CHAPTER 1

STATISTICAL MECHANICS OF THERMODYNAMIC PROCESSES

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This note is dedicated to H. Ezawa on the occasion of his 70^{th} birthday, with respect and affection.

1. Time-dependent thermodynamic processes

In this note we describe some results concerning non-relativistic quantum systems at positive temperature and density confined to macroscopically large regions, Λ, of physical space $\mathbb{R}^3$ which are under the influence of some local, time-dependent external forces. We are interested in asymptotic properties of such systems, as Λ increases to all of $\mathbb{R}^3$. It might thus appear natural to directly study such systems in the thermodynamic limit, $\Lambda \nearrow \mathbb{R}^3$. But for reasons of technical simplicity and ease of exposition we prefer to first consider finite systems and then extend our results to the thermodynamic limit. An important reference is [3]. Details of our results appear in [1,5,4].

The Hilbert space of pure state vectors of a system confined to Λ is denoted by $\mathcal{H}^\Lambda$, and its dynamics is generated by a *time-dependent* Hamiltonian H_t^Λ with the properties that H_t^Λ is a selfadjoint operator on $\mathcal{H}^\Lambda$, for each time t, that its domain of definition is time-independent, and that $\dot{H}_t^\Lambda = \frac{d}{dt} H_t^\Lambda$ is bounded by H_s^Λ, e.g. in the sense of Kato-Rellich [8], for arbitrary times t and s. If the sytem is in a state corresponding to a vector

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$\psi_s \in \mathcal{H}^\Lambda$, at time s, then its state vector, ψ_t, at time t is given by

$$\psi_t = U^\Lambda(t,s)\psi_s, \tag{1}$$

where $U^\Lambda(t,s)$ denotes the *unitary propagator* on $\mathcal{H}^\Lambda$. This operator is the solution of the equation

$$\frac{\partial}{\partial t}U^\Lambda(t,s) = -iH_t^\Lambda U^\Lambda(t,s) \tag{2}$$

with

$$U^\Lambda(s,s) = \mathbb{1} \tag{3}$$

and has the property that

$$U^\Lambda(t,s) = U^\Lambda(t,u)U^\Lambda(u,s), \tag{4}$$

for arbitrary pairs $(t,s),(t,u)$ and (u,s) of times. (We are using units such that Planck's constant $\hbar = 1$.)

The kinematics of the system is encoded in an algebra $\mathcal{F}^\Lambda$ of bounded operators on $\mathcal{H}^\Lambda$ with the properties that

$$\mathcal{F}^\Lambda \subseteq \mathcal{B}(\mathcal{H}^\Lambda), \tag{5}$$

and

$$U^\Lambda(s,t)AU^\Lambda(t,s) \in \mathcal{F}^\Lambda, \tag{6}$$

for all $A \in \mathcal{F}^\Lambda$ and all times s,t.

The time evolution of a time-dependent family of operators

$$\{A_t\}_{t\in\mathbb{R}} \subset \mathcal{F}^\Lambda$$

in the *Heisenberg picture* is given by

$$A(t) := U^\Lambda(t_0,t)A_tU^\Lambda(t,t_0) \tag{7}$$

where t_0 denotes the "initial time"; (e.g., the time when an experiment involving the system is started). We also denote the r.h.s. of (7) by

$$\alpha^\Lambda_{t_0,t}(A_t). \tag{8}$$

Then

$$A(t) = \alpha^\Lambda_{t_0,t}(A_t) = \alpha^\Lambda_{t_0,t_1} \circ \alpha^\Lambda_{t_1,t}(A_t), \tag{9}$$

for an arbitrary time t_1. One easily verifies that

$$\frac{d}{dt}A(t) = \alpha^\Lambda_{t_0,t}\left(\frac{DA_t}{Dt}\right), \tag{10}$$

where the *Heisenberg derivative*, DA_t/Dt, is defined by

$$\frac{DA_t}{Dt} = i[H_t^\Lambda, A_t] + \dot{A}_t. \tag{11}$$

We assume that the Hamiltonians H_t^Λ are of the form

$$H_t^\Lambda = H_0^\Lambda + W_t, \tag{12}$$

where the term W_t describes a time-dependent perturbation of the system. When this perturbation is turned off the propagator is given by the unitary group $\{e^{itH_0^\Lambda}\}_{t\in\mathbb{R}}$ on $\mathcal{H}^\Lambda$ implementing the Heisenberg time evolution

$$\alpha_t^{0,\Lambda}(A_t) := e^{itH_0^\Lambda} A_t e^{-itH_0^\Lambda}. \tag{13}$$

The unperturbed system may exhibit a group of dynamical internal symmetries unitarily represented on $\mathcal{H}^\Lambda$. For reasons of simplicity of our exposition, we assume that the symmetry group is a connected compact Lie group $\mathcal{G}$. Let $\mathcal{Z}$ denote an n-dimensional continuous connected subgroup contained in or equal to the centre of the group $\mathcal{G}$, and let $Q_1^\Lambda, \dots, Q_n^\Lambda$ denote the generators of the unitray representation of $\mathcal{Z}$ on $\mathcal{H}^\Lambda$. The operators $Q_1^\Lambda, \dots Q_n^\Lambda$ are selfadjoint operators on $\mathcal{H}^\Lambda$ with

$$[Q_i^\Lambda, Q_j^\Lambda] = 0, \quad \text{for all } i, j = 1, \dots, n, \tag{14}$$

(in the sense that their spectral projections commute), and, since $\mathcal{G}$ has been assumed to be a group of *dynamical* symmetries,

$$e^{i\boldsymbol{\tau}\cdot\boldsymbol{Q}^\Lambda} e^{itH_0^\Lambda} = e^{itH_0^\Lambda} e^{i\boldsymbol{\tau}\cdot\boldsymbol{Q}^\Lambda}, \tag{15}$$

for arbitrary $\boldsymbol{\tau} = (\tau_1, \dots, \tau_n)$ and arbitrary t; (here $\boldsymbol{\tau}\cdot\boldsymbol{Q}^\Lambda := \sum_{j=1}^n \tau_j Q_j^\Lambda$). We define *gauge transformations of the first kind* by

$$\phi_{\boldsymbol{\tau}}^\Lambda(A) := e^{i\boldsymbol{\tau}\cdot\boldsymbol{Q}^\Lambda} A e^{-i\boldsymbol{\tau}\cdot\boldsymbol{Q}^\Lambda}, \tag{16}$$

for arbitrary $A \in \mathcal{F}^\Lambda$. It is assumed that $\phi_{\boldsymbol{\tau}}^\Lambda$ are $*$automorphisms of $\mathcal{F}^\Lambda$. We define the C^*-algebra $\mathcal{A}^\Lambda$ of "observables" to be the fixed-point subalgebra of the algebra $\mathcal{F}^\Lambda$ with respect to the automorphism group $\{\phi_{\boldsymbol{\tau}}^\Lambda\}_{\boldsymbol{\tau}\in\mathbb{R}^n}$; i.e.,

$$\mathcal{A}^\Lambda := \{A \in \mathcal{F}^\Lambda \mid \phi_{\boldsymbol{\tau}}^\Lambda(A) = A, \ \forall\boldsymbol{\tau}\}. \tag{17}$$

