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Non-Equilibrium Liouville and Wigner Equations: Moment Methods and Long-Time Approximations

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Abstract: We treat the non-equilibrium evolution of an open one-particle statistical system, subject to a potential and to an external "heat bath" (hb) with negligible dissipation. For the classical equilibrium Boltzmann distribution, $W_{c,eq}$, a non-equilibrium three-term hierarchy for moments fulfills Hermiticity, which allows one to justify an approximate long-time thermalization. That gives partial dynamical support to Boltzmann's $W_{c,eq}$, out of the set of classical stationary distributions, $W_{c,st}$, also investigated here, for which neither Hermiticity nor that thermalization hold, in general. For closed classical many-particle systems without hb (by using $W_{c,eq}$), the long-time approximate thermalization for three-term hierarchies is justified and yields an approximate Lyapunov function and an arrow of time. The largest part of the work treats an open quantum one-particle system through the non-equilibrium Wigner function, W. W_{eq} for a repulsive finite square well is reported. W's (< 0 in various cases) are assumed to be quasi-definite functionals regarding their dependences on momentum (q). That yields orthogonal polynomials, $H_{Q,n}(q)$, for W_{eq} (and for stationary W_{st}), non-equilibrium moments, W_n, of W and hierarchies. For the first excited state of the harmonic oscillator, its stationary W_{st} is a quasi-definite functional, and the orthogonal polynomials and three-term hierarchy are studied. In general, the non-equilibrium quantum hierarchies (associated with W_{eq}) for the W_n's are not three-term ones. As an illustration, we outline a non-equilibrium four-term hierarchy and its solution in terms of generalized operator continued fractions. Such structures also allow one to formulate long-time approximations, but make it more difficult to justify thermalization. For large thermal and de Broglie wavelengths, the dominant W_{eq} and a non-equilibrium equation for W are reported: the non-equilibrium hierarchy could plausibly be a three-term one and possibly not far from Gaussian, and thermalization could possibly be justified.

1. Introduction

A large and comprehensive set of references on the philosophy and foundations of statistical mechanics (both at equilibrium and off-equilibrium), from different points of view, is collected in [1]. Non-equilibrium statistical systems of classical particles are described by non-negative Liouville distribution functions (W_c) [2–5]. For non-equilibrium statistical systems of quantum particles, Wigner functions (W) are quite suitable in a global sense [3–8] ($W < 0$ in some cases). Achieving a deeper knowledge of how open or closed (classical or quantum) statistical interacting systems evolve in time plays a key role in statistical physics. A system subject to the influence of another (in general, larger) system at thermal equilibrium (external "heat bath" or hb) is named open. A system not influenced by any such external hb is named closed. The issue of the thermodynamic asymmetry in time continues to be central [9]: in short, how an arrow of time and/or irreversibility could arise in the long-time evolution of closed classical or quantum many-particle systems [2–5,10].

The dependences of the non-equilibrium Liouville and Wigner equations on momenta have a universal character (see Equations (1), (40) and (41)), while their dependences on positions are contained inside the potentials and, then, vary from one case to another. These facts suggest the use of non-equilibrium position-dependent moments (through suitable orthogonal polynomials profiting from the universal dependences on momenta and integrations over the latter). One could ask whether those universal momenta dependences would allow, for large systems under certain conditions and in some approximation, for their thermalization towards the canonical equilibrium distributions.

We shall adopt the following standpoint, certainly different from those in [11–14] and bearing connections to and, simultaneously, differences from those in [15–22]. As a direct analysis of large systems is very difficult, we shall start with an open small statistical system, subject to an hb at thermal equilibrium at absolute temperature, T ($\neq 0$), but with negligible external dissipation, due to the hb. In such a framework, the non-equilibrium evolution of the system does not thermalize, but we shall apply suitable long-time approximations and investigate whether they yield an approximate thermalization or if the latter is physically unexpected. Even if such dissipationless systems constitute an oversimplification, they give rise to both considerable difficulties and some interesting possibilities, as we shall see. Just in case an approximate thermalization could occur under certain conditions, then such a strategy could possibly be generalized for non-equilibrium evolutions of closed statistical many-particle systems without hb, at least approximately.

We shall study the following issues, left open in [11–14]: (a) In the non-equilibrium evolution for an open classical one-particle system for long times, subject to an external hb at absolute temperature T with negligible external dissipation on the former, is there anything in the structure of its Liouville equation

allowing for certain dynamical selection of the canonical equilibrium distribution, out of the set of all stationary distributions, at least partially and/or approximately? If so, in what sense? If (a) has some positive (even if partial) answer: (b) could it be extended to non-equilibrium closed classical systems without external hb (the role of the latter being then played by a large set of internal degrees of freedom at equilibrium in the system), at least approximately? (c) Could it be extended to quantum systems by means of Wigner functions [6], at least approximately or in some regime? The present work, which will extend, non-trivially, [15–22], is devoted to study questions (a), (b) and (c).

First, we shall investigate Issue (a). See Section 2 (which will also provide a useful framework for (c) later, in Sections 3–7) and Appendices A and B.

Second (Issue (b)), we shall present a simple overview of [15] on long-time approximations and irreversibility in closed interacting many-particle classical systems (with neither hb's nor dissipation due to external sources), including some improvements from [17], in order to extract some approximate arrow of time. See Section 3 and Appendix B.

Third, we turn to the largest part of this work (Issue (c)). The genuine difficulties of quantum cases already show up in one-dimensional systems, and they deserve further study. Some generalizations of the moment method to non-equilibrium open one-particle quantum statistical systems have already been studied with external dissipation (to lowest order in Planck's constant) [21,22] and also without external dissipation [20]. Here, we shall focus on the Wigner function and equation, with negligible external dissipation due to the hb, to all orders in Planck's constant. We shall treat stationary and equilibrium Wigner functions, the issue of negativity and the orthogonal polynomials generated by them (Sections 4 and 5) and the non-equilibrium evolution (Section 6). Could one display some arrow of time in the quantum case, at least approximately in some regime? See Section 6.4 and, just for the case of large thermal and de Broglie wavelengths, Section 7. Finally, Section 8 presents some conclusions and various discussions. Several technical aspects on Issues (a) and (c) are treated in Appendices A and C–G.

The inclusion of non-negligible dissipation in open systems has been studied in detail, both in classical and quantum cases, in [22]. From the outset, in the present work, we shall deal with an open system, subject to an hb (at finite and well-defined $T \neq 0$) exerting negligible dissipation on the former. However, the very consideration of such a system could give rise to criticisms. In fact, one could argue that either the neglection of dissipation would upset the fact that the system evolves at finite T or that the system would be a closed one (then being unclear what the temperature would mean). We shall address such conceptual issues *a posteriori* in Sections 2.3 (classical) and 6.4 (quantum).

2. Open Classical One-Particle Systems

2.1. Some General Aspects

Let a classical non-relativistic particle, with mass m, position x and momentum q, be subject to a real potential $V = V(x)$, in the presence of a "heat bath" (hb) at thermal equilibrium at absolute temperature T, with $\beta = (k_B T)^{-1}$ (k_B being Boltzmann's constant). Dissipation effects on the particle due to the hb will be supposed as so small that they will be discarded completely (negligible friction).

We shall suppose that $V(x) \geq 0$, with $V(x) \to 0$ as $\mid x \mid \to +\infty$. Classical harmonic/anharmonic oscillators, treated in [17,20], will not be considered in Sections 2 and 3. The classical Hamiltonian of the particle is: $H_c = q^2/(2m) + V$. Let the classical particle be, at the initial time $t = 0$, out of thermal equilibrium with the hb, and have a Liouville probability distribution $W_{c,in} = W_{c,in}(x, q)$ (≥ 0) to be at the position, x, with momentum q. Then, the non-equilibrium particle has, at time $t(> 0)$, the probability distribution $W_c = W_c(x, q; t)(\geq 0)$, which evolves through the reversible Liouville equation:

$$\frac{\partial W_c}{\partial t} + \frac{q}{m} \frac{\partial W_c}{\partial x} - \frac{\partial V}{\partial x} \frac{\partial W_c}{\partial q} = 0 \tag{1}$$

We shall treat the temporal evolution for $t > 0$ by using Equation (1) for W_c, with the initial condition, $W_{c,in}$. Equation (1) has an infinite set of stationary (t-independent) solutions: $W_c = W_{c,st} = f(H_c)$, with an arbitrary function, $f \geq 0$, decreasing quickly as $\mid H_c \mid \to +\infty$, by assumption. Hence, $W_{c,st}$ is not Gaussian in q, in general. The equilibrium (or Boltzmann's) canonical distribution, a t-independent solution of Equation (1) describing thermal equilibrium of the particle with the hb, is Gaussian in q: $W_{c,st} = W_{c,eq} = \exp[-\beta(q^2/(2m)+V)]$. Another stationary solution, to be treated briefly in Appendix B, just as a peculiar illustration, is the stationary microcanonical distribution, $W_{c,mc}$.

