Macroscopic Observables, Thermodynamic Completeness and the Differentiability of Entropy

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Abstract

We provide a quantum statistical basis for (a) a characterisation of a complete set of thermodynamic variables and (b) the differentiability of the entropy function of these variables.

Key Words: algebraic quantum thermodynamics, extensive conserved observables, spatially ergodic states, thermodynamic completeness, KMS conditions, differentiability of entropy

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1. Introduction

The fundamental formula of classical thermodynamics is

$$TdS = dE + pdV + \sum_{j=1}^{n} y_j dQ_j,$$  \hspace{1cm} (1.1)

where $S$ is the entropy of a system, $T$ is its temperature, $p$ its pressure, $V$ its volume, $E$ its internal energy, $Q_1, \ldots, Q_n$ a further set of conserved macroscopic variables and $y_1, \ldots, y_n$ a set of real valued parameters representing the coupling of the system to external sources such that $\sum_{j=1}^{n} y_j dQ_j$ represents the work done by the system against these sources due to infinitesimal changes in the $Q_j$’s. Thus, for fixed values of the $y_j$’s, the effective energy of the system is

$$E^{(\text{eff})} = E + \sum_{j=1}^{n} y_j Q_j.$$  \hspace{1cm} (1.2)

The formula (1.1) implies that $S$ is a differentiable function of the variables $V$, $E$ and the $Q_j$’s, though it does not provide any general rule for identifying the latter variables of a system of given microscopic constitution. Thus we are confronted by the challenging problems of providing a quantum statistical basis for both a characterisation of the thermodynamic variables $(Q_1, \ldots, Q_n)$ and the differentiability of entropy. These are the problems that we shall address in this paper.

Our treatment is formulated within the operator algebraic framework of quantum statistical mechanics wherein the model of a macroscopic system is represented as an infinitely extended one, as in the thermodynamic limit, and is designed to be applicable both to lattice systems and continuous ones. The treatment is centred on (a) a set of macroscopic observables $\hat{q} = (\hat{q}_0, \hat{q}_1, \ldots, \hat{q}_n)$ that are global densities of quantum versions of the above variables $(E, Q_1, \ldots, Q_n)$, and (b) the spatially ergodic states, i.e. the extremal elements of the convex set of translationally invariant states, which correspond to pure phases [1].

The equilibrium condition on these states is assumed to be given by the maximisation of the entropy density, subject to the constraint that fixes the expectation value of $\hat{q}$ to a prescribed value $q$. The set $\hat{q}$ of macroscopic observables is then termed \textit{thermodynamically complete} if, for each realisable value of $q$, there is precisely one spatially ergodic state that satisfies this condition. In other words, the values of the macro-observables $\hat{q}$ completely determine the pure phases of the model. Further, we find that it follows from the structure of the model that thermodynamic completeness implies that the resultant state of the model satisfies the Kubo-Martin-Schwinger (KMS) condition, whereby the dynamical automorphisms are the modular ones* of the Tomita-Takesaki theory [2]. The differentiability of the entropy function then follows from the uniqueness of these automorphisms.

Our treatment proceeds as follows. In Section 2 we provide a brief resume of classical thermodynamics in a form that connects simply with our subsequent formulation of the

* Recall that the general definition of the modulars is that they constitute a one-parameter group $\{\sigma_t | t \in \mathbb{R}\}$ of automorphisms of a $W^*$-algebra $\mathcal{M}$, induced by a faithful, normal state $\omega$ according to the KMS condition that $\omega([\sigma_t A] B) = \omega(B \sigma_{t+i} A)$ for all $A, B$ in $\mathcal{M}$.\]
quantum model. In Section 3 we formulate that model in operator algebraic terms as an
infinitely extended system. In Section 4 we formulate the equilibrium and thermodynamic
completeness conditions discussed above In Section 5 we show that, under the imposed
conditions, the entropy function realised by the quantum model is indeed differentiable.
We conclude in Section 6 with some brief observations about the basis of the treatment of
quantum thermodynamics presented here.