Mixed states of the system are described by *density matrices*, ϱ, on $\mathcal{H}^\Lambda$, (i.e., by non-negative trace-class operators with $\mathrm{tr}\varrho = 1$). If the perturbation W_t of the system vanishes, i.e.,

$$H_t^\Lambda = H_0^\Lambda, \quad \text{for all times } t, \tag{18}$$

then the notion of *thermal equilibrium* of the system is meaningful. At *inverse temperature* β and *chemical potentials* $\mu_1, \ldots, \mu_n$, the equilibrium state is given by the density matrix

$$\varrho_{\beta,\boldsymbol{\mu}} := \left(\Xi^{\Lambda}_{\beta,\boldsymbol{\mu}}\right)^{-1} \exp -\beta[H_0^{\Lambda} - \boldsymbol{\mu} \cdot \boldsymbol{Q}^{\Lambda}]. \tag{19}$$

It is assumed, here, that $\exp -\beta[H_0^{\Lambda} - \boldsymbol{\mu} \cdot \boldsymbol{Q}^{\Lambda}]$ is trace-class, for arbitrary $\beta > 0$, $\boldsymbol{\mu} \in \mathbb{R}^n$; the normalization factor $\Xi^{\Lambda}_{\beta,\boldsymbol{\mu}}$, the so-called *grand partition function*, is chosen such that $\mathrm{tr}\varrho_{\beta,\boldsymbol{\mu}} = 1$, and one commonly assumes that the system is *thermodynamically stable*, in the sense that the thermodynamic potential, G^{Λ}, given by

$$\beta G^{\Lambda}(\beta, \boldsymbol{\mu}) := -\ln \Xi^{\Lambda}_{\beta,\boldsymbol{\mu}} \tag{20}$$

is *extensive*, i.e., bounded in absolute value by a constant times the volume of Λ, for arbitrary $\beta > 0, \boldsymbol{\mu} \in \mathbb{R}^n$, and $\Lambda \nearrow \mathbb{R}^3$.

If, at time t_0, the system is in a mixed state $\varrho(t_0)$ then its state at time t is given by the density matrix

$$\varrho(t) = U^{\Lambda}(t, t_0)\varrho(t_0)U^{\Lambda}(t_0, t) = \alpha^{\Lambda}_{t,t_0}(\varrho(t_0)). \tag{21}$$

Then, using equations (7) and (21), we find that

$$\langle A_t \rangle_{\varrho(t)} := \mathrm{tr}\,(\varrho(t)A_t) = \mathrm{tr}\,(\varrho(t_0)A(t)) =: \langle A(t)\rangle_{\varrho(t_0)}, \tag{22}$$

as expected.

The *entropy* of a state given by a density matrix ϱ is defined by

$$S(\varrho) = -\mathrm{tr}\,(\varrho \ln \varrho)\,. \tag{23}$$

(We use units such that Boltzmann's constant $k_B = 1$.)

Since $U^{\Lambda}(t, t_0)$ is unitary, for arbitrary t, t_0, it follows from (21) and the cyclicity of the trace that

$$S(\varrho(t)) = S(\varrho(t_0)), \tag{24}$$

for arbitrary t, t_0.

Next, we introduce the notion of a (time-dependent) *thermodynamic process*. We imagine that, for all times $t \le t_0$, the Hamiltonian $H_t^{\Lambda} = H_{t_0}^{\Lambda} =: H_0^{\Lambda}$ is *independent* of time t, and that the initial state at time t_0 of the system is given by an *equilibrium state* $\varrho_{\beta,\boldsymbol{\mu}} =: \varrho_{\beta,\boldsymbol{\mu}}(t_0)$, as defined in equation (19), for some inverse temperature β and chemical potentials $\boldsymbol{\mu}$. We are interested in studying the effects of *local, external perturbations* acting on the system. In order to make more precise what we are talking about, we assume that the systems considered in this note have a *local structure*:

if Λ_0 is an arbitrary convex subset of the convex region Λ containing the system, and $\Lambda \backslash \Lambda_0$ denotes its complement then the Hilbert space $\mathcal{H}^{\Lambda}$ of the system can be factorized into

$$\mathcal{H}^{\Lambda} = \mathcal{H}^{\Lambda_0} \otimes \mathcal{H}^{\Lambda \backslash \Lambda_0},$$

where $\mathcal{H}^{\Lambda_0}$ can be interpreted as the Hilbert space of pure state vectors of the degrees of freedom localized in Λ_0. Let $\mathcal{F}^{\Lambda_0} \subseteq \mathcal{B}(\mathcal{H}^{\Lambda_0})$ be the kinematical algebra associated to the region Λ_0, see (5). Then the subalgebra

$$\mathcal{F}^{\Lambda_0} \otimes \mathbb{1}|_{\mathcal{H}^{\Lambda \backslash \Lambda_0}} \subset \mathcal{F}^{\Lambda} \tag{25}$$

is naturally identified with $\mathcal{F}^{\Lambda_0}$. Without any essential loss of generality, we may assume that the gauge transformations $\phi^{\Lambda}_{\boldsymbol{\tau}}$ introduced in equation (16) leave the subalgebra $\mathcal{F}^{\Lambda_0}$ of $\mathcal{F}^{\Lambda}$ invariant, and when restricted to $\mathcal{F}^{\Lambda_0}$ coincide with $\phi^{\Lambda_0}_{\boldsymbol{\tau}} \otimes \mathrm{id}|_{\mathrm{Aut}(\mathcal{F}^{\Lambda \backslash \Lambda_0})}$. Then the algebra $\mathcal{A}^{\Lambda_0}$ can be identified with

$$\{A \in \mathcal{F}^{\Lambda_0} \mid \phi^{\Lambda}_{\boldsymbol{\tau}}(A) = A\} \tag{26}$$

and will be viewed as a subalgebra of $\mathcal{A}^{\Lambda}$, for arbitrary $\Lambda_0 \subset \Lambda$.