Let q_0 be some fixed x-independent momentum, to be discussed later. We shall define $y = q/q_0$. We shall consider a generic stationary $W_{c,st}$, with an arbitrary f, and we shall introduce the denumerably infinite family of all (unnormalized) polynomials in y: $H_{c,n} = H_{c,n}(y)$ ($n = 0, 1, 2, 3, \dots$), orthogonalized in y (for fixed x) by using $W_{c,st}$ as the weight function. By choosing $H_{c,0}(q) = 1$, we impose, for $n \neq n'$ and any x (left unintegrated), that:

$$\int_{-\infty}^{+\infty} dy W_{c,st}(x, q) H_{c,n}(y) H_{c,n'}(y) = 0 \tag{2}$$

The orthonormalized polynomials are $H_{c,n}(y)/(h_{c,n})^{1/2}$, with the ($x$-dependent) normalization factor:

$$h_{c,n} \equiv \int_{-\infty}^{+\infty} dy W_{c,st}(x, q) H_{c,,n}(y)^2 \tag{3}$$

The $H_{c,n}(y)$'s suggest the following new moments $W_{c,n}$ ($n = 0, 1, 2, \dots$) of W_c:

$$W_{c,n} = W_{c,n}(x; t) = \int_{-\infty}^{+\infty} dy H_{c,n}(y) W_c(x, q; t) \tag{4}$$

For $W_c = W_{c,st}(x, q)$, Equation (4) yields $W_{c,st,n} = 0$ if $n > 0$, and $W_{c,st,0} = \int_{-\infty}^{+\infty} dy W_{c,st}(x, q)$. The initial condition, $W_{c,in,n}$, for $W_{c,n}$ is obtained by replacing W_c by $W_{c,in}$ in Equation (4). One has the following (formal) expansion for W_c:

$$W_c = W_{c,st}(x, q) \sum_{n=0}^{+\infty} W_{c,n}(x; t) \frac{H_{c,n}(y)}{h_{c,n}} \tag{5}$$

2.2. $W_{c,st} = W_{c,eq}$: Three-Term Hierarchy, Operator Continued Fractions and Long-Time Approximation

Let us consider the very special case: $W_{c,st} = W_{c,eq}$, with $q_0 = (2m/\beta)^{1/2}$. The orthogonal polynomials generated by the weight function, $W_{c,eq}$, are $H_{c,n}(y) = H_n(y)$, $H_n(y)$ being the standard

(x-independent) Hermite polynomials [23]. For $W_c = W_{c,eq}(x,q)$ and $H_{c,n}(y) = H_n(y)$, Equation (4) yields $W_{c,eq,n} = 0$ if $n > 0$, and $W_{c,eq,0} = \int_{-\infty}^{+\infty} dy W_{c,eq}(x,q) = \pi^{1/2} \exp[-\beta V]$. For $H_{c,n}(y) = H_n(y)$, Equations (1) and (4) give an exact three-term non-equilibrium hierarchy for all $W_{c,n}$'s [11,12,15]. Such a three-term hierarchy, through the transformation $W_{c,n}(x;t) = [W_{c,eq,0}(x)]^{1/2} g_n(x;t)$, becomes the following exact three-term hierarchy for the g_n's for any $n = 0, 1, 2, 3....$:

$$\frac{\partial g_n}{\partial t} = -M_{c,n,n+1} g_{n+1} - M_{c,n,n-1} g_{n-1} \tag{6}$$

$$M_{c,n,n\pm1} g_{n\pm1} \equiv \left[\frac{(n + (1/2)(1 \pm 1)) k_B T}{m}\right]^{1/2} \left[\frac{\partial g_{n\pm1}}{\partial x} - \frac{(\pm 1) g_{n\pm1}}{2 k_B T} \frac{\partial V}{\partial x}\right] \tag{7}$$

with initial condition $g_{in,n} = W_{c,in,n}/W_{c,eq,0}^{1/2}$. One key fact is that $M_{c,n,n+1}$ and $-M_{c,n+1,n}$ are the adjoint of each other. Notice that Equation (7) corrects a misprint in Equation (5) in [20]. One sees directly that the $W_{c,eq,n}$'s solve the three-term recurrence relation Equations (6) and (7).

Let us consider the Laplace transforms $\tilde{g}_n = \tilde{g}_n(s) = \int_0^{+\infty} dt g_n \exp(-st)$, with inverse $g_n = \int_{c-i\infty}^{c+i\infty} (ds/2\pi i) \tilde{g}_n \exp(st)$ (c being real and such that $\tilde{g}_n(s)$ is analytic in the half-plane $Res > c$ of the complex s-plane). This definition and Equation (6) yield the three-term hierarchy for $\tilde{g}_n$:

$$s\tilde{g}_n = g_{in,n} - M_{c,n,n+1} \tilde{g}_{n+1}(s) - M_{c,n,n-1} \tilde{g}_{n-1}(s) \tag{8}$$

The hierarchy Equation (8) can be solved formally by extending to it standard procedures for solving numerical three-term linear recurrence relations in terms of continued fractions [12]. One gets all $\tilde{g}_n(s)$, for any $n = 1, \ldots$, in terms of sums of products of certain s-dependent linear operators $D[n'; s]$, $n' \geq n$, acting upon $\tilde{g}_{n-1}(s)$ and upon all $g_{in,n'}$'s, with $n' \geq n$. The following recurrence gives the $D[n;s]$'s:

$$D[n;s] = [sI - M_{c,n,n+1} D[n+1;s] M_{c,n+1,n}]^{-1} \tag{9}$$

I is the unit operator. By iteration of Equation (9), $D[n;s]$ becomes a formal infinite continued fraction of the products of the non-commuting linear operators, $M_{c,n,n+1}$ and $M_{c,n+1,n}$. The hierarchies in Equations (6)–(8) are as reversible as Equation (1). The long-time approximation below will introduce irreversibility in those hierarchies. Let us consider some real and small $\epsilon > 0$ and some integer, $n_0 \geq 1$. Then, for $n \geq n_0$, $D[n+1; \epsilon]$ is Hermitian, and all its eigenvalues are real and non-negative. The essential justification of those two properties can be easily exemplified through 2×2 matrices: let us replace $D[n+1; s]$ by a Hermitian 2×2 matrix with non-negative eigenvalues, $M_{c,n,n+1}$ and $M_{c,n+1,n}$, by two 2×2 matrices, such that $M_{c,n,n+1}$ and $-M_{c,n+1,n}$ are the adjoint of each other. Then, it is easy to see that $-M_{c,n,n+1} D[n+1; s] M_{c,n+1,n}$ is also a Hermitian 2×2 matrix with non-negative eigenvalues, and the same holds for $\epsilon I - M_{c,n,n+1} D[n+1; s] M_{c,n+1,n}$, I being now the unit 2×2 matrix. An alternative justification of the above is also given just before Equation (32). To complete the justification, one should take into account the $[(n + (1/2)(1 \pm 1)) k_B T]^{1/2}$ factors contained inside $M_{c,n,n\pm1}$ in Equation (7): the continued-fraction structure of the D's in Equation (9) implies that for adequately large n, $-M_{c,n,n+1} D[n+1; s] M_{c,n+1,n}$ decreases grossly as $n^{-1/2}$, so that, if ϵ is not large, $[\epsilon I - M_{c,n,n+1} D[n+1; s] M_{c,n+1,n}]^{-1}$ is also Hermitian and has non-negative eigenvalues. In short, the continued-fraction structure of the D's in Equation (9) justifies recurrently that if $D[n+1; \epsilon]$ is Hermitian and has only non-negative eigenvalues, the same is also true for $D[n; \epsilon]$. For more details,

