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Semiclassical densities in phase space: Wigner's distribution function for thermodynamic equilibrium

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Abstract. The quantum-mechanical joint (quasi-) density in phase space (the Wigner distribution) for thermodynamic equilibrium is studied in the semiclassical limit $\hbar \to 0$. The approximation is of an asymptotic (WKB) type and nonperturbative in character. The equilibrium phase-space distribution can be expressed in terms of classical paths satisfying certain well defined boundary conditions. These paths are complex-valued, i.e. classically forbidden. The resulting semiclassical expression for the equilibrium Wigner phase-space density agrees with the exact quantum result for the analytical solvable case of harmonic potentials for all temperatures.

1. Introduction

During the last few years an increasing utilisation of statistical-dynamical methods in several areas of physics has been observed. Such mixed techniques turned out to be almost unavoidable for the theoretical treatment of dynamical systems involving more than a 'few' (say three) and less than 'many' (say 10^{23}) particles. Typical applications can be found in nuclear physics in the theory of deep inelastic processes in heavy-ion scattering (see, for example, Agassi *et al* 1977 and references therein) and in chemical physics in the theory of chemical reactions or inelastic molecular collisions (see, for example, Schatz *et al* 1977, Billing *et al* 1978, Miller and Skuse 1978 and references therein). A natural object of interest for such a statistical–dynamical theory is the phase-space distribution function in classical physics and its quantum-mechanical analogue: the Wigner distribution function (Wigner 1932), which closely parallels the classical picture of phase-space dynamics. These developments have lead to a renewed interest in the Weyl-Wigner equivalent representation of quantum mechanics in terms of functions over phase space (Weyl 1928, Wigner 1932). For more recent work on the Weyl–Wigner formalism see Leaf (1968a, b), de Groot and Suttorp (1972), Balazs and Zipfel (1973), Remler (1975), Heller (1976, 1977), Krüger and Poffyn (1976, 1977, 1978), Berry (1977) and Bayen *et al* (1978 a, b).

In view of the importance of the Wigner function in several areas of physics and, of course, its basically interesting feature of providing a smooth transition from quantal to classical physics, it seems valuable to gain a better understanding of the Wigner phase-space distribution and its relationship to the much better understood classical phase-space densities. Such a better understanding, as well as an approximation for numerical calculations, can be provided by an asymptotic semiclassical analysis in the

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limit $\hbar \to 0$. A semiclassical approximation for the Wigner distribution has been presented recently in the case of pure states (Berry 1977, Heller 1977). It is the aim of this paper to extend the well understood semiclassical approximation scheme of pure state dynamics (see, for example, the fundamental work of van Vleck (1928) and Maslov (1972)) to the case of statistical mechanics, i.e. mixed states, which is much less well understood. As a first step towards this goal, a study of the Wigner distribution function for thermodynamic equilibrium is presented in the present paper. The treatment of the more complicated case of the time development of nonstationary mixed-state distributions is deferred to a future publication.

For the sake of simplicity, we confine ourselves to the one-dimensional case. An extension to higher dimensions is possible along the lines presented in this paper, but—contrary to common belief—this extension is straightforward only for the case of integrable (or separable) systems (see, for example, the early work by Einstein (1917), the famous paper by Henon and Heiles (1964) and the recent article by Berry (1977)). The general case of non-integrable systems (i.e. systems where no complete compatible set of global integrals of motion exists) is at present far from being understood and deserves further investigation.

2. The Weyl transform and Wigner's distribution function

In this section we present a brief outline of the Weyl–Wigner equivalent representation of quantum mechanics. For the sake of brevity, we give all equations without proofs, since these can easily be found in the literature. The transformation suggested by Weyl (1928) establishes a one-to-one correspondence between operators in Hilbert space, which can be expressed in terms of the canonical position and momentum operators, and functions over phase space. The resulting reformulation of quantum mechanics in terms of phase-space functions bears the closest possible analogy between classical and quantum descriptions of physical systems. Detailed outlines of the Weyl correspondence can be found in the book by de Groot and Suttorp (1972) and in the papers by Imre *et al* (1967), Leaf (1968a, b), Remler (1975), Heller (1976) and Krüger and Poffyn (1976, 1977, 1978). Here we will only give the basic equations, and for simplicity we confine ourselves to the one-dimensional case. The Weyl transform of an operator $\hat{A}$ is defined by

$$A^{\mathrm{W}}(p, q) = \int \mathrm{d}q' \exp^{(-\mathrm{i}pq'/\hbar)} \langle q + \tfrac{1}{2}q' | \hat{A} | q - \tfrac{1}{2}q' \rangle. \tag{1}$$

A similar integral exists in the momentum representation, but here and in the following equations we give only the coordinate representations.