2. The Classical Thermodynamic Model.

The classical phenomenological model is based on Eq. (1.1), which may be con-
veniently re-expressed in terms of the variables $Q = (Q_0 := E, Q_1, .., Q_n)$ and $\theta =
(\theta_0, \theta_1, .., \theta_n)$, where $\theta_0 = T^{-1}$ and $\theta_j = T^{-1}y_j$ for $j = 1, .., n$. Eq.(1), as expressed in
terms of these variables, then takes the form

$$dS = \theta.dQ + \phi dV,$$

(2.1)

where

$$\phi = T^{-1}p,$$

(2.2)

which is termed the reduced pressure, and where the dot denotes the $\mathbb{R}^{n+1}$ scalar product,
i.e. $\theta.dQ := \sum_{k=0}^{n}\theta_k dQ_k$. The components $\theta_k$ of $\theta$ are termed the control variables.

It is standard to classical thermodynamics [3] that
(a) the variables $V, S$ and $Q$ are extensive, while $T, \phi$ and $\theta$ are intensive; and
(b) by the demand of thermodynamic stability, the entropy $S$ is a concave function of $Q$
and $V$.

It follows from (a) that $Q$ and $S$ take the forms $Vq$ and $Vs(q)$, where $q := (q_0, q_1, .., q_n)$, $q_j =
Q_j/V$ and $s$ is a function of $q$ only. We term $q$ the thermodynamic state of the model. It
follows from these specifications and Eq. (2.1) that

$$d(s(q)V) = \theta.dqV + \phi dV,$$

i.e. that

$$(s(q) - \theta.q - \phi)dV + (ds - \theta.dq)V = 0,$$

which signifies that

$$ds = \theta.dq$$

(2.3)

and

$$\phi = s - \theta.q.$$  

(2.4)

We assume that the domains of definition of the variables $q$ and $\theta$ are convex subsets
of $\mathbb{R}^{(n+1)}$, which we denote by $Q$ and $\Theta$ and term the thermodynamic state space and
the control space, respectively: quantum statistical specifications of these states will be
provided in Section 4. Since, by (b), $S$ is a concave function of its arguments, so too is its
density, $s$. 

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Since Eq. (2.3) signifies that $\theta = s'(q)$, the differential (i.e. the $\mathbb{R}^{(n+1)}$ gradient) of $s$, it follows that, for fixed $\theta$, $q$ is a stationary point of the function $s - \theta(\cdot)$ on $Q$. Moreover, as the concavity of $s$ ensures that the tangent to the graph of $s$ at $q$ lies above that graph, it follows that

$$s(q') - s(q) \leq \theta(q' - q) \quad \forall \; q' \in Q,$$

i.e.

$$s(q) - \theta.q \geq s(q') - \theta.q' \quad \forall \; q' \in Q,$$

which signifies that the stationary point $q$ of $s - \theta(\cdot)$ is a maximum. Hence, by Eq. (2.4) the reduced pressure $\phi$ is the Legendre transform of the entropy density $s$, i.e.

$$\phi(\theta) = \max_{q \in Q} (s(q) - \theta.q),$$

which implies, by the following argument, that $\phi$ is convex. For $\theta, \theta' \in \Theta, \lambda \in (0, 1)$ and $\epsilon > 0$, it follows from Eq. (2.6) that, for some $q \in Q$,

$$\phi(\lambda\theta + (1 - \lambda)\theta') < s(q) - (\lambda\theta + (1 - \lambda)\theta') + \epsilon \equiv \lambda(s(q) - \theta.q) + (1 - \lambda)(s(q) - \theta'.q) + \epsilon \leq \lambda \phi(\theta) + (1 - \lambda) \phi(\theta') + \epsilon$$

and therefore, as $\epsilon$ is arbitrarily chosen,

$$\phi(\lambda\theta + (1 - \lambda)\theta') \leq \lambda \phi(\theta) + (1 - \lambda) \phi(\theta'),$$

which signifies that $\phi$ is convex.

To summarise, the general structure of classical thermodynamics is governed by the forms of the entropy function $s$ and the reduced pressure $\phi$, which is its Legendre transform. Further, $s$ is concave, $\phi$ is convex and the thermodynamic state $q$ is determined by the maximisation $s - \theta(\cdot)$.