see [15,16,20]. For a simpler hierarchy, without loss of generality, let us assume that $W_{c.in,n'} = 0$ for $n' \geq 1$, with $W_{c,in,0} \neq 0$. Although the long-time approximation has been justified for adequately large n, let us choose $n_0 = 1$, for simplicity. Then, Equation (8) yields:

$$s\tilde{g}_0(s) = W_{c,eq,0}^{-1/2}W_{c,in,0} - M_{c,0,1}\tilde{g}_1(s) \tag{10}$$

$$\tilde{g}_n(s) = -D[n;s]M_{c,n,n-1}\tilde{g}_{n-1}(s), \; n \geq 1 \tag{11}$$

The long-time approximation for $n \geq 1$ and small s can now be implemented as follows (with $\epsilon > 0$). One replaces any $D[n;s]$ yielding $\tilde{g}_n$ in Equation (11), $n \geq 1$, by $D[n;\epsilon]$: this approximation is not done for $n = 0$, which will be crucial. We regard $D[n;\epsilon]$ in Equation (11) as fixed (s-independent) operators. Thus, in particular, we approximate in Equation (11) for small s and $n = 1$ as: $\tilde{g}_1(s) \simeq -D[1;\epsilon]M_{c,1,0}\tilde{g}_0(s)$ (to be compared to Equation (11) for $n = 1$, before the approximation). Then, Equations (11) (after the approximation) and (10) become, by taking inverse Laplace transforms:

$$\frac{\partial g_0}{\partial t} = -M_{c,0,1}g_1 \tag{12}$$

$$g_1 \simeq -D[1;\epsilon]M_{c,1,0}g_0 \tag{13}$$

Equations (12) and (13) give the irreversible Smoluchowski-like equation for the $n = 0$ moment:

$$\partial g_0/\partial t = M_{c,0,1}D[1;\epsilon]M_{c,1,0}g_0 \tag{14}$$

In the latter, after the above long-time approximation, we employ the same initial condition $W_{c,in,0}/W_{c,eq,0}^{1/2}$ at $t = 0$; this amounts to another kind of approximation (presumably, without special importance, as long as the system will thermalize, independently on the initial condition). The solutions of the last equation for g_0 relax irreversibly, for large t and reasonable $W_{c,in,0}$, towards $W_{c,eq,0}^{1/2} \neq 0$ and $g_n \to 0$ if $n = 1,\ldots$ (thermal equilibrium). Then, the dominant moment is g_0, while any g_n with $n > 0$ is negligible. g_n ($n \geq 1$) is the smaller, the larger $t(> 0)$ and n are (due to the behaviors of $M_{c,n,n\pm1}$ and of $D[n;\epsilon]$ with n) [15,16,20]. Similar behaviors hold for $W_{c,0}$ and $W_{c,n}$ with $n > 0$. To carry out quantitative studies for large t, some ansatz or approximation (outside our scope) should be provided for $D[1;\epsilon]$ at least, consistently with the above properties. Equation (102) describes a Brownian-like random walker, subject to $V(x)$. For other applications of the operator continued fractions to the Smoluchowski equation for Brownian motion and to problems in condensed matter physics, see [24] and references therein.

For the following computation, the right-hand-side of Equation (14) should be interpreted as $\int_{-\infty}^{+\infty} dx'(M_{c,0,1}D[1;\epsilon]M_{c,1,0})(x,x')g_0(x';t)$. Let: $(f_1,f_2) = \int_{-\infty}^{+\infty} dxf_1(x)^*f_2(x)$ for suitable functions f_1 and f_2. The following properties (which follow from the general ones of $D[n;\epsilon]$ stated above) will be used to get Equation (16): (a) due to the Hermiticity of $D[1;\epsilon]$: $(f_1, M_{c,0,1}D[1;\epsilon]M_{c,1,0}f_2) = (M_{c,0,1}D[1;\epsilon]M_{c,1,0}f_1, f_2)$, thereby checking that $M_{c,0,1}D[1;\epsilon]M_{c,1,0}$ is Hermitian, as so is $D[1;\epsilon]$; (b) $(f_1, M_{c,0,1}D[1;\epsilon]M_{c,1,0}f_1) = -(M_{c,1,0}f_1, D[1;\epsilon]M_{c,1,0}f_1) \leq 0$ for arbitrary functions f_1, as all eigenvalues of $D[1;\epsilon]$ are ≥ 0. Both Properties (a) and (b) (with $D[1;\epsilon]$ replaced by $D[n+1;\epsilon]$) lie at the heart of the iterative justification that $D[n;\epsilon]$ is Hermitian and has only real and non-negative eigenvalues for $n \geq 0$. After the long-time approximation and anticipating Equation (32), let:

$$L = \frac{1}{2}(g_0, g_0) \tag{15}$$

Using Equation (14) and the preceding Properties (a) and (b):

$$\partial L/\partial t = (g_0, M_{c,0,1}D[1;\epsilon]M_{c,1,0}g_0) = -(M_{c,1,0}g_0, D[1;\epsilon]M_{c,1,0}g_0) \le 0 \qquad (16)$$

As L is a non-decreasing function in the time evolution, it can be regarded as a Lyapunov function. A function quite similar to this L has been studied for the Brownian motion of one classical particle [25] (but without having arrived to it, by starting from Equation (1)).

2.3. $W_{c,st} = W_{c,eq}$: On the Inclusion of Dissipation

The following discussion on dissipation is adequate. We do not attribute a physical meaning to temperature for a closed classical one-particle system (contrary to a closed classical many-particle one, to be treated in Section 3). There is a physical difference between a closed classical one-particle system and the meaningful open one in the presence of (and coupled to) an external hb at thermal equilibrium at finite T, with friction. By recalling [20], we shall treat briefly the inclusion of non-negligible dissipation with friction constant $\sigma > 0$ for the open classical system. Then, Equations (1), (8) and (9) are replaced, respectively, by:

$$\frac{\partial W_c}{\partial t} + \frac{q}{m}\frac{\partial W_c}{\partial x} - \frac{\partial V}{\partial x}\frac{\partial W_c}{\partial q} = \frac{1}{\sigma}\frac{\partial[(q+(m/\beta))(\partial W_c/\partial q)]}{\partial q} \qquad (17)$$

$$(s + \frac{n}{\sigma})\tilde{g}_n = W_{c,eq,0}^{-1/2}W_{c,in,n} - M_{n,n+1}\tilde{g}_{n+1} - M_{n,n-1}\tilde{g}_{n-1} \qquad (18)$$

$$D[n; s + \frac{n}{\sigma}] = [s + \frac{n}{\sigma} - M_{n,n+1}D[n+1; s + \frac{n+1}{\sigma}]M_{n+1,n}]^{-1} \qquad (19)$$

Equation (17) is a well-known dissipative Equation [11–13]. Notice the key fact that in Equations (18) and (19), σ only appears as $s + (n/\sigma)$, so that $\epsilon + (n/\sigma) > 0$ (for $s = \epsilon > 0$ and $n = 0,1,2,...$). Having in mind Equation (7) (and the T−dependences in it), one can let σ^{-1} be as small as one wishes at constant and finite T, while $D[n; \epsilon + \frac{n}{\sigma}]$ always fulfills Hermiticity and non-negativity, regardless of how its magnitude could vary (which, in turn, depends on σ^{-1}, n, ϵ and T, for given V). This is the essential argument allowing one to use a hb at finite T with very small dissipation and in trying to justify that the step $\sigma^{-1} \simeq 0$ could be permissible (those properties of $D[n; \epsilon + \frac{n}{\sigma}]$ not depending on whether σ^{-1} is very small, with $\ne 0$, or $\sigma^{-1} \simeq 0$), in the classical case. However, just for $\sigma^{-1} \simeq 0$, one could argue that the resulting σ^{-1}-free equations (namely, Equations (1), (8) and (9), containing a finite T) account for a closed classical one-particle system. We shall not delve into the conceptual issue of whether the step $\sigma^{-1} \simeq 0$ allows for the classical one-particle system in the presence of an hb at finite T to be still interpreted as open (which we have favored and employed) or leads to a closed one. We can avoid that issue for the following practical reason: (oversimplified) open classical one-particle systems are interesting, as long as they provide useful technical guides towards approximate long-time thermalization in non-equilibrium closed classical large systems (without external hb's), and that will turn out to be the case in Section 3.