In the following, we shall keep $\Lambda_0 \subset \Lambda$ fixed and view the degrees of freedom localized in Λ_0 as a finite subsystem of the entire system, while the regions Λ will be let to increase to $\mathbb{R}^3$, eventually.

The interaction term W_t, given in (12), describes the dynamical effects of an external perturbation acting on the system and is assumed to have the following properties:

(i) $W_t = 0$, for $t < t_0$; and
(ii) W_t is *local* in the sense that $W_t \in \mathcal{F}^{\Lambda_0}$, for all times t, where Λ_0 is an arbitrary, but fixed bounded, convex subset of $\mathbb{R}^3$ (*independent* of t).

A thermodynamic process is *charge-conserving* iff W_t is *gauge-invariant*, i.e., $W_t \in \mathcal{A}^{\Lambda_0}$, for all times t.

Later, we shall also assume that W_t is *small* in the sense that a suitable norm of W_t is assumed to be small, *uniformly* in t.

The perturbation W_t may describe, for example, the effects of shining a focussed beam of light into the system, or of local, time-dependent variations of an external magnetic field applied to the system, or of the motion of a piston confining particles to a time-dependent subset, Λ_t, of Λ, with $\Lambda \backslash \Lambda_t \subseteq \Lambda_0$. Thus, W_t is typically of the form

$$W_t = W(\boldsymbol{\lambda}(t)), \tag{27}$$

where $\boldsymbol{\lambda} = (\lambda_1, \ldots, \lambda_k)$ is a finite set of *external control parameters*, and the time-dependence of W_t is entirely due to a possible time-dependence of the control parameters $\boldsymbol{\lambda}$.

If the ratio volume(Λ_0):volume(Λ) is very small the subsystem in the region $\Lambda \backslash \Lambda_0$ can be interpreted as a *thermostat* for the small subsystem in Λ_0, keeping the values of the temperature and the chemical potentials constant throughout a thermodynamic process. Since we have assumed that the initial state, $\varrho(t_0) = \varrho_{t_0}$, of the entire system at time t_0 is an equilibrium state,

$$\varrho(t_0) = \varrho_{t_0} = \varrho_{\beta,\boldsymbol{\mu}}, \tag{28}$$

as defined in equation (19), with $H^\Lambda_{t_0} = H^\Lambda_0$, we are studying thermodynamic processes at constant temperature β^{-1} and constant chemical potentials $\boldsymbol{\mu}$; (at least after passing to the thermodynamic limit $\Lambda \nearrow \mathbb{R}^3$, with Λ_0 kept fixed).

The *true state* of the system at time t is given by

$$\varrho(t) = \alpha^\Lambda_{t,t_0}(\varrho(t_0)), \tag{29}$$

see equation (21). If the time-dependence of the perturbation $W_t = W(\boldsymbol{\lambda}(t))$ is *slow* it is of interest to compare the true state $\varrho(t)$ of the system with a reference state, ϱ_t, given by

$$\varrho_t := e^{\beta G^\Lambda(\beta,\boldsymbol{\mu};\boldsymbol{\lambda}(t))} \exp -\beta \left[H^\Lambda_t - \boldsymbol{\mu} \cdot \boldsymbol{Q}^\Lambda \right], \tag{30}$$

where

$$\beta G^\Lambda(\beta, \boldsymbol{\mu}; \boldsymbol{\lambda}(t)) = -\ln \mathrm{tr} \left(\exp -\beta \left[H^\Lambda_t - \boldsymbol{\mu} \cdot \boldsymbol{Q}^\Lambda \right] \right), \tag{31}$$

and $\boldsymbol{\lambda}(t)$ are the time-dependent control parameters that give rise to the time-dependence of $H^\Lambda_t = H^\Lambda_0 + W(\boldsymbol{\lambda}(t))$. We shall call the state ϱ_t in equation (30) the *reference state* at time t.

An important quantity in the characterization of thermodynamic processes is the *relative entropy* of the reference state ϱ_t with respect to the true state $\varrho(t)$ of the system, which is given by

$$S(\varrho_t | \varrho(t)) := -\mathrm{tr} \left(\varrho(t) [\ln \varrho_t - \ln \varrho(t)] \right) = -\mathrm{tr} \ (\varrho(t) \ln \varrho_t) - S(\varrho(t)), \tag{32}$$

where the entropy $S(\varrho(t))$ of $\varrho(t)$ has been defined in (23). If A is a non-negative trace-class operator and B is a strictly positive trace-class operator then

$$-\mathrm{tr} \ (A \ln B - A \ln A) \geq \mathrm{tr} \ (A - B) \, ;$$

see e.g. Lemma 6.2.21 of [3]. Setting $A = \varrho(t)$ and $B = \varrho_t$, and using that $\mathrm{tr}\,\varrho(t) = \mathrm{tr}\,\varrho_t = 1$, we conclude that

$$S(\varrho_t|\varrho(t)) \geq 0, \tag{33}$$

for all times t. By equation (24),

$$S(\varrho(t)) = S(\varrho(t_0)) =: S(t_0). \tag{34}$$

It then follows from (32) and (33) that

$$S(t) := -\mathrm{tr}\left(\varrho(t)\ln\varrho_t\right) \geq S(t_0), \tag{35}$$

for all times $t \geq t_0$. Next, we note that, by equation (30),

$$S(t) = \beta\left[\left\langle H_t^\Lambda - \boldsymbol{\mu}\cdot\boldsymbol{Q}^\Lambda\right\rangle_{\varrho(t)} - G(\beta,\boldsymbol{\mu};\boldsymbol{\lambda}(t))\right]. \tag{36}$$

It is natural to define the *internal energy*, $U^\Lambda(t)$, of the sytem at time t by

$$U^\Lambda(t) := \left\langle H_t^\Lambda\right\rangle_{\varrho(t)}, \tag{37}$$

and the various *charge densities* by

$$q_j^\Lambda(t) := \left\langle Q_j^\Lambda\right\rangle_{\varrho(t)}. \tag{38}$$

Dropping superscripts Λ, it follows that

$$G = U - \boldsymbol{\mu}\cdot\boldsymbol{q} - TS, \tag{39}$$

which is the usual relation between the Gibbs potential G and the internal energy, charge densities and the entropy. All these quantities are *extensive* and, hence, do not have a limit, as Λ increases to $\mathbb{R}^3$. It is more useful to consider their *time derivatives.* Taking the time derivative of equation (36) it follows that

$$\dot{S}(t) = \beta\dot{U}(t) - \beta\boldsymbol{\mu}\cdot\dot{\boldsymbol{q}}(t) - \beta\frac{\partial G}{\partial\boldsymbol{\lambda}}\cdot\dot{\boldsymbol{\lambda}}(t). \tag{40}$$

The combination

$$đA := -\boldsymbol{\mu}\cdot d\boldsymbol{q} - \frac{\partial G}{\partial\boldsymbol{\lambda}}\cdot d\boldsymbol{\lambda} \tag{41}$$

is commonly interpreted as the *work* done by the system during a change of state. Hence we conclude that

$$\dot{U} = T\dot{S} - \frac{đA}{dt}, \tag{42}$$

which summarizes the first and second law of thermodynamics (for *reversible processes*).