It is obvious that the Weyl transform of a product will generally differ from the products of the Weyl transforms:

$$(AB)^{\mathrm{W}}(p, q) \neq A^{\mathrm{W}}(p, q) B^{\mathrm{W}}(p, q) \tag{2}$$

(an equality is, of course, obtained in the classical limit). One of the most important features for applications of the Weyl formalism is the fact that traces can be evaluated as simple phase-space integrals (Leaf 1968a):

$$\mathrm{Tr}\, \hat{A} = \frac{1}{h} \int \mathrm{d}p\, \mathrm{d}q\, A^{\mathrm{W}}(p, q) \tag{3}$$

and

$$\mathrm{Tr}\,\hat{A}\hat{B}=\mathrm{Tr}\,\hat{B}\hat{A}=\frac{1}{h}\int \mathrm{d}p\,\mathrm{d}q\,A^{\mathrm{W}}(p,q)B^{\mathrm{W}}(p,q). \tag{4}$$

The Wigner function (or Wigner distribution) is the Weyl transform of the density operator (Wigner 1932). In the present paper we would like to discuss two special cases of these distributions: the pure states and the mixed states in thermal equilibrium, i.e. the density operators $\hat{\rho}_n=|n\rangle\langle n|$ and $\hat{\rho}_\beta=\exp(-\beta\hat{H})\cdot\hat{\rho}_\beta$ satisfies the Bloch equation

$$\partial\hat{\rho}_\beta/\partial\beta=-\hat{H}\hat{\rho}_\beta, \tag{5}$$

which is nearly the same as the time-dependent Schrödinger equation with imaginary 'time' $t=-\mathrm{i}\hbar\beta$. This formal similarity is the basis for several interesting correspondences between equilibrium statistical mechanics and time-dependent wave mechanics (see, for example, § 3).

The matrix elements of $\hat{\rho}_\beta$ in the position representation are easily expressed in terms of the wavefunctions $\psi_n(q)$:

$$\rho_\beta(q_2,q_1)=\sum_n \exp(-\beta E_n)\psi_n(q_2)\psi_n^*(q_1). \tag{6}$$

(Here and in the following we assume for simplicity that there are only bound states and no continuum.) The matrix elements (6) satisfy the equation

$$\rho_{\beta_2+\beta_1}(q_2,q_1)=\int \mathrm{d}q\,\rho_{\beta_2}(q_2,q)\rho_{\beta_1}(q,q_1), \tag{7}$$

i.e. they form a semigroup ($\rho_{\beta=0}(q_2,q_1)=\delta(q_2-q_1)$) (see, for example, Baltin 1978).

The Weyl transforms of $\hat{\rho}_n/h$ and $\hat{\rho}_\beta/h$ are usually denoted as Wigner distribution functions. For the case of a pure state we find

$$\rho_n^{\mathrm{W}}(p,q)=\frac{1}{h}\int \mathrm{d}q'\exp(-\mathrm{i}pq'/\hbar)\,\psi_n(q+\tfrac{1}{2}q')\psi_n^*(q-\tfrac{1}{2}q'). \tag{8}$$

The Wigner function for thermal equilibrium—which is the central object of the present study—is given by

$$\rho_\beta^{\mathrm{W}}(p,q)=\frac{1}{h}\int \mathrm{d}q'\exp(-\mathrm{i}pq'/\hbar)\,\rho_\beta(q+\tfrac{1}{2}q',q-\tfrac{1}{2}q') \tag{9a}$$

or—equivalently—in terms of the Wigner functions $\psi_n^{\mathrm{W}}(p,q)$:

$$\rho_\beta^{\mathrm{W}}(p,q)=\sum_n \exp(-\beta E_n)\,\rho_n^{\mathrm{W}}(p,q). \tag{9b}$$

It is widely known that the distributions $\rho^{\mathrm{W}}(p,q)$ can be regarded as quasi-densities in phase space, i.e. averages of dynamical variables can be calculated by direct integration over phase space:

$$\langle\hat{A}\rangle=\frac{\mathrm{Tr}\,\hat{A}\hat{\rho}}{\mathrm{Tr}\,\hat{\rho}}=\frac{1}{Q}\int \mathrm{d}p\,\mathrm{d}q\,A^{\mathrm{W}}(p,q)\,\rho^{\mathrm{W}}(p,q) \tag{10}$$

(see equation (4)), where $A^{\mathrm{W}}(p,q)$ is the Weyl transform of A and

$$Q=\mathrm{Tr}\,\hat{\rho}=\int \mathrm{d}p\,\mathrm{d}q\,\rho^{\mathrm{W}}(p,q). \tag{11}$$

For the pure states the distribution is normalised: $Q_n = \int \mathrm{d}p\, \mathrm{d}q\, \rho_n^{\mathrm{W}}(p, q) = 1$, and for the equilibrium distribution $Q_\beta = \int \mathrm{d}p\, \mathrm{d}q\, \rho_\beta^{\mathrm{W}}(p, q)$ is the celebrated thermodynamic partition function. It must be stressed that equation (10) is quantum-mechanically exact, despite the obvious classical structure of the right hand side.

The Wigner distribution function for the harmonic oscillator (unit mass and unit frequency) can be evaluated in closed form (Groenewold 1946):

$$\rho_n^{\mathrm{W}}(p, q) = \frac{(-1)^n}{\pi\hbar} \exp\left[-(p^2+q^2)/\hbar\right] L_n[2(p^2+q^2)/\hbar \tag{12}$$

where L_n is the Laguerre polynomial with normalisation $L_n(0) = 1$. For the ground state $n = 0$, $\rho_n^{\mathrm{W}}(p, q)$ is non-negative, but for higher quantum numbers there are regions in phase space where the (quasi-) phase-space density is negative: ρ_n^{W} shows a fringe pattern. The number of fringes (i.e. the number of curves in phase space where ρ_n^{W} vanishes) is equal to the quantum number n.