A similar practical standpoint in the (far more difficult) quantum case will be expressed in the last paragraph in Section 6.4.

2.4. Generic $W_{c,st}$: Hierarchy and Failures of the Long-Time Approximation

For a general $W_{c,st}$, with given (x-independent) q_0, we shall return to the $H_{c,n}$'s defined in Equation (2) (depending parametrically on x in general for $n \geq 2$), so that $H_{c,n} \neq H_n$. We shall write them as:

$$H_{c,n}(y) = y^n + \sum_{j=1}^{n} \epsilon_{c,n,n-j} y^{n-j} \tag{20}$$

$\epsilon_{c,n,n-j}$, being y-independent (but x-dependent, in general), is given in Appendix A for $n = 2, 3, 4, 5$ (Equations (73)–(76)). As $W_{c,st}$ is even in y, one has $\epsilon_{c,n,n-j} = 0$ for odd j, so that $H_{c,n}(-y) = (-1)^n H_{c,n}(y)$. Consistently with the general properties [26], the $H_{c,n}$'s fulfill the three-term recurrence relation:

$$y H_{c,n}(y) = H_{c,n+1}(y) + C_{c,n} H_{c,n-1}(y) \tag{21}$$

for $n = 0, 1, 2, \ldots$, with $C_{c,0} \equiv 0$. $C_{c,n}$ is y-independent (but it depends on x). Since $W_{c,st} \geq 0$, a general theorem [26] ensures that $C_{c,n} \geq 0$. Examples of the lowest $C_{c,n}$'s for the stationary microcanonical distribution are given in Appendix B. One could also express the $H_{c,n}$'s as suitable sums of Hermite polynomials: such an alternative will not be followed here, but in Section 5, in other cases.

The $H_{c,n}$'s determine new moments $W_{c,n}$ (not to be confused with those in Section 2.2 for the H_n's) through Equation (4). We shall transform Equation (1) into a linear hierarchy for the new moments, $W_{c,n}$. For that purpose, we multiply Equation (1) by $H_{c,n}(y)$, integrate over y and operate, so as to express the resulting equation solely in terms of the $W_{c,n'}$'s. We carry out cancellations and simplifications, by using Equations (1) and (20). We shall display the first five equations (for $n = 0, 1, 2, 3, 4$) in the hierarchy, for any $W_{c,st}$ and q_0:

$$\frac{\partial W_{c,0}}{\partial t} = -\frac{q_0}{m} \frac{\partial W_{c,1}}{\partial x} \tag{22}$$

$$\frac{\partial W_{c,1}}{\partial t} = -\frac{q_0}{m} \frac{\partial W_{c,2}}{\partial x} + \frac{q_0}{m} \frac{\partial}{\partial x} [(\epsilon_{c,2,0}) W_{c,0}] - \frac{1}{q_0} \frac{\partial V}{\partial x} W_{c,0} \tag{23}$$

$$\frac{\partial W_{c,2}}{\partial t} = -\frac{q_0}{m} \frac{\partial W_{c,3}}{\partial x} + \frac{q_0}{m} \frac{\partial}{\partial x} [(\epsilon_{c,3,1} - \epsilon_{c,2,0}) W_{c,1}] + \frac{q_0}{m} \frac{\partial \epsilon_{c,2,0}}{\partial x} W_{c,1} - \frac{2}{q_0} \frac{\partial V}{\partial x} W_{c,1} \tag{24}$$

$$\frac{\partial W_{c,3}}{\partial t} = -\frac{q_0}{m} \frac{\partial W_{c,4}}{\partial x} + \frac{q_0}{m} \frac{\partial}{\partial x} [(\epsilon_{c,4,2} - \epsilon_{c,3,1}) W_{c,2}] + \frac{q_0}{m} \frac{\partial \epsilon_{c,3,1}}{\partial x} W_{c,2} - \frac{3}{q_0} \frac{\partial V}{\partial x} W_{c,2} \tag{25}$$

$$\frac{\partial W_{c,4}}{\partial t} = -\frac{q_0}{m} \frac{\partial W_{c,5}}{\partial x} + \frac{q_0}{m} \frac{\partial}{\partial x} [(\epsilon_{c,5,3} - \epsilon_{c,4,2}) W_{c,3}] + \frac{q_0}{m} \frac{\partial \epsilon_{c,4,2}}{\partial x} W_{c,3} - \frac{4}{q_0} \frac{\partial V}{\partial x} W_{c,3} \tag{26}$$

Equations (77)–(80) play a key role in the computations and cancellations leading to Equations (22)–(26). The latter constitute a three-term recurrence relation for $0 \leq n \leq 4$. For any $W_{c,st} \neq W_{c,eq}$ and $V \neq 0$, the equation for $\partial W_{c,n}/\partial t$ for $n \geq 5$ contains $M_{st,n,n+1} W_{c,n+1} = (q_0/m(\partial W_{c,n+1}/\partial x$ and no other dependences on higher order moments, but it is increasingly difficult to exhibit cancellations in it for moments of order lower that n. Then, it is an open question whether the hierarchy Equations (22)–(26), when analyzed for $5 \leq n \leq +\infty$, is also a three-term one regarding moments of order lower than n. In spite of that, and for a generic $W_{c,st}(\neq W_{c,eq})$, let us conjecture, tentatively, for

a while, that, for $V \neq 0$, the $W_{c,n}$'s would fulfill an infinite three-term hierarchy, with other operators $M_{st,n,n\pm1}(\neq M_{c,n,n\pm1})$, namely:

$$\frac{\partial W_{c,n}}{\partial t} = -M_{st,n,n+1}W_{c,n+1} - M_{st,n,n-1}W_{c,n-1} \tag{27}$$

with the above $M_{st,n,n+1}$. The corresponding $M_{st,n,n-1}$'s are linear first-order differential operators, and those for $n = 0, 1, 2, 3, 4$ are obtained by comparison with Equations (22)–(26). That is, the finite hierarchy Equations (22)–(26) would be the lowest part of the infinite three-term one in Equation (27), conjectured to hold for any $5 \leq n \leq +\infty$. See Section 7 for one further development regarding such a conjecture. The initial conditions at $t = 0$ continue to be $W_{c,in,n}$. One sees directly that the stationary moments $W_{c,st,n}$'s do solve the three-term recurrence relations Equations (22)–(26), (27). A key issue for a generic $W_{c,st}(\neq W_{c,eq})$ is that $M_{st,n,n+1}$ is not the adjoint of $-M_{st,n+1,n}$ for any n in general, as Equations (22)–(26) exemplify. Moreover, we have been unable to transform exactly the hierarchy Equation (27) into another one with new $W'_{c,n}$ and $M'_{st,n,n\pm1}$, in which $M'_{st,n,n+1}$ is the adjoint of $-M'_{st,n+1,n}$ for any n, and we believe that, likely, such a transformation does not exist in general.