It is important to notice that, under our assumptions on the perturbation operator $W_t = W(\boldsymbol{\lambda}(t))$, the quantities

$$\dot{U}^\Lambda(t), \dot{\boldsymbol{q}}^\Lambda(t) \quad \text{and} \quad (\partial G^\Lambda/\partial\boldsymbol{\lambda}) \cdot \dot{\boldsymbol{\lambda}}(t)$$

have finite thermodynamic limits. By equations (29) and (37), and because

$$\frac{DH_t^\Lambda}{Dt} = \dot{H}_t^\Lambda = \dot{W}_t = \frac{\partial W(\boldsymbol{\lambda}(t))}{\partial\boldsymbol{\lambda}} \cdot \dot{\boldsymbol{\lambda}}(t)$$

it follows that

$$\dot{U}^\Lambda(t) = \left\langle \frac{\partial W(\boldsymbol{\lambda}(t))}{\partial\boldsymbol{\lambda}} \right\rangle_{\varrho(t)} \cdot \dot{\boldsymbol{\lambda}}(t). \tag{43}$$

Similarly,

$$\begin{aligned} \dot{\boldsymbol{q}}^\Lambda(t) &= \left\langle \frac{D\boldsymbol{Q}^\Lambda}{Dt} \right\rangle_{\varrho(t)} \\ &= i\Big\langle [W(\boldsymbol{\lambda}(t)), \boldsymbol{Q}^\Lambda] \Big\rangle_{\varrho(t)} = -\frac{\partial}{\partial\boldsymbol{\tau}} \Big\langle \phi_{\boldsymbol{\tau}}^\Lambda\Big(W(\boldsymbol{\lambda}(t))\Big) \Big\rangle_{\varrho(t)} \Big|_{\boldsymbol{\tau}=0}, \end{aligned} \tag{44}$$

where the gauge transformations $\phi_{\boldsymbol{\tau}}^\Lambda$ have been defined in equation (16). Under our hypotheses on $W(\boldsymbol{\lambda}(t))$, the operators $\frac{\partial W(\boldsymbol{\lambda}(t))}{\partial\boldsymbol{\lambda}}$ and $\frac{\partial\phi_{\boldsymbol{\tau}}^\Lambda(W(\boldsymbol{\lambda}(t)))}{\partial\boldsymbol{\tau}}$ are strictly *local*, in the sense that they are elements of the algebra $\mathcal{F}^{\Lambda_0} \subset \mathcal{F}^\Lambda$, see (25), and *independent* of Λ. In the next section, we shall see that the propagators in the *interaction picture*

$$U^{I,\Lambda}(t,s) := e^{itH_0^\Lambda} U^\Lambda(t,s) e^{-isH_0^\Lambda}$$

have thermodynamic limits, as $\Lambda \nearrow \mathbb{R}^3$, under standard assumptions on the unperturbed evolution generated by H_0^Λ. If expectations of local, bounded operators in the initial state, $\varrho_{t_0} = \varrho_{\beta,\boldsymbol{\mu}}$, of the system have thermodynamic limits, as $\Lambda \nearrow \mathbb{R}^3$, which is a standard assumption (or result – see [3] for examples –) then it follows that the thermodynamic limit of the quantities on the r.h.s. of equations (43) and (44) exist.

Finally, from the definition of G^Λ, equation (31), and using the cyclicity of the trace, we find that

$$\frac{\partial G^\Lambda}{\partial\boldsymbol{\lambda}}(\beta, \boldsymbol{\mu}; \boldsymbol{\lambda}(t)) \cdot \dot{\boldsymbol{\lambda}}(t) = \left\langle \dot{H}_t^\Lambda \right\rangle_{\varrho_t} = \left\langle \frac{\partial W(\boldsymbol{\lambda}(t))}{\partial\boldsymbol{\lambda}} \right\rangle_{\varrho_t} \cdot \dot{\boldsymbol{\lambda}}(t),$$

hence

$$\frac{\partial G}{\partial\boldsymbol{\lambda}}(\beta, \mu; \boldsymbol{\lambda}(t)) = \left\langle \frac{\partial W(\boldsymbol{\lambda}(t))}{\partial\boldsymbol{\lambda}} \right\rangle_{\varrho_t}, \tag{45}$$

which, under the same standard assumptions, has a well defined thermodynamic limit. We have thus proven the equation

$$\dot{S}(t) = \beta \left[\left\langle \frac{\partial W(\boldsymbol{\lambda}(t))}{\partial \boldsymbol{\lambda}} \right\rangle_{\varrho(t)} - \left\langle \frac{\partial W(\boldsymbol{\lambda}(t))}{\partial \boldsymbol{\lambda}} \right\rangle_{\varrho_t} \right] \cdot \dot{\boldsymbol{\lambda}}(t) + \beta \boldsymbol{\mu} \cdot \frac{\partial}{\partial \boldsymbol{\tau}} \left\langle \phi_{\boldsymbol{\tau}}^{\Lambda} \left(W(\boldsymbol{\lambda}(t)) \right) \right\rangle_{\varrho(t)} \Big|_{\boldsymbol{\tau}=0} \tag{46}$$

for the rate of change in time of the entropy $S(t)$, and we have convinced ourselves that all three terms on the r.h.s. of equation (46) have well defined thermodynamic limits.