The harmonic oscillator distribution for thermal equilibrium is given by

$$\rho_\beta^{\mathrm{W}}(p, q) = (h \cosh \tfrac{1}{2}\hbar\beta)^{-1} \exp\left[-\hbar^{-1}(p^2+q^2) \tanh \tfrac{1}{2}\hbar\beta\right] \tag{13}$$

(see, for example, Meijer 1966). In this case the phase-space density is positive. The same may be true for other potentials or even generally; we are not aware of an example of a quantum-mechanical equilibrium phase-space density which is negative somewhere. The semiclassical approximation to $\rho_\beta^{\mathrm{W}}(p, q)$ derived in § 3 of this paper is also positive throughout, which supports the conjecture that $\rho_\beta^{\mathrm{W}}(p, q)$ is indeed non-negative (for well behaved potentials). This point deserves further investigation.

3. Semiclassical Wigner densities in phase space

The classical limit ($\hbar \to 0$) of the Weyl transform and of Wigner's phase-space distribution function is, of course, the usual classical description of phase-space mechanics: $\rho_n^{\mathrm{W}}(p, q)$ approaches a δ function on the energy shell $E_n = H(p, q)$ and $\rho_\beta^{\mathrm{W}}(p, q)$ goes to the classical Boltzmann distribution

$$h\rho_\beta^{\mathrm{W}}(p, q) \xrightarrow[\hbar \to 0]{} \rho_\beta^{\mathrm{CL}}(p, q) = \exp(-\beta H(p, q)) \tag{14}$$

and with $H(p, q) = p^2/2m + V(q)$ one obtains the classical density in coordinate space:

$$h\tilde{\rho}_\beta(q) \to \tilde{\rho}_\beta^{\mathrm{CL}}(q) = (2\pi m/\beta)^{1/2} \exp(-\beta V(q)). \tag{15}$$

The traditional semiclassical approximations in statistical mechanics try to account for quantum effects by means of perturbation expansions in terms of a small parameter, i.e. in terms of powers of $\hbar$. An example is the well known Wigner–Kirkwood expansion of the density in coordinate space (Wigner 1932, Kirkwood 1933, Mayer and Band 1947, Hornstein and Miller 1972, Miller 1973, Onofri 1978, Baltin 1978).

In contrast to these series expansions the semiclassical WKB-type approximation scheme developed in the last decade (see, for example, the fundamental works of van Vleck (1928) and Maslov (1972), and the review articles by Berry and Mount (1972) and Miller (1974, 1975)) is essentially nonperturbative in character. It leads to a self-consistent semiclassical mechanics which differs both from classical and quantum mechanics. The main ingredients of this semiclassical description are the classical paths (with the inclusion of classically forbidden, complex-valued trajectories (see, for example, Korsch and Leissing (1976) and references therein), and on the other hand specific algebraic methods for the asymptotic evaluation of matrix elements, integrals, or sums (Berry and Mount 1972, Dingle 1973). From the beginning of the development of semiclassical dynamics, the formal similarity between the time dependence of pure states and the $\beta = 1/kT$ dependence in equilibrium statistical mechanics (compare the Bloch equation (5)) lead to a number of semiclassical applications to statistical mechanics (Feynman and Hibbs 1965, Miller 1971, 1973, 1974, Stratt and Miller 1978). A self-consistent semiclassical statistical mechanics, however, is still lacking. The present paper is considered as a step in this direction.

There are several ways to obtain a semiclassical expression for equilibrium density matrices. One is based on the formal similarity between the time-dependent propagator $\hat{U}(t) = \exp[-(i/\hbar)\hat{H}t]$ and the density operator $\hat{\rho}_\beta = \exp(-\beta\hat{H})$. In this approach the well known semiclassical approximations are carried over to statistical mechanics by replacing the time t by $-i\hbar\beta$ (Miller 1971, 1973, 1974, Hornstein and Miller 1972, Stratt and Miller 1978). This recipe is, of course, heuristic but quite successful. The other approach is exact but mathematically involved: it demands an analysis of Feynman path integrals (Feynman and Hibbs 1965) for statistical mechanics, i.e. Wiener integrals (see, for example, Truman 1977, Bach *et al* 1978). Both approaches have been used to derive a semiclassical approximation to the off-diagonal and diagonal matrix elements of $\hat{\rho}_\beta$ in the position representation. Needless to say that the results of both approaches are identical. It is not clear at the moment if a direct extension of these methods to the objects of our interest, the Wigner distributions in equilibrium, is possible.