Let us consider the Laplace transforms $\tilde{W}_{c,n} = \tilde{W}_{c,n}(s) = \int_0^{+\infty} dt W_{c,n} \exp(-st)$. This definition yields an infinite three-term hierarchy for $\tilde{W}_{c,n}$'s similar to Equation (8) which, in turn, can be solved formally in terms of other operator continued fractions, $D_{st}[n;s]$'s. The latter are defined recurrently through:

$$D_{st}[n;s] = [sI - M_{st,n,n+1}D_{st}[n+1;s]M_{st,n+1,n}]^{-1} \tag{28}$$

As $M_{st,n,n+1}$ and $-M_{st,n+1,n}$ are not adjoint to each other, it follows that $D_{st}[n+1;\epsilon]$ is not Hermitian in general, and no general statement can be made regarding its eigenvalues, if they exist. Then, *a priori*, it is unlikely that a long-time approximation and a long-time approach to equilibrium for $n \geq n_0 \geq 1$ could be justified for the $\tilde{W}_{c,n}$'s in the three-term Equation (27), for an arbitrary $W_{c,st}$. Upon recalling at this stage that the validity of the three-term structure in Equation (27) has not even been established if $V \neq 0$ for $5 \leq n \leq +\infty$, the possibility of formulating a long-time approximation for a generic $W_{c,st}(\neq W_{c,eq})$ becomes even more unlikely. It is unclear whether the microcanonical distribution $W_{c,st} = W_{c,mc}$ could be an exception, somehow: see Appendix B.

Then, the developments in Section 2.2 and in the present one appear to indicate that, if $\epsilon > 0$, there would exist some sort of (at least, partial) dynamical selection of the canonical equilibrium distribution, $W_{c,eq}(x, q)$, out of the set of all stationary distributions, $W_{c,st}$, solving the Liouville equation. On the other hand, the general recurrence Equations (22)–(26) and the arguments on the D_{st}'s in this subsection will turn out to be very useful in Sections 6 and 7.

3. Closed Classical Many-Particle Systems: Long-Time Approximation and the Arrow of Time

We treat a closed large system of many ($N \gg 1$) classical non-relativistic particles, in d spatial dimensions ($d = 1, 2, 3$), with spatial coordinates $\mathbf{x}_1, \ldots, \mathbf{x}_N$ ($\equiv [x]$) and momenta $\mathbf{q}_1, \ldots, \mathbf{q}_N$ ($\equiv [q]$): a real gas. All particles, which are identical, have mass m. Let $x_{i,\alpha}$ and $q_{i,\alpha}$ be the Cartesian components of $\mathbf{x}_i$ and $\mathbf{q}_i$, respectively ($i = 1, \ldots, N$, $\alpha = 1, \ldots d$). Neither a hb, nor external friction mechanisms, nor external forces are included. The interaction potential among all particles is: $V = \Sigma_{i,j=1,i<j}^N V_{i,j}(| \mathbf{x}_i - \mathbf{x}_j |)$. By assumption, all $V_{i,j}(| \mathbf{x}_i - \mathbf{x}_j |)$ are repulsive (≥ 0) and tend quickly to zero for large $| \mathbf{x}_i - \mathbf{x}_j |$. The non-equilibrium classical distribution function is: $W_c = W_c([x], [q]; t)$. The reversible Liouville equation reads:

$$\frac{\partial W_c}{\partial t} = \Sigma_{i=1}^N \Sigma_{\alpha=1}^d \big[\frac{\partial V}{\partial x_{i,\alpha}} \frac{\partial W_c}{\partial q_{i,\alpha}} - \frac{q_{i,\alpha}}{m} \frac{\partial W_c}{\partial x_{i,\alpha}} \big] \tag{29}$$

See [3,5,27] for studies of non-equilibrium states. The initial $W_{c,in}$ [3,5,15], given by assumption, describes the following non-equilibrium distribution at $t = 0$. There is a very large set (s_1) of degrees of freedom in the system, which are at thermal equilibrium at temperature T with one another, and they play the role of an effective (internal) hb. The gas at $t = 0$ also contains a large set of degrees of freedom (s_2), which are off-equilibrium with the previous set, s_1, and among themselves. We may suppose that the set, s_1, is located at large distances and is larger than the set, s_2 (located, in turn, at finite distances). We shall focus on Boltzmann's equilibrium distribution at temperature T: $W_{c,eq} = \exp[-\beta H_{c,N}]$, where $H_{c,N} = (2m)^{-1}\Sigma_{i=1}^N \Sigma_{\alpha=1}^d q_{i,\alpha}^2 + V$ is the classical N-particle Hamiltonian. Let $[n]$ denote a set of non-negative integers ($n(i = 1, \alpha = 1), \ldots, n(i = N, \alpha = d)$), and let $n = \Sigma_{l=1}^N \Sigma_{\alpha=1}^d n(l, \alpha)$. Let $[dq] = \prod_{i=1}^N \prod_{\alpha=1}^d dq_{i,\alpha}$.

We introduce non-equilibrium moments $W_{[n]}$ of W (using products of the Hermite polynomials orthogonalized through $W_{c,eq}$, by generalizing Equation (4)):

$$\int [dq] \prod_{i=1}^N \prod_{\alpha=1}^d \frac{H_{n(i,\alpha)}(q_{i,\alpha}/(2mk_BT)^{1/2})}{(\pi^{1/2}2^{n(i,\alpha)}n(i,\alpha)!)^{1/2}} W_c([x], [q], t) \equiv W_c(x; [n]; t) = W_c([n]) \tag{30}$$

with the choice $q_0 = (2m/\beta)^{1/2}$. If $W_c = W_{c,eq}$, then $W_{c,eq}([0]) = \pi^{3N/4}q_0^{3N}\exp[-\beta V]$ ($[0] = (0, 0, \ldots, 0)$) and $W_{c,eq}([n]) = 0$, $[n] \neq [0]$ ($n > 0$). Equation (30) can also be applied to $W_{c,in}$ and gives the corresponding initial moments, $W_{c,in}([n])$. We shall work with the symmetrized moments $g([n]) = W_{c,eq}([0])^{-1/2}W_c([n])$. The resulting infinite reversible three-term hierarchy for $g([n])$'s (for any $[n]$, generalizing Equations (6) and (7)) and the long-time approximation and evolution towards $W_{c,eq}$, have been justified previously [15,20]. In principle, the long-time approximation also requires here a similar $\epsilon > 0$; see [15,20] for the possibility of letting $\epsilon \to 0$ here (as N is very large and $d > 1$, in the thermodynamical limit). One expects that if $W_{c,in}$ is not too far from $W_{c,eq}$, then the thermalization of the whole system at constant T throughout it occurs. The arguments in Section 2.2, based upon Hermiticity and non-negativity and justifying partially the dynamical selection of $W_{c,eq}$, also hold in the present case; the details will be omitted. *A posteriori*, the formal similarity between Equations (6) and (7) and the actual three-term hierarchy for N particles (with vanishing external dissipation) [15] justify the usefulness of the studies in Section 2 for hb's with negligible dissipation.

Both the exact hierarchy for the $g([n])$'s and the closed approximate one for them after the long-time approximation are genuinely different from the non-equilibrium classical BBGKY (Bogoliubov-Born-Green-Kirkwood-Yvon) hierarchy [2–4]. In the latter, in the equation for the distribution function for $n(> 0)$ particles, one leaves unintegrated their position vectors and momenta, while those for the remaining $N - n$ particles are integrated over. Moreover, such an equation also depends on the distribution function for $n + 1$ particles, but not on that for $n - 1$ ones, a feature that, beyond the approximate framework of the standard Boltzmann equation (for $n = 1$) [2–4], does not seem to shed much light on the long-time approach to thermal equilibrium for larger n. By contrast, in the equation for $g([n])$ in the actual non-equilibrium hierarchy based upon $W_{c,eq}$, the contributions from $g([n + 1])$'s are neatly different from (and, for large n, approximately smaller by a factor of $\simeq n^{-1/2}$ than) those coming from $g([n])$'s, at least in the long-time approximation [15,20].

As an example, let us consider the following irreversible Smoluchowski-like equation for the $[n = 0]$ moment, which follows from long-time approximation [15,22]. It generalizes Equation (14) ($[n = 0]$ meaning $n(1, 1) = 0, \ldots, n(j, \beta) = 0, \ldots, n(N, d) = 0$):

$$\frac{\partial g([n = 0])}{\partial t} = \Sigma_{l=1}^N \Sigma_{\alpha=1}^d M_{l,\alpha;n(l,\alpha)=0;+} \times$$
$$(\Sigma_{l'=1}^N \Sigma_{\alpha'=1}^d [D[[n = 1]; \epsilon]]_{l,\alpha;l',\alpha'} M_{l',\alpha';n(l',\alpha')=1;-}) g([n = 0]) \tag{31}$$

The (continued fraction) operator $D[[n = 1]; \epsilon]$ is Hermitian with non-negative eigenvalues and has, as a square matrix, the matrix elements $[D[[n = 1]; \epsilon]]_{l,\alpha;l',\alpha'}$ (possibly, with $\epsilon \to 0$). The justification generalizes that for $D[1; \epsilon]$ in Section 2.2; see [15,16,20]. The initial condition is $W_{c,eq}([0])^{-1/2} W_{c,in}([0])$. Equation (102) describes the Brownian-like motion of N random walkers: the interaction of each walker with the other $N - 1$ ones is contained in V.