Returning to equations (32), (33) and (35), one may ask under what conditions the inequalities in (33) and (35) are saturated. The answer is given in Lemma 6.2.21 of [3]:

$$S(\varrho_t|\varrho(t)) = 0 \quad \text{iff} \quad \varrho_t = \varrho(t), \tag{47}$$

i.e., iff the reference state ϱ_t coincides with the true state $\varrho(t)$. In view of equation (46) one may expect that a similar result holds in the thermodynamic limit. Equation (46) proves that the thermodynamic limit of

$$\Delta S(t) := S(t) - S(t_0) = \int_{t_0}^{t} \dot{S}(t')dt' \tag{48}$$

exists, and one expects that if $\Delta S(t) = 0$ then the true state of the system at time t is given by the thermodynamic limit of the reference states ϱ_t; (see [4]). Furthermore, if, at time t, the restrictions of the true and the reference state to the subalgebra $\mathcal{F}^{\Lambda_0}$ coincide in the thermodynamic limit then $\Delta\dot{S}(t) = \dot{S}(t) = 0$, as follows from equation (46).

Of course, if W_t depends non-trivially on time t, for $t > t_0$, there is no reason why the true and the reference state should ever coincide at times $t > t_0$. Then a relevant and interesting problem is to study the rate of change of the entropy under the assumption that the perturbation W_t depends slowly on time,

$$W_t = W(\boldsymbol{\lambda}(t/T)),$$

for some large T. In this situation one would like to prove an *adiabatic theorem* yielding sharp estimates on the rate at which $\dot{S}(t)$ tends to 0, as $T \to \infty$. More interestingly, such a theorem would tell us at which rate the differences of expectation values of local operators in the true state and in the reference state tend to 0, as $T \to \infty$. In this note we shall not address this problem.

The essential features of our definition of the entropy $S(t)$ can be summarized as follows:

(1) It is compatible with the first and second law of thermodynamics; see equations (40)-(42).

(2) $S(t) \geq S(t_0)$, for all $t \geq t_0$, i.e., entropy tends to increase.

(3) The thermodynamic limit of $\dot{S}(t)$, and hence of $\Delta S(t) = S(t) - S(t_0)$ exists, for all times t.

(4) If the time evolution is *adiabatic*, in the sense that the norm of the difference of the restrictions of the true and of the reference state to the algebra $\mathcal{F}^{\Lambda_0}$ is bounded by some small, positive number $\epsilon > 0$, for all times $t \leq t_1$, then $|\dot{S}(t)| < O(\epsilon)$ and $\Delta S(t) < O(\epsilon)$, for $t \leq t_1$, i.e., the entropy remains approximately constant. For more detail, see [5].

In the following, we consider two typical examples of time-dependent thermodynamic processes.

Process (I). The perturbation W_t converges to a limiting operator $W_\infty \neq 0$, as $t \to \infty$, with

$$\int^\infty \|W_t - W_\infty\| dt < \infty. \tag{49}$$

For such perturbations we study the phenomenon of *return to equilibrium*: Under suitable assumptions on the unperturbed dynamics in the thermodynamic limit ("dispersiveness") and assuming that a suitable norm of W_∞ is small enough, we show that, in the thermodynamic limit, the true state of the system converges to an equilibrium state w.r.t. the dynamics determined by $H^\Lambda_\infty = H^\Lambda_0 + W_\infty$ at temperature β^{-1}, as $t \to \infty$, if the initial state is an equilibrium state of the unperturbed dynamics at temperature β^{-1} or a local perturbation thereof. For earlier results, see [11,7,1]. Our analysis is an extension of results in [6,11,2] and is based on methods developed in [4].
The result described here is a kind of adiabatic theorem and shows that thermodynamic processes with perturbations W_t as specified above are *reversible*. It implies that, in the thermodynamic limit,

$$\lim_{t\to\infty} \dot{S}(t) = 0, \quad \text{and hence} \quad \lim_{t\to\infty} \lim_{\Lambda \nearrow \mathbb{R}^3} \dot{\boldsymbol{q}}^\Lambda(t) = 0, \tag{50}$$

i.e., the entropy production rate and the rate of change of the charges $\boldsymbol{q}^\Lambda(t)$ vanish in the thermodynamic limit, as time tends to infinity.

Process (II). For $t \geq t_0$, the perturbation W_t depends *periodically* on time t, with period T, see [9], and [10,12] for recent experiments involving time-periodic perturbations. Under the same assumptions on the unperturbed dynamics in the thermodynamic limit as in (I) and if a suitable norm of W_t is small enough, for all $t \in [t_0, t_0 + T]$, we prove that, in the thermodynamic limit, the true state of the system converges to a *time-periodic state* of period T, as time t tends to infinity. It is not hard to generalize this to perturbations W_t with the property that

$$\int^{\infty} \|W_t - W_t^{\infty}\| dt < \infty, \tag{51}$$

where W_t^{∞} is periodic in t with some period T.

2. Processes (I) and (II) in the thermodynamic limit

In this section we study the thermodynamic limit, $\Lambda \nearrow \mathbb{R}^3$, of thermodynamic processes, in particular of processes (I) and (II) described at the end of Section 1. It is convenient to introduce a C^*-algebra, $\mathcal{F}$, of operators for the infinite system. We define

$$\mathring{\mathcal{F}} = \bigvee_{\Lambda \nearrow \mathbb{R}^3} \mathcal{F}^{\Lambda} \tag{52}$$

to be the algebra generated by all the algebras $\mathcal{F}^{\Lambda}$, for an increasing sequence of bounded convex regions $\Lambda \nearrow \mathbb{R}^3$. The C^*-algebra $\mathcal{F}$ is defined as the closure of $\mathring{\mathcal{F}}$ in the operator norm. For an operator $A \in \mathcal{F}^{\Lambda}$ and a set $\Lambda' \supseteq \Lambda$, one can define

$$\alpha_t^{0,\Lambda'}(A) := e^{itH_0^{\Lambda'}} A e^{-itH_0^{\Lambda'}}. \tag{53}$$

It is a standard assumption (that can be verified in physically relevant examples – see Section 3) that the norm-limit

$$n - \lim_{\Lambda' \nearrow \mathbb{R}^3} \alpha_t^{0,\Lambda'}(A) =: \alpha_t^0(A) \tag{54}$$

exists, for all $A \in \mathcal{F}^{\Lambda}$, for an arbitrary bounded convex set $\Lambda \subset \mathbb{R}^3$. Since $\alpha_t^{0,\Lambda'}(A)$ belongs to $\mathcal{F}^{\Lambda'}$, it follows that $\alpha_t^0(A) \in \mathcal{F}$. By continuity, α_t^0 can be extended to a $*$automorphism group of the C^*-algebra $\mathcal{F}$.