The present approach pursues another idea. Because of the impressive mass of material available in nonstatistical semiclassical mechanics—a semiclassical expression for the pure-state Wigner function has been derived recently (Berry 1977, Heller 1977)—we found it very promising to establish a direct connection between statistical and nonstatistical semiclassical mechanics. In other words, we want to study the following diagram in the framework of the semiclassical theory:

$$\begin{array}{ccc} \psi_n(q) & \rightarrow & \rho_\beta(q_2, q_1) \\ \downarrow & & \downarrow \\ \rho_n^{\mathrm{W}}(p,q) & \rightarrow & \rho_\beta^{\mathrm{W}}(p,q)\,. \end{array} \tag{16}$$

The exact quantum formulae, which express the desired equilibrium Wigner function $\rho_\beta^{\mathrm{W}}(p,q)$ in terms of the pure-state wavefunctions $\psi_n(q)$ are given in the preceding section. It turns out to be instructive to study the semiclassical limit of both routes leading from the wavefunctions $\psi_n(q)$—which are by no doubt the best studied objects in semiclassical (WKB) mechanics—to the Wigner distributions $\rho_\beta^{\mathrm{W}}(p,q)$ in phase space: the route via the matrix elements $\rho_\beta(q_2, q_1)$ is explored in § 3.1 and the route via the pure-state Wigner function in § 3.2.

3.1. Semiclassical density matrix and equilibrium phase-space distributions

The semiclassical (WKB) bound-state wavefunctions can be written as a linear combination:

$$\psi(q, I) = \frac{1}{\sqrt{2}}(\psi^+(q, I) + \psi^-(q, I)) \tag{17}$$

(in the classically allowed region $q_< < q < q_>$; $q_{\gtrless}$ are the classical turning points) of the elementary semiclassical wavefunctions

$$\psi^{\pm}(q, I) = \left(\mp \frac{\mathrm{i}}{\pi} \frac{\partial^2 S}{\partial q\, \partial I}\right)^{1/2} \exp[\pm(\mathrm{i}/\hbar) S(q, I)]. \tag{18}$$

Here

$$S(q, I) = \int_{q_<}^{q} p(q', I)\, \mathrm{d}q' \tag{19}$$

is the classical position-dependent action, and I is the classical action variable, defined by

$$I(p, q) = I(H(p, q)) = \frac{1}{2\pi} \oint p\, \mathrm{d}q. \tag{20}$$

The conjugate angle variable $\phi(p, q)$ is given by

$$\phi(p, q) = (\partial/\partial I) S(q, I). \tag{21}$$

The WKB quantum condition

$$I = I_n = (n + \tfrac{1}{2})\hbar \tag{22}$$

determines the bound-state energies E_n. With $\partial S/\partial q = p$ ($S(q, I)$ is the generating function for the canonical transformation $(p, q) \to (I, \phi)$) we find a more familiar looking expression:

$$\frac{\partial^2 S}{\partial q\, \partial I} = \frac{\partial p}{\partial I} = \frac{\partial H}{\partial I} \frac{\partial p}{\partial H} = \omega(I) \frac{m}{p(q)} \tag{23}$$

with $\omega(I) = \dot{\phi} = \partial H/\partial I$. The $\psi^{\pm}(q, I)$ of equation (18) are normalised to unity in the classically accessible region:

$$\int_{q_<}^{q_>} |\psi^{\pm}(q)|^2\, \mathrm{d}q = 1. \tag{24}$$

In order to obtain the semiclassical limit of the matrix elements of the statistical operator $\hat{\rho}_\beta$ in the coordinate representation, we replace the bound-state wavefunctions $\psi_n(q)$ in equation (6) by the semiclassical expressions (17) and convert the sum over the quantum number n into an integral over the continuous action variable $I = (n + \frac{1}{2})\hbar$ by means of the (exact!) Poisson summation formula in close analogy to the well known semiclassical evaluation of the angular momentum sums in potential scattering (see, for example, Berry and Mount 1972, Korsch and Leissing 1976, Berry and Tabor 1976, 1977, and references therein):

$$\begin{aligned}\rho_\beta(q_2, q_1) &= \sum_n \exp(-\beta E_n) \psi_n(q_2) \psi_n^*(q_1) \\ &= \frac{1}{\hbar} \sum_{M=-\infty}^{+\infty} \exp(-\mathrm{i}\pi M) \int_0^\infty \mathrm{d}I \exp(-\beta E(I) + 2\pi \mathrm{i} M I/\hbar)\, \psi(q_2, I) \psi^*(q_1, I) \\ &= \frac{1}{\hbar} \sum_{M=-\infty}^{+\infty} \exp(-\mathrm{i}\pi M)\, (J_M^{++} + J_M^{+-} + J_M^{-+} + J_M^{--})\end{aligned} \tag{25}$$

with

$$J_M^{\pm\pm}=\int_0^\infty \mathrm{d}I\left(\mp\frac{\mathrm{i}}{2\pi}\frac{\partial^2 S}{\partial q_2\,\partial I}\right)^{1/2}\left(\mp\frac{\mathrm{i}}{2\pi}\frac{\partial^2 S}{\partial q_1\,\partial I}\right)^{1/2}$$
$$\times\exp\left(-\beta E(I)\pm\frac{\mathrm{i}}{\hbar}S(q_2,I)\pm\frac{\mathrm{i}}{\hbar}S(q_1,I)+\frac{\mathrm{i}}{\hbar}2\pi MI\right) \tag{26}$$

where the first (second) $\pm$ sign of $J_M^{\pm\pm}$ refers to the terms involving q_2 (q_1). We now evaluate the integrals (26) by the stationary phase approximation (or the method of steepest decent if the stationary points are complex) (see, for example, Dingle 1973). We obtain the stationarity condition (with $\phi=\partial S/\partial I$ and $\omega(I)=\partial H/\partial I$)

$$-\beta\omega(I)+(\mathrm{i}/\hbar)\phi_2\pm(\mathrm{i}/\hbar)\phi_1+(\mathrm{i}/\hbar)2\pi M=0. \tag{27}$$