### 3. The Quantum Model

In a standard way [1, 4-8], we represent the quantum model of a macroscopic system, $\Sigma$, as an infinitely extended body: this corresponds to a treatment of the system in the thermodynamic limit. Specifically, we take the model to comprise a system of interacting particles that occupies an infinitely extended space, $X$, which may be either a Euclidean space, $\mathbb{R}^d$, or a lattice, $\mathbb{Z}^d$, with $d$ finite. Correspondingly, space translations are represented by $X$, considered as an additive group.

**The Algebra $\mathcal{A}$.** The model of $\Sigma$ is centred on a $C^*$-algebra, $\mathcal{A}$, constructed in the following standard way. We denote by $L$ the set of bounded open subregions $\Lambda$ of $X$. For each $\Lambda \in L$ we then construct, according to the general rules of quantum mechanics, a model $\Sigma(\Lambda)$ of a finite system of particles of the given species confined to $\Lambda$. Thus, the bounded observables of this system are represented by the self-adjoint elements of a type I primary $W^*$-algebra $\mathcal{A}(\Lambda)$ in a separable Hilbert space $\mathcal{H}(\Lambda)$, The constructions of the
algebras $\mathcal{A}(\Lambda)$ is effected so as to meet the canonical requirements of isotony and local commutativity, i.e.

$$\mathcal{A}(\Lambda_1) \subseteq \mathcal{A}(\Lambda_2) \text{ and } \mathcal{H}(\Lambda_1) \subseteq \mathcal{H}(\Lambda_2) \text{ if } \Lambda_1 \subseteq \Lambda_2$$

and

$$\mathcal{A}(\Lambda_1) \subseteq \mathcal{A}(\Lambda_2)' \text{ if } \Lambda_1 \cap \Lambda_2 = \emptyset$$

where the prime denotes commutant. Thus, $\bigcup_{\Lambda \in L} \mathcal{A}(\Lambda)$ is a normed $^\ast$-algebra, $\mathcal{A}_L$, of the local observables of the system $\Sigma$. We define $\mathcal{A}$ to be its norm completion. Thus $\mathcal{A}_L$ and $\mathcal{A}$ are naturally identified as the algebras of local and quasi-local bounded observables, respectively, of $\Sigma$. Its unbounded local observables are represented by the unbounded self-adjoint operators affiliated to $\mathcal{A}_L$ [9]. In particular, the local Hamiltonian operator, $H(\Lambda)$, is the energy observable for the region $\Lambda$, and either belongs or is affiliated to $\mathcal{A}(\Lambda)$.

**The Extensive Conserved Observables.** We assume that each $\Lambda$ in $L$ harbours a set of intercommuting, linearly independent, possibly unbounded, extensive observables $Q(\Lambda) = (Q_0(\Lambda), Q_1(\Lambda), \ldots, Q_n(\Lambda))$, with $Q_0(\Lambda)$ the internal energy $H(\Lambda)$. These are designed to be the thermodynamic observables that correspond, for large $\Lambda$, to the classical variables $Q$ of Section 2. Their extensivity condition is that

$$\hat{Q}(\Lambda \cup \Lambda') = \hat{Q}(\Lambda) + \hat{Q}(\Lambda') \text{ if } \Lambda \cap \Lambda' = \emptyset.$$

**The Space Translational Automorphisms.** We represent space translations by a homomorphism, $\sigma$, of the group $X$ into the automorphisms of $\mathcal{A}$ satisfying the covariance conditions

$$\sigma(x)\mathcal{A}(\Lambda) = \mathcal{A}(\Lambda + x) \quad (3.1)$$

and

$$\sigma(x)\hat{Q}(\Lambda) = \hat{Q}(\Lambda + x). \quad (3.2)$$

We define the effective energy observable, $H_\theta^\text{eff}(\Lambda)$, for the region $\Lambda$ to be the canonical counterpart to that given by Eq. (1.2) for the phenomenological model. Thus, by our definition of $\theta$ and its components $\theta_j$ in terms of $y_1, \ldots, y_n$ and $T$,

$$H_\theta^\text{eff}(\Lambda) = \theta_0^{-1}\theta_0\hat{Q}(\Lambda). \quad (3.3)$$