For a finite system confined to a region $\Lambda \supset \Lambda_0$, we define the *propagator in the interaction picture* by

$$U^{I,\Lambda}(t,s) := e^{itH_0^{\Lambda}} U^{\Lambda}(t,s) e^{-isH_0^{\Lambda}}. \tag{55}$$

Assuming that the perturbation W_t is norm-continuous in t, we can expand $U^{I,\Lambda}(t,s)$ in a Dyson series that converges in norm, uniformly in Λ, and with the property that all terms in the series have a thermodynamic limit. Setting

$$W_t^{I,\Lambda} := \alpha_t^{0,\Lambda}(W_t),$$

and

$$W_t^I := \alpha_t^0(W_t), \tag{56}$$

we find that

$$U^{I,\Lambda}(t,s) = \mathbb{1} + \sum_{n\geq 1}(-i)^n \int_s^t dt_1 \cdots \int_s^{t_{n-1}} dt_n \; W_{t_1}^{I,\Lambda} \cdots W_{t_n}^{I,\Lambda}$$

and this operator converges in norm to

$$U^I(t,s) = \mathbb{1} + \sum_{n\geq 1}(-i)^n \int_s^t dt_1 \cdots \int_s^{t_{n-1}} dt_n \; W_{t_1}^I \cdots W_{t_n}^I, \tag{57}$$

as $\Lambda \nearrow \mathbb{R}^3$. The propagator $U^I(t,s)$ solves the differential equation

$$\begin{array}{c} \frac{\partial}{\partial t} U^I(t,s) = -iW_t^I U^I(t,s), \\ U^I(s,s) = \mathbb{1} \end{array} \tag{58}$$

and $U^I(t,s) \in \mathcal{F}$, for all finite times t, s.

These remarks enable us to define the time evolution of an operator $A \in \mathcal{F}$ in the Heisenberg picture from time s to time t by

$$\alpha_{s,t}(A) = n - \lim_{\Lambda \nearrow \mathbb{R}^3} \alpha_{s,t}^\Lambda(A) = \alpha_{-s}^0\left(U^I(s,t)\alpha_t^0(A)U^I(t,s)\right); \tag{59}$$

see equations (55) and (8). Equation (59) shows that $\alpha_{s,t}$ is a $*$automorphism of the algebra $\mathcal{F}$, for arbitrary times s and t, with

$$\alpha_{s,t} = \alpha_{s,t'} \circ \alpha_{t',t}.$$

Next, we describe two key hypotheses enabling us to study thermodynamic processes, such as processes (I) and (II) described at the end of Section 1, in the thermodynamic limit.

Hypothesis (A) There is a class $\mathcal{W}$ of (time-dependent) interactions s.t. the $*$automorphisms α_t^0 and $\alpha_{s,t}$, defined in (54) and (59), with $W_t \in \mathcal{W}$, satisfy the following property: for arbitrary $A \in \mathcal{F}$,

$$n - \lim_{s \to \mp\infty} \alpha_s^0(\alpha_{s,0}(A)) =: \sigma_\pm(A) \tag{60}$$

exists and defines a $*$endomorphism of $\mathcal{F}$.

Hypothesis (B) For $H_{t_0}^{\Lambda} = H_0^{\Lambda}$, the thermodynamic limit of the equilibrium states $\varrho_{\beta,\boldsymbol{\mu}}$ defined in equation (19) exists on the C^*-algebra $\mathcal{F}$ and satisfies the KMS condition (see e.g. [3,4]), for arbitrary $\beta > 0$, $\boldsymbol{\mu} \in \mathbb{R}^n$.

These two hypotheses can be verified in some simple, but physically relevant examples; see Section 3 and [4]. We now use them to discuss processes (I) and (II). Let

$$\omega^0 = \omega_{\beta,\boldsymbol{\mu}} \tag{61}$$

denote the state of $\mathcal{F}$ obtained as the thermodynamic limit of the equilibrium states $\varrho_{\beta,\boldsymbol{\mu}}$ of equation (19). We are interested in understanding the time dependence of the states

$$\omega_t(A) := \omega^0(\alpha_{t_0,t}(A)), \qquad A \in \mathcal{F}. \tag{62}$$

We first study this problem for **process (I)**, with a limiting interaction $W_\infty \in \mathcal{W}$. Let $\alpha_{s,t}^{\infty} \equiv \alpha_{t-s}^{\infty}$ denote the $*$automorphism of $\mathcal{F}$ constructed in equation (59) in the example where $H_t^{\Lambda} = H_0^{\Lambda} + W_\infty$, for all t; (H_t^{Λ} is then time-independent, hence $\alpha_{s,t}^{\infty} \equiv \alpha_{t-s}^{\infty}$ only depends on time differences). We consider the operator

$$\mathcal{E}_A(t,s) := \alpha_{t_0,t}(\alpha_{s-t}^{\infty}(A)). \tag{63}$$

The fundamental theorem of calculus yields

$$\mathcal{E}_A(t,s) = \mathcal{E}_A(t_0,s) + \int_{t_0}^{t} \mathcal{E}_A{}'(u,s)du,$$

with

$$\mathcal{E}_A{}'(u,s) := \frac{\partial}{\partial u}\mathcal{E}_A(u,s) = i\alpha_{t_0,u}\left([W_u - W_\infty, \alpha_{s-u}^{\infty}(A)]\right). \tag{64}$$

Note that

$$\|\mathcal{E}_A{}'(u,s)\| \leq 2\|A\|\,\|W_u - W_\infty\|, \tag{65}$$

and the r.h.s. in (65) tends to 0, as $u \to \infty$, at an integrable rate, see (49). Hence

$$\mathcal{E}_A(t,s) = \alpha_{s-t_0}^{\infty}(A) + i\int_{t_0}^{t} du\ \alpha_{t_0,u}\left([W_u - W_\infty, \alpha_{s-u}^{\infty}(A)]\right). \tag{66}$$

Since ω^0 is invariant under the unperturbed time evolution α_t^0 (see equation (54), (61)), it follows that

$$\omega^0(\mathcal{E}_A(t,s)) = \omega^0(\alpha_{t_0-s}^{0}(\alpha_{s-t_0}^{\infty}(A)) + i\int_{t_0}^{t} du\ \omega_u\left([W_u - W_\infty, \alpha_{s-u}^{\infty}(A)]\right), \tag{67}$$

see (64), (62), and the integral on the r.h.s. of (67) converges uniformly in t.