Using $\phi=\omega t$ and making the convenient change of variables $\tau=\mathrm{i}t$ and $\bar{p}=\mathrm{d}q/\mathrm{d}\tau=-\mathrm{i}p$ (Stratt and Miller 1978) the stationary phase condition (33) can be rewritten as

$$\hbar\beta=\pm\tau_2\pm\tau_1+2\pi\mathrm{i}M/\omega(I). \tag{28}$$

The sum over M separates the classical paths according to their topology. Normally only the lowest terms contribute, and in the following we take only the dominant part $M=0$ into account† (for a more detailed discussion see Berry and Mount (1972) and Korsch and Leissing (1976)). A solution of (28) exists only for the sign combination J^{+-} (the trajectory must be forward in time), and the energy which makes the integral stationary is obtained from the solution of

$$\hbar\beta=\Delta\tau=m\int_{q_1}^{q_2}\bar{p}^{-1}(q,E_s)\,\mathrm{d}q \tag{29}$$

with $\bar{p}=[2m(-E_s+V(q))]^{1/2}$. The second derivative of the exponent at the stationary point is

$$\frac{\mathrm{d}^2}{\mathrm{d}I^2}\left(-\beta E+\frac{\mathrm{i}}{\hbar}S(q_2,I)-\frac{\mathrm{i}}{\hbar}S(q_1,I)\right)_{I=I_s}=\frac{m^2\omega^2(I_s)}{\hbar}\int_{q_1}^{q_2}\bar{p}^{-3}\,\mathrm{d}q. \tag{30}$$

Defining

$$\begin{aligned}\Phi(q_2,q_1;\tau)&=E\tau+\bar{S}(q_2,q_1;E)\\ \bar{S}(q_2,q_1;E)&=\int_{q_1}^{q_2}\bar{p}\,\mathrm{d}q\end{aligned} \tag{31}$$

and using the well known relation for the second derivatives of Legendre transforms (see Gutzwiller 1967, appendix B)

$$\frac{\partial^2\Phi}{\partial q_2\,\partial q_1}=\frac{\partial^2\bar{S}}{\partial q_2\,\partial q_1}-\frac{\partial^2\bar{S}}{\partial q_2\,\partial E}\frac{\partial^2\bar{S}}{\partial q_1\,\partial E}\frac{\partial E^2}{\partial^2\bar{S}} \tag{32}$$

(here the first term on the right-hand side vanishes because of our restriction to one dimension) we finally obtain the desired result:

$$\rho_\beta(q_2,q_1)=\left(-\frac{\partial^2\Phi}{\partial q_2\partial q_1}\right)^{1/2}\exp(-\Phi(q_2,q_1;\hbar\beta)/\hbar). \tag{33}$$

† It is expected, however, that terms with $M\neq0$ are important for potentials with a double well, where the index M counts the number of oscillations in the central barrier of the potential.

This result is, of course, identical to the formula given by Miller (Miller 1971, 1973, 1974, Hornstein and Miller 1972, Stratt and Miller 1978), which was based on more heuristic arguments. For completeness we note the simple closed form expression for the second derivative:

$$\left(-\frac{\partial^2\Phi}{\partial q_2\,\partial q_1}\right)^{-1}=\bar{p}(q_2)\bar{p}(q_1)\int_{q_1}^{q_2}\bar{p}^{-3}\,\mathrm{d}q. \tag{34}$$

From a general point of view it is interesting to note that—within the self-consistent framework of semiclassical mechanics—the semiclassical density matrix elements satisfy the semigroup property (9) (see Baltin 1978). Replacing $\rho_{\beta_2}(q_2, q)$ and $\rho_{\beta_1}(q, q_1)$ on the right-hand side of equation (7) by the semiclassical approximation (33) and evaluating the integral by the method of stationary phase, we obtain the stationarity condition

$$\begin{aligned}0&=(\mathrm{d}/\mathrm{d}q)(\Phi(q_2, q\,;\hbar\beta_2)+\Phi(q, q_1;\hbar\beta_1))\\&=\bar{p}(q_2, q\,;\hbar\beta_2)-\bar{p}(q, q_1;\hbar\beta_1),\end{aligned} \tag{35}$$

i.e., at the stationary point $q=q_s$ the final momentum on the trajectory from q_1 to q_s (with time $-\mathrm{i}\hbar\beta_1$) equals the initial momentum of the trajectory from q_s to q_2 (time $-\mathrm{i}\hbar\beta_2$), so that the combined path is differentiable at q_s and hence the classical trajectory going from q_1 to q_2 in time $-\mathrm{i}\hbar(\beta_1+\beta_2)$. Obviously we have