**The State Space $S$.** We take this to comprise the positive normalised linear functionals on $\mathcal{A}$ whose restrictions to the local algebras $\mathcal{A}(\Lambda)$ are normal: this last condition is needed, in the case of continuous systems, to ensure that the number of particles in each bounded region $\Lambda$ is finite [10]. Thus, the restriction, $\rho_\Lambda$, of a state $\rho$ to the region $\Lambda$ is represented by a density matrix, which we also denote by $\rho_\Lambda$, i.e.

$$\rho(A) = Tr_{\mathcal{H}(\Lambda)}(\rho_\Lambda A) \quad \forall A \in \mathcal{A}(\Lambda), \Lambda \in L.$$
We denote by \( S_X \) the set of translationally invariant states of \( \Sigma \), as defined by the condition that \( \rho = \rho \circ \sigma(x) \) for all \( x \in X \). Evidently \( S_X \) is convex. We denote the set of its extremal elements by \( \mathcal{E}_X \). These are the spatially ergodic states of the system, characterised by the property that the space averages of the local observables are dispersionless in these states [1], i.e., defining the space average of a local observable \( A \) to be

\[
\tilde{A}_\Lambda := |\Lambda|^{-1} \int_\Lambda dx \sigma(x) A,
\]

where \( |\Lambda| \) is the volume of \( \Lambda \); and for spatially ergodic \( \rho \),

\[
\lim_{\Lambda \uparrow X} [\rho(\tilde{A}_\Lambda^2) - \rho(\tilde{A})^2] = 0,
\]

the limit being taken in the sense of Van Hove.

In particular, a folium, of states is defined [11] to be a norm closed convex subset, \( \mathcal{F} \), of \( S \) that is stable under quasi-local modifications \( \{ \rho \to \rho(B^* \cdot B) / \rho(B^* B | B \in A) \} \). The normal folium of a state \( \rho \) then corresponds to the set of normal states on the GNS representation of \( A \) induced by \( \rho \).

**Dynamics of the Model.** We assume that the dynamics of the finite system \( \Sigma_\Lambda \) is given by the unitary transformations generated by the effective local Hamiltonian \( H_\theta^{\text{eff}}(\Lambda) \) on a time scale whose unit is \( \theta_0 \). Thus, by Eq. (3.3),

\[
\alpha_{\theta_{\Lambda}}(t) A = \exp(i\theta \hat{Q}(\Lambda) t) A \exp(-i\theta \hat{Q}(\Lambda) t) \quad \forall \ t \in \mathbb{R}, \ A \in A(\Lambda).
\]  

(3.4)

It follows from this formula and Eq. (3.1) that

\[
\sigma(x) \alpha_{\theta_{\Lambda}}(t) = \alpha_{\theta, \Lambda_{+x}}(t) \sigma(x).
\]  

(3.5)

In order to formulate the dynamics of the infinitely extended system \( \Sigma \), we first recall that, in general, the model does not support an infinite volume norm limit of the automorphisms \( \alpha_{\theta_{\Lambda}} \) (cf. [12, 13])*. To cope with this situation we formulate the dynamics of the model, in the Schroedinger representation [13], as a one-parameter group, \( \{ \tau(t) \mid t \in \mathbb{R} \} \), of normalised affine transformations of a folium \( \mathcal{F} \) of its states that supports the infinite volume limit of the dual of \( \alpha_{\theta_{\Lambda}}(\mathbb{R}) \) given by the formula

\[
\langle \tau(t) \rho; A \rangle = \lim_{\Lambda \uparrow X} \langle \rho; \alpha_{\theta_{\Lambda}}(t) A \rangle \quad \forall \ \rho \in \mathcal{F}, \ A \in \mathcal{A}_{\Lambda}, \ t \in \mathbb{R}.
\]  

(3.6)

A consequence of this assumption is that [13]

\[
\lim_{\Lambda \uparrow X} \langle \rho; B_1[\alpha_{\theta_{\Lambda}}(t) A] B_2 \rangle = \langle \rho; \pi(B_1)[\hat{\alpha}(t) \pi(A)] \pi(B_2) \rangle \quad \forall \ \rho \in \mathcal{F}, \ A, \ B_1, \ B_2 \in \mathcal{A}_{\Lambda}, \ t \in \mathbb{R},
\]

(3.7)