By Hypothesis (A),

$$\lim_{s\to\infty} \omega^0(\alpha^0_{t_0-s}(\alpha^\infty_{s-t_0}(A)) = \omega^0(\sigma_+(A)) \tag{68}$$

exists, for arbitrary $A \in \mathcal{F}$. Furthermore, for arbitrary $u < \infty$,

$$\lim_{s\to\infty} \omega_u \left([W_u - W_\infty, \alpha^\infty_{s-u}(A)]\right) = \lim_{s\to\infty} \omega_u \left([W_u - W_\infty, \alpha^0_{s-u}(\sigma_+(A))]\right),$$

again by Hypothesis (A), and it follows from the property of return to equilibrium for the unperturbed time evolution, α^0_s, that

$$\omega_u \left([W_u - W_\infty, \alpha^0_{s-u}(\sigma_+(A))]\right) \to 0, \tag{69}$$

as $s \to \infty$; see Section 3 for an example where return to equilibrium holds for α^0_s, and [7,4].

In conclusion, the limit

$$\lim_{t\to\infty} \omega^0(\alpha_{t_0,t}(A)) = \lim_{t\to\infty} \omega^0(\mathcal{E}_A(t,t)) = \omega^0(\sigma_+(A)), \quad A \in \mathcal{F}, \tag{70}$$

exists, by equations (66), (68) and (69). It is known from [3] that the state $\omega^0(\sigma_+(\cdot))$ is an equilibrium (i.e. KMS) state for the asymptotic dynamics α^∞_t.

We note that equation (70) is valid for any initial state ω^0 which is invariant under α^0_t and has the property of return to equilibrium, see also Section 3. This completes our discussion of the thermodynamic process (I).

Next, we examine **process (II)**. Since we are interested in times $t \geq t_0$ we may consider the interaction W_t to be periodic with period T for *all* times, $W_{t+T} = W_t$, for $t \in \mathbb{R}$. It follows that

$$\alpha_{s,t}(A) = \alpha_{s+nT,t+nT}(A), \tag{71}$$

for arbitrary times s, t, $n \in \mathbb{Z}$ and $A \in \mathcal{F}$. Decomposing the time variable $t \in \mathbb{R}$ uniquely as $t = n(t)T + \tau(t)$, with $n(t) \in \mathbb{Z}$ and $\tau(t) \in [0,T)$ we obtain from (71) the equation

$$\alpha_{t_0,t}(A) = \alpha_{t_0-n(t)T,0}\left(\alpha_{0,\tau(t)}(A)\right).$$

The invariance of ω^0 under α^0_t and Hypothesis (A) then imply that

$$\lim_{t\to\infty} \left|\omega^0(\alpha_{t_0,t}(A)) - \omega^0\left(\sigma_+\left(\alpha_{0,\tau(t)}(A)\right)\right)\right| = 0, \tag{72}$$

for all $A \in \mathcal{F}$.

The state given by

$$\omega^P_t(A) := \omega^0\left(\sigma_+(\alpha_{0,\tau(t)}(A))\right), \quad A \in \mathcal{F},$$

is periodic in t with period T (because $t \mapsto \tau(t)$ is). This shows that ω_t approaches a *time-periodic* state as $t \to \infty$. Notice that (72) holds for an arbitrary α_t^0-invariant initial state ω^0.

Remark. The approach to the asymptotic state (which is stationary for Process (I) and time-periodic for Process (II)), for large times, holds for arbitrary initial states which are normal w.r.t. the state ω^0 given in (61). In other words, relations (70) and (72) hold if we replace $\omega^0(\alpha_{t_0,t}(A))$ by $\omega(\alpha_{t_0,t}(A))$, for any state ω on $\mathcal{F}$ which is normal w.r.t. ω^0. The proof can be found in [4].

3. Thermodynamic processes for a reservoir of non-relativistic non-interacting fermions

We consider an ideal quantum gas of fermionic particles, e.g. modelling non-interacting, non-relativistic electrons in a metal or a semi-conductor, subject to a time-dependent perturbation. For the purpose of exposition, we concentrate here on spinless fermions; a more general treatment can be found in [5,4].

The Hilbert space of pure states of the system confined to a bounded region $\Lambda \subset \mathbb{R}^3$ is given by the fermionic Fock space over $L^2(\Lambda, d^3x)$,

$$\mathcal{H}^\Lambda := F_-(L^2(\Lambda, d^3x)) = \bigoplus_{n\geq 0} P_- \left(L^2(\Lambda, d^3x)\right)^{\otimes n}, \tag{73}$$

where P_- denotes the projection operator onto the subspace of antisymmetric functions, and where the subspace for $n = 0$ is $\mathbb{C}$.

The non-interacting Hamiltonian is given by

$$H_0^\Lambda := \bigoplus_{n\geq 0} h_n^\Lambda, \tag{74}$$

where h_n^Λ acts on $P_-(L^2(\Lambda, d^3x))^{\otimes n}$ as

$$h_n^\Lambda = \sum_{k=1}^n \mathbb{1} \otimes \cdots \otimes \mathbb{1} \otimes (-\Delta) \otimes \mathbb{1} \cdots \otimes \mathbb{1},$$

and $-\Delta$ is the Laplacian on $L^2(\Lambda, d^3x)$ with selfadjoint (e.g. Dirichlet-, Neumann-, or periodic) boundary conditions, acting on the k-th factor. We set $h_0^\Lambda = 0$.

We define the field algebra as the CAR algebra (CAR for "canonical anti-commutation relations")

$$\mathcal{F}^\Lambda := \mathrm{CAR}\left(L^2(\Lambda, d^3x)\right),$$

which is the C^*-algebra generated by creation- and annihilation operators,

$$\{a^\#(f) \mid f \in L^2(\Lambda, d^3x)\}.$$

The symbol $a^\#$ denotes either a or a^*; recall that the annihilation operator $a(f)$ acts on a wave-function $\psi \in F_-(L^2(\Lambda, d^3x))$ as

$$(a(f)\psi)_n(x_1, \ldots, x_n) = \sqrt{n+1} \int \overline{f(x_{n+1})} \psi_{n+1}(x_1, \ldots, x_n, x_{n+1}) d^3x_{n+1},$$

where ψ_n is the projection of ψ onto the n-particle subspace of Fock space. The creation operators $a^*(f)$ (adjoint of $a(f)$) and annihilation operators satisfy the canonical anti-commutation relations

$$\begin{gathered}\{a(f), a^*(g)\} := a(f)a^*(g) + a^*(g)a(f) = \int \overline{f(x)} g(x) d^3x \\ \{a^*(f), a^*(g)\} = \{a(f), a(g)\} = 0,\end{gathered}$$

for any $f, g \in L^2(\Lambda, d^3x)$. Notice that the C^*-algebra $\mathcal{F}^\Lambda$ is weakly dense in $\mathcal{B}(\mathcal{H}^\Lambda)$,

$$\left(\mathcal{F}^\Lambda\right)'' = \mathcal{B}(\mathcal{H}^\Lambda)$$

(double commutant). The non-interacting Hamiltonian (74) generates a $*$automorphism group $\alpha_t^{0,\Lambda}$ of $\mathcal{F}^\Lambda$, according to formula (13), given by

$$\alpha_t^{0,\Lambda}\left(a^\#(f)\right) = a^\#(e^{-it\Delta} f), \quad f \in L^2(\Lambda, d^3x).$$