$$\Phi(q_2, q_s;\hbar\beta_2)+\Phi(q_s, q_1;\hbar\beta_1)=\Phi(q_2, q_1;\hbar(\beta_2+\beta_1)), \tag{36}$$

and with the relation

$$\begin{aligned}&\frac{\partial^2\Phi(q_2, q_s;\tau_2)}{\partial q_2\,\partial q_s}\frac{\partial^2\Phi(q_s, q_1;\tau_1)}{\partial q_s\,\partial q_1}\left(\frac{\partial^2\Phi(q_2, q_s;\tau_2)}{\partial q_s^2}-\frac{\partial^2\Phi(q_s, q_1;\tau_1)}{\partial q_s^2}\right)^{-1}\\&\quad=-\frac{\partial^2\Phi(q_2, q_1;\tau_2+\tau_1)}{\partial q_1\,\partial q_2}\end{aligned} \tag{37}$$

between the second derivatives (compare Berry and Mount 1972, § 7.2) we finally reproduce the semiclassical approximation (33) to the left-hand side of equation (7).

As a last point it should be noted that for the harmonic oscillator (unit mass and frequency) the action Φ can be calculated in closed form:

$$\Phi(q_2, q_1;\hbar\beta)=\frac{1}{2\sinh\hbar\beta}\,[(q_2^2+q_1^2)\cosh\hbar\beta-2q_2q_1]. \tag{38}$$

The resulting expression for the semiclassical density matrix elements (33) agrees with the exact quantum result, as already stated by Miller (1974).

The central object of this paper, the semiclassical phase-space density for thermodynamic equilibrium $\rho_\beta^{\mathrm{W}}(p, q)$, can now be derived from the integral (9*a*). Approximating the matrix element $\rho_\beta(q+\frac{1}{2}q', q-\frac{1}{2}q')$ by the semiclassical expression (33) we obtain

$$\begin{aligned}\rho_\beta^{\mathrm{W}}(p, q)&=\frac{1}{h}\int\mathrm{d}q'\exp(-\mathrm{i}pq'/\hbar)\rho_\beta(q_2, q_1)\\&=\frac{1}{h}\int\mathrm{d}q'\left(-\frac{1}{\hbar}\frac{\partial^2\Phi}{\partial q_2\,\partial q_1}\right)^{1/2}\exp[-(\mathrm{i}/\hbar)pq'-\Phi(q_2, q_1;\hbar\beta)/\hbar]\end{aligned} \tag{39}$$

with $q_2 = q + \frac{1}{2}q'$ and $q_1 = q - \frac{1}{2}q'$. The integral (39) is again evaluated by the method of stationary phase. The stationarity condition is

$$\tfrac{1}{2}\mathrm{i}(\bar{p}(q + \tfrac{1}{2}q_s; E_s) + \bar{p}(q - \tfrac{1}{2}q_s; E_s)) = p, \tag{40}$$

or in short notation $\frac{1}{2}\mathrm{i}(\bar{p}_2 + \bar{p}_1) = p$ and $\frac{1}{2}(q_2 + q_1) = q$. The same stationary phase conditions have been obtained for the semiclassical pure-state Wigner function (Berry 1977; see also § 3.2 this paper). The energy E_s is, of course, determined by equation (29):

$$\hbar\beta = \Delta\tau = m\int_{q-\frac{1}{2}q_s}^{q+\frac{1}{2}q_s} \bar{p}^{-1}\,\mathrm{d}q. \tag{41}$$

For the second derivative we obtain

$$\frac{\mathrm{d}^2}{\mathrm{d}q'^2}\Phi(q + \tfrac{1}{2}q', q - \tfrac{1}{2}q')\bigg|_{q'=q_s} = \frac{1}{4}\left(\frac{\partial^2\Phi}{\partial q_2^2} + \frac{\partial^2\Phi}{\partial q_1^2} - 2\frac{\partial^2\Phi}{\partial q_2\,\partial q_1}\right), \tag{42}$$

so that the final result for the semiclassical Wigner density in phase space is given by

$$\rho_\beta(p, q) = \frac{1}{\pi\hbar}\left(2 - \frac{(\partial^2\Phi/\partial q_2^2) + (\partial^2\Phi/\partial q_1^2)}{\partial^2\Phi/\partial q_2\,\partial q_1}\right)^{-1/2} \exp(-B(p, q; \hbar\beta)/\hbar) \tag{43}$$

with $q_2 = q + \frac{1}{2}q_s$, $q_1 = q - \frac{1}{2}q_s$ and

$$B(p, q; \hbar\beta) = \mathrm{i}pq + \Phi(q_2, q_1; \hbar\beta). \tag{44}$$

Because of the imaginary time interval $-\mathrm{i}\hbar\beta$, the trajectories determined by the boundary conditions (40) and (41) are complex-valued, i.e. classically forbidden. The stationary point q_s is purely imaginary and the energy E_s is generally smaller than the energy $p^2/2m + V(q)$ at the phase-space point (p, q), so that (p, q) lies outside the energy shell $H = E_s$ (compare § 3.2 and figure 2).