* To be more specific, such a limit is supported by spin systems with short range interactions [14-17], but not, in general, by continuous systems.
where $\pi$ is the GNS representation of the state $\rho$, $\hat{\rho}$ is its canonical extension to the $W^*$-algebra $A_F := \pi(A)'$ and $\{\hat{\alpha}(t)|t \in \mathbb{R}\}$ is the one parameter group of automorphisms of that algebra defined by the formula

$$\hat{\alpha}(t) \pi(A) = \pi(\hat{\alpha}(t) A) \quad \forall A \in A_L, \ t \in \mathbb{R}. \quad (3.8)$$

where the limit is taken over an increasing sequence of cubes with parallel axes. Thus, the automorphisms $\hat{\alpha}(\mathbb{R})$ represent the dynamics of the model in the folium $F$. Furthermore, defining the space translational automorphisms $\hat{\sigma}(x)$ of $A_F$ by the formula

$$\hat{\sigma}(x) \pi(A) = \pi(\sigma(x) A) \quad \forall A \in A, \ x \in X, \quad (3.9)$$

it follows from Eqs. (3.5), (3.8) and (3.9) that the space and time automorphisms, $\hat{\sigma}(x)$ and $\hat{\alpha}(t)$, intercommute.

4. The Quantum Thermodynamic Picture

We base the quantum thermodynamic picture on

(a) a set of intercommuting, possibly unbounded, intensive observables $\hat{q} = (\hat{q}_0, \hat{q}_1, .., \hat{q}_n)$, given by the global space average of $\hat{Q}(\Lambda)$ and designed to be the quantum counterpart of the classical variables $q$ of Section 2; and

(b) a global entropy density function, $s$, on the range, $Q$, of expectation values of $\hat{q}$ in the spatially ergodic states: we term $Q$ the thermodynamic state space.

Specifically $\hat{q}$ is the observable at infinity [18] whose action on the spatially ergodic states given by the following formula.

$$\hat{q}(\rho) = \lim_{\Lambda \uparrow X} |\Lambda|^{-1} \rho(\hat{Q}(\Lambda)) \equiv \lim_{\Lambda \uparrow X} |\Lambda|^{-1} Tr(\rho |\Lambda\rangle \langle |\Lambda|) \quad \forall \rho \in \tilde{E}_X, \quad (4.1)$$

$\tilde{E}_X$ being its domain of definition as the subset of $E_X$ on which the r.h.s. is well defined. In particular, the spatial ergodicity of $\tilde{E}_X$ ensures that $\hat{q}$ is sharply defined there, i.e. that its dispersion vanishes.

The construction of the entropy function, $s$, proceeds as follows. We take the entropy, $S(\rho_\Lambda)$, of the restriction, $\rho_\Lambda$, of the state $\rho$ to the region $\Lambda (\in L)$, to be given by Von Neumann’s formula i.e.

$$S(\rho_\Lambda) = -Tr_{H(\Lambda)}(\rho_\Lambda \log(\rho_\Lambda)). \quad (4.2)$$

in units where Boltzmann’s constant is unity. The entropy density functional $\hat{s}$ of the translationally invariant states given by the following formula [19], which stems from the strong subadditivity property of $S_\Lambda$, established by Lieb and Ruskai [20].

$$\hat{s}(\rho) = \lim_{\Lambda \uparrow X} \frac{S(\rho_\Lambda)}{|\Lambda|} \quad \forall \rho \in S_X. \quad (4.3)$$

Key properties of $\hat{s}$ are that it is affine and upper semi-continuous [1]. The entropy function, $s$, on the thermodynamic space, $Q$ is defined by the formula

$$s(q) = \sup_{\rho \in \tilde{E}_X} \{\hat{s}(\rho)|\hat{q}(\rho) = q\}. \quad (4.4)$$
Thus the macroscopic picture provided by the quantum model is given by the global observable $\hat{q}$, the thermodynamic state space $Q$ and the entropy density $s$ on $Q$. Moreover, it follows from Eq. (4.4) and the affine property of $\hat{s}$ that the function $s$ is concave. Hence the tangents to the graph of $s$ at the point $q$ lie above that graph. Thus the set, $T_s(q)$, of these tangents comprises the control variables $\theta$ that satisfy the condition

$$s(q') - s(q) \leq \theta(q' - q) \quad \forall \theta \in T_s(q), \; q' \in Q,$$

which signifies that

$$s(q) - \theta.q \geq s(q') - \theta.q' \quad \forall q' \in Q. \quad (4.5)$$

Consequently

$$s(q) - \theta.q \geq \sup_{q' \in Q} (s(q') - \theta.q') := \phi(\theta) \quad \forall \theta \in T_s(q), \; q \in Q.$$  

