Journal of Statistical Physics, Vol. 103, Nos. 3/4, 2001

Periodic Thermodynamics

Walter Kohn[1]

Received August 18, 2000

This paper develops the thermodynamics of quantum Floquet systems, i.e., quantum systems driven by an arbitrarily strong periodic perturbation, which are in weak interaction with a heat bath. The physics differs in an essential way from that of undriven systems, because the usual energy conservation law, for interactions between the system and heat bath, is changed to $\Delta\varepsilon + \Delta E = 0$, $\pm\omega$, $\pm 2\omega$,... where ω is the driving frequency, $\Delta\varepsilon$ is the difference of the so-called quasi-energies of the Floquet states and ΔE the excitation energy of the bath. That is, a transition between two given physical Floquet states will be accompanied by bath transitions with many *different* energy changes, $\Delta E = -\Delta\varepsilon + m\omega$, where m is an arbitrary integer. This results in a breakdown of detailed balance. There is a steady state in which the system has periodic fluctuations of period $T = 2\pi/\omega$. The steady state density matrix is diagonal in the Floquet states, with all Floquet states having finite weights, *even at zero temperature*. Experimentally favorable conditions for studying periodic thermodynamics are briefly discussed.

KEY WORDS: Floquet systems coupled to heat bath; steady state density matrix.

PERSONAL FOREWORD

Quin Luttinger and I collaborated over a period of 14 years, from 1953–1966, resulting in 10 joint papers; our close friendship extended to the end of his life in 1997, over almost half a century. Science has many rewards but none greater than such a deep friendship born of a scientific resonance and gradually spreading over all aspects of our lives.

Quin and I were, I think, a rather odd couple. He (apart from a decade's interruption) a bachelor and bohemian, the life of every party, with a long succession of girlfriends, with all of whom—to the best of my knowledge—he remained on friendly terms; I, "square," married, do-goodish.

---

[1] Department of Physics, University of California, Santa Barbara, California 93106.

Scientifically too we were quite different. I will come back to Quin's science a little further down.

Quin had a wonderful affinity for "his" children: his own daughter Catherine, his three stepchildren, Sara, Jennifer and Ralph, my daughters, Marilyn and Ingrid—there was no end. They literally flew into his arms as soon as he appeared on the scene.

He had a rare, largely mathematical, originality. Physical importance of a theory was of less interest to him than some beautiful, radically new mathematical structure. His work on one-dimensional interacting Fermi systems, now called "Luttinger liquids," essentially different from three-dimensional systems, is a case in point. This followed his complete perturbative explication (along with others) of three-dimensional Landau Fermi liquids and his perturbative proof of the beautiful "Luttinger Theorem," the conservation of the *k*-space volume enclosed by the Fermi Surface, when electron-electron interactions are "turned on." I often felt that in scientific style, Quin and Lars Onsager rather resembled each other. They both left unforgettable marks on theoretical physics.

My collaboration and friendship with Quin was one of the great experiences of my life. On one occasion a person who knew some of our joint work referred to me as Dr. Kohn-Luttinger. I liked that name very much.

I offer this modest paper as my contribution to the special Luttinger volume of the Journal of Statistical Physics. I would like to think it would have given him some small pleasure. Quin loved Statistical Mechanics and many students of his Columbia course remember it as their best. His own research contributions, e.g., his magisterial analysis of Landau's Fermi Liquid Theory and his brilliant demonstration that a Fermi gas in one dimension has an essentially different character from a 3-dimensional Fermi gas, shine in their mathematical originality and sophistication. Alas, by contrast, the present paper is mathematically elementary. But I feel that it has a generality and simplicity that he used to enjoy. I miss having a chance to talk with him about it.