It is also quite suggestive to rewrite the boundary condition (41) as

$$(1/\beta)\Delta\tau = \hbar, \tag{45}$$

which closely resembles the energy $(1/\beta = kT)$ – time uncertainty relation (Stratt and Miller 1978). During the time interval $\Delta\tau$ the trajectory explores the neighbourhood of the phase-space point (p, q) of interest. There is a reciprocal relationship between the temperature T and the time interval $\Delta\tau$, and in the extreme classical (high-temperature) limit the time interval goes to zero and the trajectory shrinks into the point (p, q). In this limit the pre-exponential factor in equation (43) approaches $1/h$ and the exponent $B(p, q)$ goes to $H(p, q)\hbar\beta$, so that we recover the classical Boltzmann distribution (14).

It is worthwhile to discuss the analytically solvable case of the harmonic oscillator (unit mass and frequency) in more detail. The trajectory satisfying the boundary conditions (46) and (47) is given by

$$q(\tau) = \frac{1}{\cosh(\frac{1}{2}\hbar\tau)}(q\cosh(\tau - \tfrac{1}{2}\hbar\beta) + \mathrm{i}p\sinh(\tau - \tfrac{1}{2}\hbar\beta)); \tag{46}$$

and we have $q(0) = q - \frac{1}{2}q_s$, $q(\hbar\beta) = q + \frac{1}{2}q_s$ with

$$q_s = -2\mathrm{i}p\tanh(\tfrac{1}{2}\hbar\beta) \tag{47}$$

and

$$E_s = \tfrac{1}{2}(p^2 + q^2)/\cosh^2(\tfrac{1}{2}\hbar\beta). \tag{48}$$

Equation (46) describes a hyperbola in the complex q plane (see figure 1); the focal point of this hyperbola is the classical turning point $q_0 = (2E_s)^{1/2}$. The trajectory does *not* pass through the phase-space point (p, q) under consideration. Recently Stratt and Miller (1978) suggested a relationship between phase-space densities and classical trajectories which start at the phase-space point (p, q). But this would necessarily require $E_s = H(p, q)$, which is clearly inconsistent with the boundary conditions (40) and (41). A short calculation using the two-point action function (38) shows that the semiclassical phase-space density (43) agrees with the exact result (13) for all values of the temperature. This is, of course, a special feature of the harmonic potential. It can be expected, however, that the semiclassical formula (43) also gives a reasonable approximation for anharmonic potentials at low temperatures.

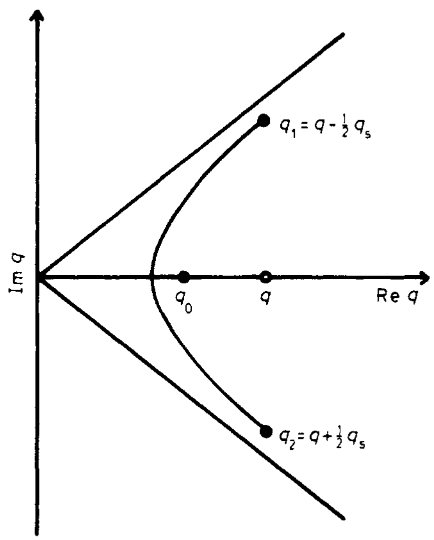

Figure 1. Complex-valued classical path in coordinate space which determines the semiclassical phase-space density $\rho_\beta^W(p, q)$ at the point (p, q). For the harmonic oscillator the trajectory is a hyperbola going from $q_1 = q - \frac{1}{2}q_s$ to $q_2 = q + \frac{1}{2}q_s$ ($q_s = 2\mathrm{i}p \tanh(\frac{1}{2}n\beta)$) in time $\Delta t = -\mathrm{i}\hbar\beta$. q_0 is the classical turning point.

3.2. Pure-state Wigner functions and equilibrium phase-space densities

It is instructive to give a brief discussion of an alternative route leading to the semiclassical phase-space densities for thermodynamic equilibrium. A semiclassical expression for the Wigner distribution for pure states has recently been derived by Berry (1977) (see also Heller 1977):

$$\rho_n^W(p, q) = \frac{2\cos(A(p, q; E_n) - \frac{1}{4}\pi)}{\pi\sqrt{\hbar}(I_q(2)I_p(1) - I_p(2)I_q(1))^{1/2}}. \tag{49}$$

Here I_p and I_q denote the p- and q-derivatives of the action variable (20) evaluated at the two solutions 1 and 2 of the stationarity condition

$$\tfrac{1}{2}\{p(q + \tfrac{1}{2}q_s, E_n) + p(q - \tfrac{1}{2}q_s, E_n)\} = p, \tag{50}$$

which determines the two points $q_{1,2} = q \mp \frac{1}{2}q_s$ and the momenta $p_{1,2} = p \mp \frac{1}{2}p_s$ on the energy shell $H(p_1, q_1) = H(p_2, q_2) = E_n$. The situation is illustrated by figure 2. The stationarity condition (50) shows that the phase-space point of interest (p, q) bisects the chord joining the stationarity points 1 and 2. The modified action $A(p, q; E)$ is given by

$$A(p, q; E) = \int_{q_1}^{q_2} p(q', E)\,\mathrm{d}q' - pq_s, \tag{51}$$

i.e. $A(p, q; E)$ is the shaded area in figure 2 between the chord and the energy shell. It is obvious that we have

$$\hbar^{-1}|A(p, q; E_n)| \leq 2\pi I_n/\hbar = 2\pi(n + \tfrac{1}{2}), \tag{52}$$