Hence

$$s(q) - \theta.q = \phi(\theta) \quad \forall \theta \in T_s(q), \quad (4.6)$$

where

$$\phi(\theta) = \sup_{q' \in Q} (s(q') - \theta.q'). \quad (4.7)$$

Eq. (4.6) is just the condition for global thermodynamic stability (GTS), discussed in [8]. Further $\phi$, as defined by Eq. (4.7), is the reduced pressure of the quantum model [21] and is the quantum counterpart of the function denoted by the same symbol for the phenomenological one in Section 2. Moreover, by Eq. (4.6), it is convex. We take the control space, $\Theta$, to be the subset of $R^{n+1}$ on which $\phi$ is finite. As we shall infer from Eq. (4.15), it follows from Eqs. (4.1)-(4.4) that this is just \{ $\theta \in R^{n+1} \mid \lim_{\Lambda \uparrow X} |\Lambda|^{-1} \text{Tr} [\exp (-\theta \hat{Q}(\Lambda))] \leq \infty$ \}.

**The Equilibrium Condition.** We assume that the equilibrium condition for the model is that the entropy $\hat{s}$ is maximised, subject to the constraint that fixes the expectation value of $\hat{q}$. Moreover, as $\hat{s}$ is affine, any maximum over the states $S_X$ must be achieved over the extremals $E_X$. Hence we have the following definition of thermodynamic completeness.

**Definition 4.1.** We term the macroscopic observables $Q$ thermodynamically complete if, for each $q$ in $Q$, there is precisely one spatially ergodic state, $\rho_q$, that satisfies the equilibrium condition of maximal entropy density subject to the constraint that fixes the expectation value of $\hat{q}$ to be $q$. Thus, this constraint fixes not only the expectation value of the macroscopic observables $\hat{q}$ but also the full microstate of the model at the value $\rho_q$. Moreover, it follows from this definition that

$$\hat{s}(\rho_q) = s(q) \quad (4.8)$$

and

$$\hat{q}(\rho_q) = q. \quad (4.9)$$
Comment. Evidently thermodynamic completeness is a condition on the chosen macroscopic observables. A very simple example, which exhibits the significance of this condition, is provided by a ferromagnetic system, such as the much studied two-dimensional Ising model*. Here the energy density observable $\hat{e}$ of that model is manifestly incomplete, since there are two spatially ergodic states with equal and opposite polarisation that maximise its entropy, subject to the condition that the expectation value $e$, of $\hat{e}$ is less than a certain critical value $e_0$. However, on supplementing the energy density $\hat{e}$ with a polarisation observable $\hat{m}$, one obtains a thermodynamically complete pair $(\hat{e}, \hat{m})$, for which the equilibrium state $\rho_{e,m}$ is spatially ergodic.

The Generalised Grand Canonical Property. In view of Def. (4.1), we may re-express the formula (4.6) as the following global thermodynamic stability (GTS) condition [8] for the equilibrium state $\rho$.

$$\hat{s}(\rho) - \theta.\hat{q}(\rho) = \phi(\theta) \quad \forall \theta \in T_s(q). \quad (4.10)$$

It follows from Eqs. (4.1) and (4.2) that this condition may be expressed in terms of the observables $Q$ by the formula

$$\lim_{\Lambda \uparrow X} |\Lambda|^{1} \text{Tr} \left[ \rho_{\Lambda} \log \rho_{\Lambda} + \rho_{\Lambda} \theta.\hat{Q}(\Lambda) \right] + \phi(\theta) = 0 \quad (4.11)$$