The general principles of the thermodynamics of quantum systems S governed by a time-*independent* Hamiltonian H, which date back to the classical theories of Boltzmann and Gibbs,$^{(1)}$ have been well established since the beginning of this century. We recall the key elements:

One considers the system S as weakly coupled to a large heat bath at temperature τ, with the total Hamiltonian

$$H^{\text{tot}} = H + H^{b} + \gamma H' \tag{1}$$

where H^b and H' are respectively the bath and coupling Hamiltonians and γ is a small coupling constant. We denote the eigenstates and eigenvalues of H and H^b by ψ_j, ε_j and Ψ_ν, E_ν. The total energy of the system is conserved. The bath is so large that its spectrum E_ν may be treated as continuous. The spectrum ε_j of H is taken to be discrete. The combined system may be regarded as in a dynamical equilibrium in which $\gamma H'$ causes energy conserving transitions in both directions between eigenstates $\psi_j \Psi_\nu$ and $\psi_{j'} \Psi_{\nu'}$ of the uncoupled Hamiltonian $H + H^b$ with

$$\varepsilon_j + E_\nu = \varepsilon_{j'} + E_{\nu'}. \tag{2}$$

The occupation probability P_ν of the bath-eigenstate ν is given by the Boltzmann distribution

$$P_\nu = e^{-\beta E_\nu}/Z^b, \qquad \text{where} \quad Z^b \equiv \sum_\nu e^{-\beta E_\nu} \quad (\beta \equiv (k\tau)^{-1}), \tag{3}$$

assumed to be unaffected by its weak coupling to the system S. The quantum system is described by an incoherent mixture of its eigenstates j with time-dependent, normalized occupation probabilities $p_j(t)$. These satisfy the rate equations.

$$\dot{p}_j = -p_j \sum_{j'} R_{jj'} + \sum_j p_{j'} R_{j'j}, \tag{4}$$

where $R_{jj'}$, the transition rate of the system from j to j', is given by the golden rule

$$R_{jj'} = \frac{2\pi}{\hbar} \gamma^2 \sum_\nu P_\nu \, |(j, \nu| \, H' \, |j'\nu')|^2 \, \rho(E_{\nu'}) \tag{5}$$

with $E_{\nu'} = E_\nu + (\varepsilon_j - \varepsilon_{j'})$, and $\rho(E_{\nu'})$ the bath density of states at the energy $E_{\nu'}$. These rates are known to satisfy the detailed balance relations

$$R_{jj'} e^{-\beta\varepsilon_j} = R_{j'j} e^{-\beta\varepsilon_j'} \tag{6}$$

The equilibrium condition, $\dot{p}_j = 0$, has the normalized solution, independent of γ and H',

$$p_j = e^{-\beta\varepsilon_j}/Z, \qquad \text{where} \quad Z \equiv \sum e^{-\beta\varepsilon_j}. \tag{7}$$

We now turn to the thermodynamics of Floquet systems. Especially since the advent of the laser there has been increasing interest in time-periodic so-called Floquet systems, driven by a strong, external, coherent, harmonic perturbation

$$H^e(x, t) \equiv h^e(x) \cos \omega t \tag{8}$$

(or any time periodic perturbation with period $T = 2\pi/\omega$), where x represents all spatial coordinates. The wave-functions of such systems satisfy the time-dependent Schroedinger equation

$$i \frac{\partial \psi(x, t)}{\partial t} = H^F(x, t)\, \psi(x, t), \tag{9}$$

where we have set $\hbar = 1$, and the Floquet hamiltonian H^F is

$$H^F \equiv H + H^e. \tag{10}$$

The Schroedinger equation (9) has an infinite complete set of orthonormal, quasi-periodic, so-called Floquet-solutions of the form

$$\psi_j(x, t) = u_j(x, t)\, e^{-i\varepsilon_j t}, \tag{11}$$

where $u_j(x, t)$ is periodic with period T and the real quantity ε_j is called the quasi-energy.$^{(2)}$ Simultaneous multiplication of u by $e^{im\omega t}$ and of $e^{-i\varepsilon_j t}$ by $e^{-im\omega t}$ shows that neither u_j nor ε_j are uniquely defined but can be made so (except for trivial phase factors multiplying the u_j) by imposing the condition