In this paper, we limit our discussion to only one dynamical symmetry, namely the one corresponding to the charge operator

$$N^\Lambda := \bigoplus_{n \geq 0} n \mathbb{1}\big|_{P_-(L^2(\Lambda, d^3x))^{\otimes n}}, \tag{75}$$

i.e., the particle number operator. We refer the reader to [5,4] for a discussion involving more general charges. It is obvious that the commutation relation (15) is satisfied for $\boldsymbol{Q}^\Lambda = N^\Lambda$ and H_0^Λ given by (75) and (74), and that the charge (75) generates a $*$automorphism group ϕ_τ^Λ on $\mathcal{F}^\Lambda$, according to (16). The observable algebra $\mathcal{A}^\Lambda$ defined in (26) corresponds to the C^*-algebra generated by monomials in creation- and annihilation operators (smeared out with functions in $L^2(\Lambda, d^3x)$) in which the number of creation operators equals the number of annihilation operators.

We take the initial state of the system, at some fixed time t_0, to be given by the density matrix

$$\varrho_{\beta,\mu} := \left(\Xi_{\beta,\mu}^\Lambda\right)^{-1} \exp -\beta\left[H_0^\Lambda - \mu N^\Lambda\right]. \tag{76}$$

It is a standard result (see e.g. Section 5.2.4 of [3]) that the dynamics $\alpha_t^{0,\Lambda}$ has a thermodynamic limit, α_t^0, in the sense of equation (54) and moreover, that the equilibrium state (76) has a thermodynamic limit in the sense that

$$\lim_{\Lambda\nearrow\mathbb{R}^3} \left(\Xi_{\beta,\mu}^{\Lambda}\right)^{-1} \mathrm{tr}\,(\varrho_{\beta,\mu} A) =: \omega_{\beta,\mu}(A)$$

exists for all $A \in \mathrm{CAR}(L^2(\Lambda', d^3x))$ and any bounded $\Lambda' \subset \mathbb{R}^3$ and defines an equilibrium (KMS) state at inverse temperature β and chemical potential μ on the C^*-algebra

$$\mathcal{F} = \mathrm{CAR}(L^2(\mathbb{R}^3, d^3x)) = \overline{\bigvee_{\Lambda\nearrow\mathbb{R}^3} \mathrm{CAR}(L^2(\Lambda, d^3x))}. \tag{77}$$

This means that Hypothesis (B) is verified.

It is known that the property of return to equilibrium holds for the KMS state $\omega_{\beta,\mu}$ (relative to the dynamics α_t^0), see [7,1,4]; this means that

$$\lim_{t\to\pm\infty} \omega^0(B\alpha_t^0(A)C) = \omega^0(BC)\omega^0(A),$$

for all $A, B, C \in \mathcal{F}$.

So far, we have verified that our example is structurally compatible with the theory outlined in Sections 1,2, and that the α_t^0-invariant initial state ω^0 satisfies the property of return to equilibrium. We are left with the specification of a class $\mathcal{W}$ of interactions satisfying Hypothesis (A).

The description of such a class has been given in [4] for time-independent interactions, and we indicate here an extension to time-dependent ones. Set $x^{(N)} := (x_1, \ldots, x_N)$, $x_j \in \mathbb{R}^3$ and similarly for $y^{(N)}$, and let

$$w^N(t, x^{(N)}, y^{(N)})$$

be a function which is bounded and continuously differentiable in $t \in \mathbb{R}$ and smooth and with support in a compact region Λ_0 in each variable $x_j, y_j \in \mathbb{R}^3$. We denote by

$$\boldsymbol{a}^*(x^{(N)}) := a^*(x_1)\cdots a^*(x_N)$$

the product of creation operators $a^*(x_j)$ at positions $x_j \in \mathbb{R}^3$; $\boldsymbol{a}(y^{(N)})$ is defined similarly. The operator

$$W_t^N := \int \boldsymbol{a}^*(x^{(N)}) w^N(t, x^{(N)}, y^{(N)}) \boldsymbol{a}(y^{(N)}) dx^{(N)} dy^{(N)}, \tag{78}$$

where we integrate over all spatial variables x_j and y_j in Λ_0, defines an element of the C^*-algebra $\mathcal{F}$ introduced in (77). A norm-summable sequence of operators $\{W_t^N\}_{N\geq 1}$ of the form (78) determines an operator

$$W_t := \sum_{N\geq 1} W_t^N \in \mathcal{F}. \tag{79}$$

The class $\mathcal{W}$ consists of interactions of the form (79) which satisfy the smallness condition

$$\|W_t\|'_\infty < \frac{1}{24\pi},$$

where we have introduced the norm

$$\|W_t\|'_\infty := \sum_{N\geq 1} 2^{5N} N \sup_{t\in\mathbb{R}} \|w^N(t,\cdot,\cdot)\|'_{6N},$$

with

$$\|f\|'_M := \frac{1}{2^{3M/2}} \left\langle f, \prod_{k=1}^{M} \left(-\frac{d^2}{dx_k^2} + x_k^2 + 1\right)^3 f \right\rangle_{L^2(\mathbb{R}^M)}^{1/2},$$

for a function $f \in L^2(\mathbb{R}^M)$ and where $\langle\cdot,\cdot\rangle_{L^2(\mathbb{R}^M)}$ is the inner product in $L^2(\mathbb{R}^M)$.

It is shown in [4] that the limit (60) exists, for time-independent interactions in $\mathcal{W}$; the proof of convergence given there generalizes readily to the time-dependent case, hence Hypothesis (A) holds.

Remark. One can explicitly calculate relevant physical quantities, such as rates of change in time of internal energy, $\dot{U}(t)$, charge, $\dot{q}(t)$, or entropy, $\dot{S}(t)$ (see (43), (44), (46)) in the thermodynamic limit in a *perturbative way* by using a Dyson series expansion (which is norm-convergent uniformly in time); see equations (63)-(70). Furthermore, expectations in the reference state ϱ_t have a convergent perturbation expansion, as well. Thus, our methods are quantitative.

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