$$

Since from (19), $d\mathcal{F}_B/dU = T$, then

$$\frac{d\mathcal{F}_B}{dS} = \frac{dU}{dS}\frac{d\mathcal{F}_B}{dU} = T^2, \tag{23}$$

and finally, combining (22) and (23),

$$\mathcal{F}_U = T\frac{d\mathcal{F}_B}{dT}, \tag{24}$$

which is formally analogous to the relationship between the heat capacity and the entropy, $C = TdS/dT$.

We conclude by discussing the link of the present analysis with Serrin's theory [3,4,41], which provides an alternative formulation of thermodynamics based on heat (i.e., temperature) and heat flow, without assuming internal energy and entropy as primitive concepts (similar concepts were developed by Silhavy [5,6]; see also [7]). The theory is formulated using an accumulation function, $A(T)$, defined for cyclic processes as the total heat added in a process at a temperature lower than or equal to T,

$$\oint \frac{dQ}{T} = \int_0^\infty \frac{A(T)}{T^2}dT \leqslant 0. \tag{25}$$

Based on this definition, $A(T)$ is 0 in adiabatic processes as well as whenever the input and output of heat cancel at every temperature, while it is a step function for the isothermal process. Considering an infinitesimal reversible transformation with heat transfer only,

$$dS = \frac{dQ^{\text{rev}}}{T} = \frac{A(T)}{T^2}dT = \frac{d\mathcal{F}_B}{T^2}. \tag{26}$$

Thus, it follows that

$$A(T) = \frac{d\mathcal{F}_B}{dT} = CT = \frac{1}{T}\mathcal{F}_U, \tag{27}$$

which establishes our last connection to previous work.

VII. CONCLUSIONS

We have highlighted in detail some interesting connections among alternative formulations of equilibrium thermodynamics. Following the original spirit of Biot's work, the elegant structure endowed by the properties of the exponential family distributions may prove to be also practically useful for the solution of problems of nonequilibrium thermodynamics using variational formulations.

Our considerations have been limited to the case of heat processes at constant volume and mass in simple systems. A logical way to extend the analysis to processes including mechanical work or mass flow would be to consider generalized Gibbs ensembles [1,42,43], along with their Fisher information matrices. Such an extension and its consequences for field theories of thermodynamics, especially for the case in which mechanical work is involved, as in compressible fluids, will be explored in future contributions.

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APPENDIX

For convenience, we briefly review here the main definitions and properties related to the Fisher information and the exponential family distributions. For the case of interest here, a univariate probability density function, $p(\hat{x};\theta)$, with one parameter θ, the maximum likelihood estimate of the parameter $\hat{\theta}$, based on n independent observations of x, solves for $\theta = \tilde{\theta}$ the equation

$$\frac{\partial}{\partial\theta}\left(\sum_{i=1}^{n} \ln p(\hat{x}_i;\theta)\right) = 0, \tag{A1}$$

where the left-hand side is the so-called score function, considered as a function of θ for given (observed) values $\hat{x}_i$ assumed to be extracted from the distribution $p(\hat{x};\theta)$. The score can be shown to have zero mean, while its variance is the Fisher information [25],

$$\begin{aligned}\mathcal{F}_x(\theta) &= \int \left(\frac{\partial \ln p(\hat{x};\theta)}{\partial\theta}\right)^2 p(\hat{x};\theta)d\hat{x}\\ &= -\int \frac{\partial^2 \ln p(\hat{x};\theta)}{\partial\theta^2}\, p(\hat{x};\theta)d\hat{x},\end{aligned} \tag{A2}$$

where the second form follows by integration by parts and holds under suitable regularity conditions met here. The Fisher information is thus the expected curvature of the log-likelihood: the greater the curvature, the sharper the inference for a given number of observations.