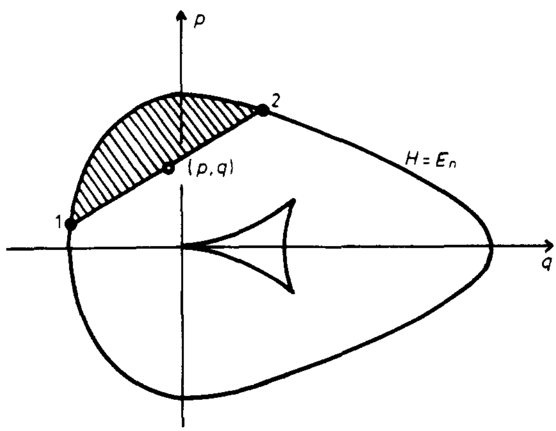

Figure 2. The pure-state Wigner density at the phase-space point (p, q) is related to the classical trajectory on the energy shell $H = E_n$. The two points (p_1, q_1) and (p_2, q_2) on the energy shell determined by $\frac{1}{2}(p_1 + p_2) = p$ and $\frac{1}{2}(q_1 + q_2) = q$ contribute to the density at (p, q). The region outside the energy shell is classically forbidden, i.e. the points 1 and 2 become complex-valued. The phase-space action function $A(p, q; E_n)$ is equal to the shaded area between the energy shell and the chord joining (p_1, q_1), (p, q), and (p_2, q_2).

so that the phase-space distribution shows n fringes. For phase-space points outside the energy shell the stationary points are complex-valued and the action integral $A(p, q; E_n)$ is purely imaginary. This leads to a monotonically decreasing distribution in this region. On the energy shell the semiclassical Wigner function (49) diverges because of the coalescence of the stationary points. A second catastrophy of $\rho_n^{\mathrm{W}}(p, q)$ occurs at the boundary of a second classically forbidden region, where the denominator of equation (49) vanishes. For points inside this region there is more than one solution of the stationary phase condition (50). The boundary line of this region shows typical cusps (an odd number, normally three). For a detailed discussion see the recent article by Berry (1977), who also gives a uniform semiclassical approximation for the Wigner function.

In view of the harmonic oscillator results discussed in the preceding section for the semiclassical equilibrium Wigner density it should be noted that equation (49) does *not* give the exact result for the harmonic oscillator. This is, of course, obvious from the discussion of the catastrophes given above.

The semiclassical phase-space densities $\rho_\beta^{\mathrm{W}}(p, q)$ can now be derived by converting the sum in equation (9*b*) into an integral, again using the Poisson summation formula (compare § 3.1):

$$\rho_\beta^{\mathrm{W}}(p,q)=\sum_n \exp(-\beta E_n)\,\rho_n^{\mathrm{W}}(p,q)$$

$$=\frac{1}{\hbar}\sum_{M=-\infty}^{+\infty}\exp(-\mathrm{i}\pi M)\int_0^\infty \mathrm{d}I\,\exp(-\beta E(I)+2\pi\mathrm{i}MI/\hbar)\,\rho_I^{\mathrm{W}}(p,q). \qquad (53)$$

In a second step we replace $\rho_I^{\mathrm{W}}(p,q)$ by the semiclassical approximation (49) and evaluate the integrals again by the method of stationary phase. After some calculation the semiclassical formula (43) of § 3.1 is rediscovered. The equilibrium phase-space action $B(p,q;\hbar\beta)$ defined in equation (44) is related to the phase-space action at fixed energy by the simple formula

$$B(p,q;\hbar\beta)=\hbar\beta E_{\mathrm{s}}-\mathrm{i}A(p,q;E_{\mathrm{s}}), \qquad (54)$$

in close analogy to the well known relation between the time-dependent and the time-independent classical action function in coordinate space (see, for example, Gutzwiller 1967). The energy E_{s} and $\hbar\beta$ in equation (54) are interrelated by the boundary conditions (40) and (41).

4. Concluding remarks

The semiclassical limiting form of the Wigner phase-space density for thermodynamic equilibrium has been derived. As a byproduct a rederivation of the semiclassical matrix elements of the density operator in coordinate space has been given. The approximation agrees with the exact quantum result for the harmonic potential.

The semiclassical phase-space density should be useful in two ways. From the general point of view it offers a way for a better (more 'classical') understanding of quantum effects arising in statistical mechanics, and may be a first step towards the development of a self-consistent semiclassical statistical dynamics. On the other hand, it provides a valuable and considerably easy calculable phase-space weighing function, which is superior to the classical Boltzmann distribution and takes account of some of the quantum effects. Statistical averages of dynamical observables and—last but not least—the thermodynamic partition function can be calculated as simple phase-space integrals by means of equations (10) and (11).

The present treatment is, of course, not exhaustive. Future work should remove the restriction to one dimension and, probably even more interesting, the restriction to the time-independent case of pure states or thermodynamic equilibrium, and to derive a semiclassical theory of the time development of nonstationary phase-space distributions.

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