The structure of Equation (31), with $V_{i,j} \neq 0$ between any pair of particles and $D[[n = 1]; \epsilon]$ replaced by a constant, is similar to that of the linear Smoluchowski equation in the standard Rouse model for (linear) polymer dynamics [25], except for the following difference. For the polymer, one deals with a linear three-dimensional chain of many atoms, and the interaction is $\neq 0$ only (or dominant) between successive pairs of neighboring atoms along the chain (each of which performs Brownian-like motion). Another physical motivation of our approach would be to provide irreversible evolution equations for the actual (real gas) system, which, being different from those in the standard non-equilibrium BBGKY hierarchy, would have, in the simplest case (Equation (31)), a structure mimicking the one in the standard Rouse model for polymer dynamics, namely, resembling Brownian motion for N interacting random walkers, and would allow for generalizations (by using $g([n])$, with $n > 0$).

Let $d = 3$. We shall introduce the t-dependent Lyapunov function:

$$L = \frac{1}{2} \int \prod_{i=1}^N \prod_{\alpha=1}^3 dx_{i,\alpha} g([n = 0])^2 \tag{32}$$

upon integrating in $-\infty < x_{i,\alpha} < +\infty$ for any i, α. Like for Equation (15) in Section 2.2, Equation (31) implies:

$$\partial L/\partial t \leq 0 \tag{33}$$

Then, the actual L is a non-decreasing function in the time evolution. The generalization of a Lyapunov function for $n_0 > 1$, also fulfilling the generalization of Equation (33), can be made by extending [15,17] and will be omitted here. Let the classical many-particle system be at thermal equilibrium at T. Then:

$$L = \frac{1}{2} \int \prod_{i=1}^{N} \prod_{\alpha=1}^{3} dx_{i,\alpha} q_0^{3N} \pi^{3N/4} \exp[-\beta V] \equiv L_{eq} \tag{34}$$

As is well known, in equilibrium statistical mechanics, the equilibrium entropy, S_{eq}, is defined, up to a constant $S_{eq,0}$, by:

$$\exp[\frac{S_{eq} - S_{eq,0}}{k_B}] = \int [\prod_{i=1}^{N} \prod_{\alpha=1}^{3} dx_{i,\alpha}] \int [dq] \, W_{c,eq} \tag{35}$$

Upon comparing Equations (34) and (35), we get:

$$\exp[\frac{S_{eq} - S_{eq,0}}{k_B}] = 2\pi^{3N/4} L_{eq} \tag{36}$$

In our statistical mechanics approach, the situation seems somewhat paradoxical. In fact, let us start out from the t-independent structure in Equation (36) in order to go beyond equilibrium by letting t vary. That is, one would try tentatively a non-equilibrium entropy $S(t)$, such that $\exp[\frac{S(t)}{k_B}]$ would be proportional to $L(t)$. However, in so doing, one faces a paradox: as $L(t)$ decreases as t increases, such an $S(t)$ would also be forced to decrease, which strongly contradicts, in principle, what one expects from any physically acceptable non-equilibrium entropy. Then, if a t-dependent non-equilibrium entropy exists, it should not be related to $L(t)$ through some structure like "$\exp[\frac{S(t)}{k_B}]$ proportional to $L(t)$". Alternatively, we recall that, at thermal equilibrium, one introduces the information, I_{eq}, as $-S_{eq}$, and that if a non-equilibrium information, $I(t)$, could be defined in general, one would expect that it would decrease as t increases. Then, an attempt to introduce such a non-equilibrium information, $I(t)$, through a structure like "$\exp[\frac{-I(t)}{k_B}]$ proportional to $L(t)$", would not work either; as such, an $I(t)$ would be an increasing function.

There has been much interesting work aimed at extending, in different frameworks (thermodynamical, statistical, *etc.*), the definition of a t-dependent entropy, $S(t)$, to non-equilibrium phenomena, in such a way that the inequality $dS(t)/dt \geq 0$ would hold. Rate equation dynamics following the path of steepest entropy ascent constitute an interesting research subject [28]. At present, several different non-equilibrium entropies have been proposed and do characterize, in general settings, the notion of evolution [29–32] (to the best of the present author's knowledge). So far, neither a general agreement seems to have been reached on a unique non-equilibrium entropy $S(t)$ valid for different frameworks [29,32], nor an accepted definition of it on the basis of non-equilibrium statistical mechanics appears to exist (to the best of the present author's knowledge). Further perspectives are given by other interesting presentations, like [33].

Both in case that a general definition of a unique non-equilibrium entropy does not exist or, in the case that it could be formulated at the end, our proposal for a partial way out towards the characterization of, at least, an approximate arrow of time in the actual moment approach to non-equilibrium classical statistical mechanics is the following. Once the long-time approximation has been carried out as indicated above, we have studied a t-dependent function, L, through Equation (32), the variation of which seems to

be adequate to define an arrow of time, although it does fail to provide a non-equilibrium entropy! A previous study of L was limited to the framework of classical Brownian motion [25] and did not relate it to either non-equilibrium classical statistical mechanics for N particles or (to our knowledge) to any sort of non-equilibrium entropy. Our proposal could possibly complement partially different proposals by other authors characterizing evolution; see [1–4,9,29–34].

4. Open Quantum-Mechanical One-Dimensional System without Dissipation: General Aspects

4.1. Some General Aspects

We shall consider a quantum Brownian particle (qBp) of mass m (> 0) and momentum operator $-i\hbar(\partial/\partial x)$, in one spatial dimension, x, with (Hermitian) quantum Hamiltonian:

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V \tag{37}$$

with a real potential $V = V(x)$ ($\hbar$ being Planck's constant). We shall suppose that $V(x) \geq 0$ and, having in mind possible generalizations to many degrees of freedom, that $V(x) = V(-x)$ (parity being a constant of motion). We shall also suppose that $V(x)$ and all $d^n V(x)/dx^n$, $n = 1, 2, 3...$, are continuous for any x; a study for V's with finite discontinuities will be reported later (see, in particular, Appendices C and D). If $\varphi_j(x)$ is a suitably normalized eigenfunction of H: $H\varphi_j(x) = E_j\varphi_j(x)$, j being a suitable label. We shall deal with two classes of potentials, $V(x)$, depending on their behavior as $\mid x \mid \to +\infty$, and characterized as follows. The first class of $V(x)$'s fulfills $V(x) \to 0$ quickly, as $\mid x \mid \to +\infty$. Then, all eigenvalues, E_j, of H sweep the continuous positive real half-line: $0 \leq E_j < +\infty$. Such a purely continuous spectrum has, typically, a double degeneracy, associated with two different asymptotic conditions (incoming plane waves) at $x \to \pm\infty$, with the same energy, E_j. Then, j is a continuous variable ($-\infty < j < +\infty$), which labels all states and distinguishes degenerate ones (see Appendices D and G). The second class of $V(x)$'s fulfill as $\mid x \mid \to +\infty$, $V(x) \to +\infty$ (proportional to x^{2n}, for positive integer n), and they correspond specifically to harmonic/anharmonic oscillators (polynomials; see Section 5.1, where the spectra of the corresponding Hamiltonians is discussed). All items in this Section will apply to both classes of $V(x)$'s, unless otherwise stated.