Exponential family distributions are typically defined as [24]

$$p(\hat{x};\theta) = e^{-\phi(\theta)+\theta\hat{x}+\alpha(\hat{x})}, \tag{A3}$$

where θ is known as the canonical parameter. The cumulant generating function is $\kappa(t) = \phi(t-\theta) - \phi(t)$, so that the cumulants can be obtained directly by differentiating $\phi(\theta)$ with respect to θ,

$$\kappa_r = \frac{d^r\phi}{d\theta^r}, \tag{A4}$$

where κ_r is the rth cumulant; for this reason, $\phi(\theta)$ is called the cumulant transform [24]. Its second derivative can also be shown to be equal to the Fisher information. As a result,

$$\frac{\partial\phi}{\partial\theta} = \langle\hat{x}\rangle = x \tag{A5}$$

and

$$\frac{\partial^2\phi}{\partial\theta^2} = \mathcal{F}_x(\theta) = \langle(\hat{x}-x)^2\rangle = \sigma^2. \tag{A6}$$

The form used in thermodynamics, (1), differs in the sign of the canonical parameter,

$$p(\hat{x};\vartheta) = e^{-\varphi(\vartheta)-\vartheta\hat{x}-h(\hat{x})}. \tag{A7}$$

This sign difference is responsible for the appearance of a sign change in front of the the odd cumulants, when adopting (1); see Eq. (2).

A final important result is that $\phi(\theta)$ is a convex function whose Legendre transform is the maximized log-likelihood function (Theorem 6.1, Eq. (6.42), in [24]). The Legendre transform used in mathematics and statistics, $\phi^*(x)$, is different from the one used in thermodynamics, $\phi^\dagger(x)$, which uses the opposite sign:

$$\phi^*(x) = \theta x - \phi(\theta) = -\phi^\dagger(x). \tag{A8}$$

Both $\phi(\theta)$ and $\phi^*(x)$ can be differentiated infinitely often, and (Theorem 6.1, Eq. (6.42), in [24])

$$\frac{\partial\phi}{\partial\theta} = x, \quad \frac{\partial\phi^*}{\partial x} = \theta, \tag{A9}$$

$$\frac{\partial^2\phi}{\partial\theta^2} = \sigma^2, \quad \frac{\partial^2\phi^*}{\partial x^2} = \frac{1}{\sigma^2}. \tag{A10}$$

In thermodynamics, the sign difference in the exponential family distributions, that is, $\theta = -\vartheta$ and $\phi(\theta) = \varphi(\vartheta) = \varphi(-\theta)$, results in

$$\frac{\partial\varphi}{\partial\vartheta} = -x \tag{A11}$$

[see Eq. (2)] and

$$\frac{\partial^2\varphi}{\partial\vartheta^2} = \sigma^2 \tag{A12}$$

[see Eq. (3)]. Moreover, combined with the different convention for the Legendre transform, it follows that

$$\varphi^\dagger(x) = \varphi(\vartheta) - \vartheta\frac{\partial\varphi}{\partial\vartheta} = \phi(\theta) - \theta x = -\phi^*(x), \tag{A13}$$

whence

$$\frac{\partial\varphi^\dagger}{\partial x} = -\theta = \vartheta, \tag{A14}$$

as in Eq. (11), and

$$\frac{\partial^2\varphi^\dagger}{\partial x^2} = -\frac{1}{\sigma^2},$$

as in (13).

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[1] H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (John Wiley & Sons, New York, 1965).

[2] A. Bejan, *Advanced Engineering Thermodynamics*, 3rd ed. (Wiley, Hoboken, NJ, 2006).

[3] J. Serrin, Arch. Rat. Mech. Anal. **70**, 355 (1979).

[4] J. Serrin, in *New Perspective in Thermodynamics* (Springer, Heidelberg, 1986), pp. 3–31.

[5] M. Silhavy, Arch. Rat. Mech. Anal. **81**, 221 (1983).

[6] M. Silhavy, in *New Perspective in Thermodynamics* (Springer, Heidelberg, 1986), pp. 33–47.

[7] E. H. Lieb and J. Yngvason, Phys. Today **53**, 32 (2000).