$$0 \leqslant \varepsilon_j < \omega. \tag{12}$$

Thus, in the finite interval $[0, \omega)$ there is an infinite set of quasi-energies, ε_j, and corresponding Floquet solutions ψ_j, necessarily entailing an infinite number of degeneracies or near-degeneracies. The resulting mathematical intricacies were discussed and, to a considerable extent, clarified in a previous publication.$^{(3)}$ In the present paper the emphasis will be on coupling of Floquet systems to a heat bath. We shall work within the *finite*-dimensional Hilbert space of the N lowest eigenstates of H and assume that there are no degeneracies among the N quasi-energies, ε_j ($j = 1,..., N$). The challenging problem of degeneracies or near-degeneracies will be postponed to a later time.

An eigenfunction of a time-*independent* Hamiltonian has a time-dependence $e^{-i\varepsilon_j t}$ with a single frequency ε_j. While this frequency can be arbitrarily changed by reckoning the energy from an arbitrary reference value, the *difference* of two eigenvalues ε_j and $\varepsilon_{j'}$, satisfying (12), *is* unique, giving rise to a unique energy change of the heat bath, $E_{\nu'} - E_\nu$ for a transition from system state j to j', the famous Bohr condition

$$j \to j' : E_{\nu'} - E_\nu = \varepsilon_j - \varepsilon_{j'} \tag{13}$$

By contrast each Floquet state, *j*, contains *all* frequencies of the form $\varepsilon_j + m\omega$ $(-\infty < m < \infty)$ (of course most with small amplitudes). This leads to the important modification of the Bohr condition (13) to

$$j \to j' \colon E_{\nu'} - E_\nu = \varepsilon_j - \varepsilon_{j'} + m\omega, \tag{14}$$

where m is an arbitrary integer. This modified Bohr condition can be interpreted as signifying that the radiative transition can be accompanied by the simultaneous exchange of an arbitrary number of photons with the external periodic driver. In this paper we prefer to take the point of view that, when Floquet systems are involved, energy conservation becomes quasi-energy conservation, modulo ω.

Can one associate an energy, rather than a quasi-energy, with a Floquet state? Of course one can, for example

$$\eta_j \equiv T^{-1} \int_0^T dt \int dx\, \psi_j^*(x, t)\, H\psi_j(x, t). \tag{15}$$

We have found this "energy" to be of qualitative interest; but since, due to the coupling of the system to the external classical driver, it does not obey strict energy conservation relations, it appears to be of little quantitative significance.

We are now ready to deal with the subject of this paper, a periodic quantum system in interaction with a heat bath. We take as our total Hamiltonian

$$H^{tot} = H + h^e \cos\ \omega t + H^b + \gamma H', \tag{16}$$

whose constituents were defined earlier. (Thus we regard only the system but not the bath as periodically driven). The system-bath coupling hamiltonian $\gamma H'$ causes simultaneous transitions between two system Floquet states and two bath eigenstates, satisfying the modified energy conservation condition (13).

If the coupling constant γ is sufficiently small we may assume that at temperature T the bath can be described by the standard equilibrium ensemble probabilities,

$$P_\nu = e^{-\beta E_\nu}/Z^b, \qquad \text{where} \quad Z^b \equiv \sum e^{\beta E_\nu}. \tag{17}$$

We expect, and will show, that the system is also described by a well defined periodic density matrix of Floquet states, given by

$$\rho(x, x', t) \equiv \sum_j p_j \varphi_j^*(x, t)\, \varphi_j(x', t), \tag{18}$$

where the positive weights p_j are *independent of the magnitude* γ *of the system-bath coupling*, *but*, *in contrast to undriven systems*, *dependent on its form.* Of course

$$\sum_j p_j = 1. \tag{19}$$

The p_j are *not* proportional to $e^{-\beta(\varepsilon_j + m_j\omega)}$ for any m_j nor to $e^{-\beta\eta_j}$. Instead they are determined by the specifics of the Hamiltonians H^F, H^b and H'. Of course, in the weak driving limit, when the Floquet solutions differ only slightly from the unperturbed eigenstates of H, then

$$p_j \approx e^{-\beta\bar{\varepsilon}_j}/\bar{Z}, \qquad \text{where} \quad \bar{Z} \equiv \sum e^{-\beta\bar{\varepsilon}_j}, \quad \bar{\varepsilon}_j = \varepsilon_j + m_j\omega, \tag{20}$$

with the m_j chosen so as to minimize $\sum |\bar{\varepsilon}_j - \eta_j|^2$.