Hence, defining the generalised canonical state $\psi_\theta$ by the formula

$$\psi_{\theta_{\Lambda}} := \exp\left(-\theta.\hat{Q}(\Lambda)\right)/\text{Tr(idem)} \quad \forall \Lambda \in L, \quad (4.12)$$

and introducing the relative entropy [23]

$$S(\rho_{\Lambda}|\psi_{\theta_{\Lambda}}) = \text{Tr}(\rho_{\Lambda} \log \rho_{\Lambda} - \rho_{\Lambda} \log \psi_{\Lambda}), \quad (4.13)$$

we infer from Eqs. (4.7) and (4.11)-(4.13) that

$$\phi(\theta) = \sup_{\rho \in \mathcal{E}_{X}} \lim_{\Lambda \uparrow X} |\Lambda|^{-1} \left[ -S(\rho_{\Lambda}|\psi_{\theta_{\Lambda}}) + \log \text{Tr} \exp(-\theta.\hat{Q}(\Lambda)) \right]. \quad (4.14)$$

Consequently since $S(\xi|\eta)$, the entropy of a state $\phi$ relative to a fixed state $\psi$, is minimised at the value zero when $\xi = \eta$ [We], it follows from Eq. (4.14) that the supremum on the r.h.s. of that formula is attained when $\rho = \psi_\theta$ and that

$$\phi(\theta) = \lim_{\Lambda \uparrow X} |\Lambda|^{-1} \log \text{Tr} \exp(-\theta.\hat{Q}(\Lambda)). \quad (4.15)$$

Thus, the solution of the GTS condition (4.10) is that $\rho$ is the generalised canonical state $\psi_\theta$.

* The argument presented here can be recast in terms of the more usual canonical one of Eq. (4.10) (cf. [22])
Proposition 4.1. Under the above definitions and assumptions, the state \( \hat{\rho} \) satisfies the KMS condition, which may be expressed in the following form (cf. [HHW]).

\[
\int_{\mathbb{R}} df(t) \langle \hat{\rho}; [\hat{\alpha}(t)\pi_\rho(A)]\pi_\rho(B) \rangle = \int_{\mathbb{R}} df(t-i) \langle \hat{\rho}; \pi_\rho(B)[\hat{\alpha}(t)\pi_\rho(A)] \rangle, \quad \forall \ A, B \in \mathcal{A}, \ f \in \hat{\mathcal{D}}(\mathbb{R}),
\]

where \( \hat{\mathcal{D}}(\mathbb{R}) \) is the Fourier transform of the L. Schwartz space of infinitely differentiable functions on \( \mathbb{R} \) with compact support.

**Proof.** By Eqs. (3.7) and (3.8) and the identification of \( \rho \) with the generalised canonical state \( \psi_\theta \), the left and right sides of Eq. (4.16) are equal to

\[
\int_{\mathbb{R}} df(t) \langle \hat{\psi}_\theta; [\pi_\rho(\alpha_\theta(t)A)]\pi_\rho(B) \rangle
\]

and

\[
\int_{\mathbb{R}} df(t-i) \langle \hat{\psi}_\theta; \pi_\rho(B)[\pi_\rho(\alpha_\theta(t)A)] \rangle,
\]

respectively. Moreover, for sufficiently large \( \Lambda \), \( \hat{\psi}_\theta \) reduces to \( \hat{\psi}_{\theta\Lambda} \) in these formulae. The left and right hand sides of Eq. (4.16) may therefore be expressed as

\[
\int_{\mathbb{R}} df(t) \langle \psi_{\theta\Lambda}; [\alpha_{\theta\Lambda}(t)A]B \rangle
\]

and

\[
\int_{\mathbb{R}} df(t-i) \langle \psi_{\theta\Lambda}; B[\alpha_{\theta\Lambda}(t)A] \rangle,
\]

respectively. Hence, in order to establish the formula (4.16), it suffices to show that

\[
\int_{\mathbb{R}} f(t) \langle \psi_{\theta\Lambda}; [\alpha_{\theta\Lambda}(t)A]B \rangle = \int_{\mathbb{R}} f(t-i) \langle \psi_{\theta\Lambda}; B[\alpha_{\theta\Lambda}(t)A] \rangle,
\]

i.e., by Eq. (4.12), that

\[
\int_{\mathbb{R}} f(t) \text{Tr}[\exp((it - 1)\theta.\hat{Q}(\Lambda))A \exp(-i\theta.\hat{Q}(\Lambda))B] = \\
\int_{\mathbb{R}} f(t-i) \text{Tr}[\exp(-\theta.\hat{Q}(\Lambda))B \exp(i\theta.\hat{Q}(\Lambda)t)A \exp(-i\theta.\hat{Q}(\Lambda)t)].
\]