[8] A. E. Green and P. M. Naghdi, Proc. Roy. Soc. Lond. A **432**, 171 (1991).
[9] I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes*, 3rd ed. (Interscience, New York, 1967).
[10] I. Gyarmati, *Non-equilibrium Thermodynamics: Field Theories and Variational Principles* (Springer, New York, 1970).
[11] V. Bertola and E. Cafaro, Int. J. Heat Mass Transf. **51**, 1907 (2007).
[12] Q. Chen, H. Zhu, N. Pan, and Z.-Y. Guo, Proc. Roy. Soc. Lond. A **467**, 1012 (2011).
[13] M. A. Biot, J. Appl. Phys. **27**, 240 (1956).
[14] M. A. Biot, *Variational Principles in Heat Transfer* (Clarendon Press, Oxford, UK, 1970).
[15] Z.-Y. Guo, H. Zhu, and X. Liang, Int. J. Heat Mass Transf. **50**, 2545 (2007).
[16] G. Grazzini, R. Borchiellini, and U. Lucia, J. Non-Equilib. Thermodyn. **38**, 259 (2013).
[17] B. R. Frieden, Am. J. Phys. **57**, 1004 (1989).
[18] B. R. Frieden, Phys. Rev. A **41**, 4265 (1990).
[19] B. R. Frieden and B. H. Soffer, Phys. Rev. E **52**, 2274 (1995).
[20] B. R. Friden, *Science from Fisher Information: A Unification* (Cambridge University Press, Cambridge, UK, 2004).
[21] B. R. Frieden, A. Plastino, A. R. Plastino, and B. H. Soffer, Phys. Rev. E **60**, 48 (1999).
[22] F. Pennini and A. Plastino, Phys. Rev. E **71**, 047102 (2005).
[23] O. E. Barndorff-Nielsen, *Information and Exponential Families in Statistical Theory* (John Wiley & Sons, Chichester, UK, 1978).
[24] O. E. Barndorff-Nielsen and D. R. Cox, *Asymptotic Techniques for Use in Statistics* (Chapman and Hall, London, 1989).
[25] A. Davison, *Statistical Models* (Cambridge University Press, Cambridge, 2000).
[26] R. K. Pathria and P. D. Beale, *Statistical Mechanics*, 3rd ed. (Academic Press, New York, 2011).
[27] R. F. Green and H. B. Callen, Phys. Rev. **83**, 1231 (1951).
[28] H. B. Callen, Am. J. Phys. **33**, 919 (1965).
[29] P. G. Debenedetti, J. Chem. Phys. **85**, 2132 (1986).
[30] P. Frauddorf, Am. J. Phys. **71**, 1142 (2003).
[31] B. Mandelbrot, Ann. Math. Stat. **33**, 1021 (1962).
[32] L. Tisza and P. M. Quay, Ann. Phys. **25**, 48 (1963).
[33] G. Ruppeiner, Phys. Rev. A **20**, 1608 (1979).
[34] D. Brody and N. Rivier, Phys. Rev. E **51**, 1006 (1995).
[35] P. Salamon, J. Nulton, and E. Ihrig, J. Chem. Phys. **80**, 436 (1984).
[36] R. Gilmore, Phys. Rev. A **31**, 3237 (1985).
[37] B. H. Lavenda, Int. J. Theor. Phys. **27**, 451 (1988).
[38] H. B. Prosper, Am. J. Phys. **61**, 54 (1992).
[39] J. Uffink and J. van Lith, Found. Phys. **29**, 655 (1999).
[40] M. Falcioni, D. Villamaina, A. Vulpiani, A. Pulgisi, and A. Saracino, Am. J. Phys. **79**, 777 (2011).
[41] M. J. Lampinen and J. Vuorisalo, J. Appl. Phys. **69**, 597 (1991).
[42] H. S. Leff, Am. J. Phys. **37**, 65 (1969).
[43] H. W. Graben and J. R. Ray, Mol. Phys. **80**, 1183 (1993).