For general aspects on quantum open systems, see [34–38] and the references therein. We consider the non-equilibrium statistical evolution of a qBp subject to $V(x)$ and in the presence of a hb at thermal equilibrium at T, with negligible external dissipation, due to the hb. The time evolution for $t > 0$ of the qBp is given by the density operator $\rho = \rho(t)$ (a statistical mixture of quantum states), with the initial condition $\rho(t = 0) = \rho_{in}$. $\rho(t)$ for $t > 0$ and ρ_{in} are Hermitian and positive-definite linear operators acting in the Hilbert space spanned by the set of all eigenfunctions, $\varphi_j(x)$, of H. Unless otherwise stated, we shall not impose that $\rho(t)$ be normalized. The time evolution of the qBp is described by the operator equation ($[H, \rho] = H\rho - \rho H$):

$$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar}[H, \rho] \tag{38}$$

We consider the matrix element, $\langle x - y|\rho(t)|x + y\rangle$, of $\rho(t)$ in generic eigenstates, $|x - y\rangle$, $|x + y\rangle$, of the quantum position operator. The quantum Wigner function $W = W(x, q; t)$, determined by ρ, is [6,7]:

$$W(x, q; t) = \frac{1}{\pi\hbar} \int_{-\infty}^{+\infty} dy \exp[\frac{i2qy}{\hbar}]\langle x - y|\rho(t)|x + y\rangle \tag{39}$$

The initial non-equilibrium Wigner function at $t = 0$ is W_{in}, given by Equation (39) if $\rho = \rho_{in}$. For $t > 0$, the exact dissipationless quantum master equation for W [6,7] is:

$$\frac{\partial W(x, q; t)}{\partial t} = -\frac{q}{m}\frac{\partial W(x, q; t)}{\partial x} + M_Q W \tag{40}$$

$$M_Q W = \int_{-\infty}^{+\infty} dq' W(x, q'; t) \int_{-\infty}^{+\infty} \frac{idy}{\pi\hbar^2}[V(x + y) - V(x - y)]$$

$$\times \exp[\frac{i2(q - q')y}{\hbar}] = \frac{dV}{dx}\frac{\partial W}{\partial q} - \frac{\hbar^2}{3!2^2}\frac{d^3V}{dx^3}\frac{\partial^3 W}{\partial q^3} + \cdots \tag{41}$$

As $\hbar \to 0$, Wigner's Equation (40) becomes, formally, by dropping all $\hbar$-dependent terms (containing $\partial^n W/\partial q^n$, $n = 3, 5, ...$) in Equation (41), the classical Liouville Equation (1), with $W \to W_c$ [6,7]. All terms in the series in Equation (41) contribute, in general, to V's in the first class. For V's in the second class, there is some n_1, such that $d^n V/dx^n \equiv 0$ for $n > n_1$. We shall suppose that, as $| q | \to +\infty$, $W(x, q; t) \to 0$ quickly, for fixed x and t, so that $\int_{-\infty}^{+\infty} dqW(x, q; t)q^n$ converges, for any integer $n \geq 0$. We shall check the validity of such an assumption in specific cases in Section 4.4 and Appendix C. Under the latter assumption, Equation (40) readily implies that $(\partial/\partial t) \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dqW(x, q; t) = 0$.

A stationary density operator, ρ_{st}, for the system fulfills Equation (38), with $\partial\rho/\partial t = 0$. Then, $\rho_{st} = f(H)$ is a function of H only (in the actual one-dimensional system, the constants of motion being H and parity). Then, ρ_{st} has the matrix elements:

$$\langle x - y|\rho_{st}|x + y\rangle = \sum_j f(E_j)\varphi_j(x - y)\varphi_j(x + y)^* \tag{42}$$

For a continuous spectrum, $\sum_j$ is a short-hand notation denoting integration over the whole continuous spectrum of j ($\int_{-\infty}^{+\infty} dj$), with $\sum_j \varphi_j(x)\varphi_j(y)^* = \delta(x - y)$, δ denoting the Dirac delta function. For a purely discrete spectrum, $\sum_j$ stands for the infinite sum over the denumerably infinite set of all E_j's: see Section 5.1. $f(E_j)$ are real and non-negative constants, for all E_j. In turn, ρ_{st} determines the stationary Wigner function, $W_{st}(x, p)$, through Equation (39). Then, W_{st} fulfills:

$$-\frac{q}{m}\frac{\partial W_{st}}{\partial x} + M_Q W_{st} = 0, \quad \frac{\partial W_{st}}{\partial t} = 0 \tag{43}$$

We shall also suppose that $W_{st} \to 0$ quickly for $| q | \to +\infty$. The general structure of ρ_{in} is:

$$\langle x - y|\rho_{in}|x + y\rangle = \sum_{j,j'} c_{j,j'}\varphi_j(x - y)\varphi_{j'}(x + y)^* \tag{44}$$

where $c_{j,j'}$ define a Hermitian non-negative matrix. In general, $[H, \rho_{in}] \neq 0$. See [38] for theorems and constructive methods to find stationary solutions of Equation (43).

There exist two exact integral relationships for any W fulfilling Equation (40), for any V, x and t:

$$\frac{\partial[\int dqW(x, q; t)^2]}{\partial t} = -\frac{1}{m}\frac{\partial[\int dqqW(x, q; t)^2]}{\partial x} \tag{45}$$

$$\frac{\partial[\int dqW_{st}(x, q)W(x, q; t)]}{\partial t} = -\frac{1}{m}\frac{\partial[\int dqqW_{st}(x, q)W(x, q; t)]}{\partial x} \tag{46}$$

the integrations over q being performed in $-\infty < q < +\infty$. W_{st} is an arbitrary stationary Wigner function. Equation (45) is proven by multiplying Equation (40) by W, integrating over q, performing partial integrations and recalling that as $| q |\to +\infty$, $W(x, q; t) \to 0$ quickly. Equation (46) is derived by multiplying Equation (40) by W_{st}, operating similarly and using the first Equation (43). Equations (45) and (46) are new, to the best of the present author's knowledge.

The main part of this work will generalize, wherever possible, the developments in Section 2.2 to the (much more difficult) Wigner Equation (40).

4.2. W and W_{st} As Quasi-Definite Functionals in Momentum

We now remind ourselves of the known quantum difficulty: neither W nor W_{st} can be warranted to be ≥ 0 (negativity), in general [6,7]. As stated in [39], a necessary and sufficient condition for the Wigner function associated with a Schrodinger wave function being ≥ 0 is that the latter is the exponential of a quadratic polynomial [39]. See also [40,41]. As a nontrivial illustration, the Wigner functions, W, associated with several eigenstates of the Morse potential, have been studied by combining analytical and numerical methods: negative values of the W associated with the ground state are reported in [42,43]. The latter two references and [44] present negative values of the W's associated with some excited states. Even if $W_{st} < 0$, the domain in which that occurs cannot be large and has to be consistent with the fact that both $\int_{-\infty}^{+\infty} dx W_{st}$ and $\int_{-\infty}^{+\infty} dq W_{st}$ are ≥ 0.

In order to be able to proceed in spite of $W < 0$, we shall now invoke, in an outline, an acceptable mathematical framework based upon the theory of orthogonal polynomials [26]. Let us consider a kernel $K = K(y)$ (which could be ≤ 0), a set of functions $f = f(y)$ and the following functional, L_K, determined by the kernel, K: $f \to L_K[f] = \int_{-\infty}^{+\infty} dy K(y) f(y)$. We shall suppose that all integrals over y are convergent. Let us consider, successively: $\mu_n = L_K[y^n]$, $n = 0, 1, 2, 3...$, the set of all $(S+1) \times (S+1)$ matrices M_S ($S = 0, 1, 2, 3, ...$) with the (i, j)-th element equal to μ_{i+j} $(i, j = 0, ..., S)$ and their determinants, $Det[M_S]$. By definition, the functional, L_K, is quasi-definite if $Det[M_S] \neq 0$ for any $S = 0, 1, 2, 3, ...$ [26]. If L_K is a quasi-definite functional, then a theorem [26] implies: (i) the existence of a family of orthogonal polynomials, named here as $H_{Q,n} = H_{Q,n}(y)$, with weight function K (even if $K < 0$ in some domain in y); and (ii) that the polynomials, $H_{Q,n}$, fulfill a three-term recurrence relation analogous to Equation (21), in which the (y-independent) counterparts of the $C_{c,n}$'s are not warranted to be > 0.