(4.17)

By the change of variable from \( t \) to \( (t-i) \), the l.h.s. takes the form

\[
\int_{\mathbb{R}} f(t-i) \text{Tr}[\exp(i\theta.\hat{Q}(\Lambda)t)A \exp(-i\theta.\hat{Q}(\Lambda)(t-i))B];
\]

and, in view of the cyclicity of Trace, this is equal to

\[
\int_{\mathbb{R}} f(t-i) \text{Tr}[B \exp(i\theta.\hat{Q}(\Lambda)t)A \exp(-i\theta.\hat{Q}(\Lambda)t)\exp(-\theta.\hat{Q}(\Lambda))],
\]
which, again by the cyclicity of Trace, is equal to the r.h.s. of Eq. (4.17), as required.

5. Differentiability of Entropy

The condition for differentiability of the entropy function $s$ is simply that the tangent space, $T_s(q)$ at each point $q$ of $Q$ is one-dimensional. We shall now relate this condition to the dynamics of the model, subject to the following assumption, that appears to be natural in view of the definition (3.8) of the dynamical automorphisms $\hat{\alpha}_\theta(R)$.

**Assumption 5.1.** $\hat{\alpha}_{\theta_1}(t) = \hat{\alpha}_{\theta_2}(t) \forall t \in R$ if and only if $\theta_1 = \theta_2$.

**Proposition 5.1** Under the Assumptions 5.1, the entropy function $s$ is differentiable.

**Proof.** Assume that $s$ is not differentiable at the point $q$. Then the tangent space $T_s(q)$ contains at least two different elements, $\theta_1$ and $\theta_2$, of $\Theta$. Hence, by Prop. 4.1, the state $\rho$ satisfies the KMS condition with respect to the automorphism groups $\hat{\alpha}_{\theta_1}$ and $\hat{\alpha}_{\theta_2}$. On the other hand, the thermodynamic completeness of the observables $Q$ ensures the uniqueness of the spatially ergodic equilibrium state $\hat{\rho}_q$ under the prevailing conditions. Therefore this state must satisfy the KMS conditions with respect to the automorphisms $\hat{\alpha}_{\theta_1}$ and $\hat{\alpha}_{\theta_2}$, and consequently, by the uniqueness of the modular automorphisms [2], the groups $\hat{\alpha}_{\theta_1}(R)$ and $\hat{\alpha}_{\theta_2}(R)$ must coincide. Hence, by Assumption 5.1, $\theta_1$ and $\theta_2$ must be equal, which is contrary to hypothesis. We conclude that $T_s(q)$ must be one-dimensional and consequently, as $q$ is an arbitrary point of $Q$, that $s$ is differentiable.

6. Concluding Remarks

An aim of this article has been to present a model independent approach to quantum thermodynamics, based on the assumptions of thermodynamic completeness, defined in Def. 4.1, and the condition (3.6), whereby the folium $F$ supports a dynamics given by the infinite volume limit of that of a corresponding finite system. These assumptions serve to extend the quantum thermodynamic picture from the lattice systems, on which much of the constructive work on the subject is based [6, 15-18], to continuous ones. Further, the resultant dynamics is given by the automorphisms $\hat{\alpha}_\theta(R)$, dual to $F$, defined by Eq. (3.8).

We note here that, apart from its intrinsic significance, the completeness condition plays a key role in the derivation of the differentiability of entropy, which, in turn, represents consistency between the quantum and phenomenological pictures. This consistency appears to be nontrivial, since, in the phenomenological picture, this differentiability is just Caratheodory’s theorem, whereas in the quantum picture, it arises from Von Neumann’s formula (4.1) for the entropy, which appears to be quite different.

Finally, we remark that the theory presented here is centred on the entropy function, $s$, whereas the previous works on quantum thermodynamics are based largely on its Legendre transform $\phi$, which is just the reduced pressure function. A radical difference between the properties of $s$ and $\phi$ is that, while the former is differentiable, the latter is generally not so, as phase transitions occur at just those values of the control variables where the reduced
pressure is not differentiable [1].

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