There cannot be any off-diagonal terms with $j \neq j'$ in the density matrix $\rho(x, x', t)$ of Eq. (18), since such terms would lead to time-dependencies of the form $\cos[(\varepsilon_j - \varepsilon_{j'} + m\omega)\, t + \theta]$ which do not have the required period T.

The form of the rate equation (4) for the p_j is unchanged. But because of the modification of energy conservation, the $R_{jj'}$ are now represented by an infinite series

$$R_{j,\, j'} = \sum_{m=-\infty}^{+\infty} R^m{}_{jj'}, \tag{21}$$

where

$$R^m{}_{jj'} = \frac{2\pi}{\hbar}\gamma^2 \sum_\nu P_\nu (j\nu|\, H'\, |j'\nu')\, \rho(E_{\nu'}), \tag{22}$$

and

$$E_{\nu'} = E_\nu + \varepsilon_j - \varepsilon_{j'} + m\omega, \tag{23}$$

i.e., a transition between Floquet states j and j', will be accompanied by bath transitions with $E_{\nu'} - E_\nu = \varepsilon_j - \varepsilon_{j'}$ or $\varepsilon_j - \varepsilon_{j'} \pm \omega$, etc.

The detailed balance equations (6) no longer hold and are replaced by

$$R^m{}_{jj'} e^{-\beta(\varepsilon_j + m\omega)} = R^m{}_{j'j} e^{-\beta\varepsilon_{j'}} \tag{24}$$

For strong driving fields, the periodic steady states of course differ strongly from Boltzmann equilibrium distributions. For a relatively *weak* driving field the general condition for observing the deviations between the periodic thermodynamics, described in this paper, and the traditional Boltzmann–Gibbs thermodynamics of equilibrium systems is that the Floquet density matrix differs substantially from that of undriven eigenstates and exhibits strong periodic fluctuations with period T. This requires: (1) proximity to a resonance condition; (2) weak coupling to the heat bath, which does not excessively broaden the resonance; and (3) a well-defined driving frequency ω.

A final remark: A Floquet system, uncoupled to a heat bath, has quasi energies ε_j which, however, can be defined only to within additive constants $\pm m_j \omega$. Thus, there is no generally valid definition of a "lowest" quasienergy. One may define the ground state of a Floquet system by the condition $\eta_j =$ minimum, but, except for weak periodic deriving, this is not a fruitful convention. When weakly coupled to a specific heat bath at $\tau \to 0$, a Floquet system is described by a definite density matrix of the form (18), with all weights p_j remaining finite, although one or a few may carry most of the weight. Further the p_j will depend on the specific heat bath and coupling Hamiltonians. Thus, again no general definition of a ground state emerges.

We hope to return at a later time to the unavoidable problem of near-degeneracies (see ref. 3) as well as to the problem of the line shapes of radiative transitions between Floquet states coupled to a heat bath.

ACKNOWLEDGMENTS

The author gratefully acknowledges discussions with N. Argaman, D. Hone, R. Ketzmerick, H. Metiu and M. Sherwin, as well as the financial support of NSF Grants DMR-96-30452, DMR9976457 and QUEST 91-20007.

REFERENCES

1. For example, D. Ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, New York, 1956).
2. H. Sambe, *Phys. Rev. A* **7**:2203 (1973).
3. D. W. Hone *et al.*, *Phys. Rev. A* **56**:4045 (1997).