Let q_0 be some fixed (x-independent) momentum and let us replace q by $y = q/q_0$. We shall suppose in all that follows that, regarding their y-dependences, the Wigner function, W, and any W_{st} determine, respectively, quasi-definite functionals, L_W (for any x and t) and $L_{W_{st}}$ (for any x). The interest of the assumption is obvious: if it holds (as we suppose), it implies the existence of orthogonal polynomials. To check that assumption for any W and W_{st}, in general, lies outside our scope: its validity for $L_{W_{st}}$ will be checked (and confirmed) in one interesting case in Section 5.2 and in Appendix E.

4.3. Equilibrium Wigner Function

We shall now consider the equilibrium Wigner function $W_{st} = W_{eq}$, fulfilling Equation (43) and accounting for thermal equilibrium at T of the qBp with the hb. Like in the classical case, the solutions

of Equations (40) and (41) are not expected to approach W_{eq} exactly, unless some approximation is made. W_{eq} arises from the canonical (t-independent) density operator $\rho_{eq} = \exp[-\beta H]$. Then:

$$\langle x - y | \rho_{eq} | x + y \rangle = \sum_j \exp[-\beta E_j] \varphi_j(x - y) \varphi_j(x + y)^* \tag{47}$$

$\sum_j$ in Equation (47) has the same meaning as in Equation (42). ρ_{eq} determines $W_{eq}(x, q)$, through Equation (39). $W_{eq}(x, q)$ is neither Gaussian in q nor known in closed form in general [6,7], and the dependences on q and x do not factorize. $W_{eq}(x, q)$ for a repulsive finite square well is given in Appendix D.

It is easy to show that the imaginary part, $Im W_{eq}(x, q)$, of $W_{eq}(x, q)$ vanishes for any x and q, that is, $W_{eq}(x, q)$ is real. Let E_j sweep the continuous positive real half-line: $0 \leq E_j < +\infty$ (V in first class). Let β become complex ($\beta = Re\beta + iIm\beta$) and wander in the right-half-plane $Re\beta > 0$. Then, one sees that $W_{eq}(x, q)$ is an analytic function of β in the right-half-plane $Re\beta > 0$, for fixed x and q.

4.4. Orthogonal Polynomials $H_{Q,n}$ Generated by W_{st} and by W_{eq}

We shall introduce the (unnormalized) polynomials in $y(= q/q_0)$, $H_{Q,n} = H_{Q,n}(y)$ ($n = 0, 1, 2, 3, \dots$), orthogonalized in y (for fixed x) by using a generic stationary W_{st} (Equation (43)) as the weight function. By choosing $H_{Q,0}(q) = 1$, for $n \neq n'$ and any x (left unintegrated), we impose:

$$\int_{-\infty}^{+\infty} dy W_{st} H_{Q,n}(y) H_{Q,n'}(y) = 0 \tag{48}$$

The $H_{Q,n}$'s, depending parametrically on x for $n \geq 1$, will be used for the time evolution. For V's belonging to the first class, we shall look for the $H_{Q,n}(y)$'s as:

$$H_{Q,n}(y) = y^n + \sum_{j=1}^{n} \epsilon_{Q,n,n-j} y^{n-j} \tag{49}$$

$\epsilon_{Q,n,n-j}$ being y-independent (but x-dependent, in general). One has $\epsilon_{Q,n,n-j} = 0$ for odd j, so that $H_{Q,n}(-y) = (-1)^n H_{Q,n}(y)$. The $\epsilon_{Q,n,n-j}$'s are given by equations entirely similar to those yielding the $\epsilon_{c,n,n-j}$'s in Appendix A (Equations (73)–(76)), provided that the quantum $< y^n >$ be now understood as $\int_{-\infty}^{+\infty} dy W_{st} y^n / \int_{-\infty}^{+\infty} dy W_{st}$. The orthonormalized polynomials are $H_{Q,n}(q)/(h_{Q,n})^{1/2}$, with an ($x$-dependent) normalization factor, $h_{Q,n}$, defined through Equation (3), by replacing $W_{c,st}$ by W_{st} and $H_{c,n}$ by $H_{Q,n}$. One could also express the same $H_{Q,n}$'s as suitable sums of Hermite polynomials: such an alternative, although consistent, will not be followed for V's in the first class (but it will in Section 5.1, for V's in the second class). The above definitions and statements also hold, in particular, for the polynomials $H_{Q,eq,n} = H_{Q,eq,n}(y)$ determined by $W_{st} = W_{eq}$, with suitable choices of q_0 (to be discussed later). For another discussion of the $H_{Q,eq,n}$'s, see [20].

We shall not focus on cases in which $V(x) \to 0$ quickly for $| x | \to +\infty$ and can be ≤ 0 (attractive), except for the following comments (and a short one in Section 5.1). In such a case, H has a general spectrum; both discrete (finite number of bound states) plus continuous spectra. We shall justify briefly the motivation for such an exclusion. Let us consider for a short while the attractive δ-function potential $V(x) = -V_0 \delta(x)$, V_0 being a positive constant. Then, H has a unique bound state, namely,

$\varphi_0(x) = A \exp[-\alpha \mid x \mid]$, with $\alpha = mV_0/\hbar^2 > 0$, $A = \alpha^{1/2}$. A direct computation of W_{eq} at $x = 0$ in Equation (39), by using Equation (47) and keeping only the contribution of $\varphi_0(x)$ (say, at very low T), shows that such a contribution to $W_{eq}(x = 0, q)$ equals a constant times $[\alpha^2 + (q/\hbar)^2]^{-1}$. The latter contribution to $W_{eq}(x = 0, q)$ has a slow decrease as q increases, and hence, it does not allow one to define orthogonal polynomials, $H_{Q,eq,n}(y)$, for $n \geq 2$, because one finds divergent integrals in q. A similar study for $V(x)$ corresponding to an attractive finite square well having, for simplicity, only one bound state yields a contribution to $W_{eq}(x = 0, q)$ having another slow decrease as q, which also prevents the construction of an infinite family of $H_{Q,eq,n}(y)$'s.

5. Denumerably Infinite Purely Discrete Spectrum

5.1. Some General Aspects

Here, we treat V's in the second class (polynomials: harmonic/anharmonic oscillators). Then, H is defined in a denumerably infinite Hilbert space, and it has a nondegenerate denumerably infinite discrete spectrum, E_j, $j = 1, \ldots$ ($E_j \geq 0$, without loss of generality), the continuous spectrum being absent. Let φ_0 be the ground state with energy E_0, and let the successive nondegenerate eigenvalues be ordered as $j = 1, 2, 3....$, with $E_0 < E_1 < E_2 < E_3 < ....$. All eigenfunctions, φ_j, are square-integrable and, by assumption, normalized. As $V(x) = V(-x)$, one has : $\varphi_j(-y) = (-1)^j \varphi_j(y)$. Then, Equations (47) and (39), with $f(E_j) = \exp(-\beta E_j)$ give:

$$W_{eq}(x = 0, q = 0) = \frac{1}{\pi\hbar} \int_{-\infty}^{+\infty} dy \sum_j \exp[-\beta E_j]\varphi_j(-y)\varphi_j(y)^* =$$

$$\frac{1}{\pi\hbar}[(\exp[-\beta E_0] - \exp[-\beta E_1]) + (\exp[-\beta E_2] - \exp[-\beta E_3]) + ...] \tag{50}$$

It follows that $W_{eq}(x = 0, q = 0) > 0$ for any T. The same argument indicates that, for sufficiently low T and adequately small $\mid x \mid$ and $\mid q \mid$, $W_{eq}(x, q) \simeq (\pi\hbar)^{-1} \exp[-\beta E_0]$, which is non-negative: that is, $W_{eq}(x, q)$ is dominated by the ground state φ_0 with energy E_0. This dominance of φ_0 for small T, x and q formally holds for V's having a general (discrete finite plus continuous) spectrum.

Let $T = 0$ strictly. It follows that: (i) W_{eq} is proportional to $(\pi\hbar)^{-1} \int_{-\infty}^{+\infty} dy \exp[\frac{i2qy}{\hbar}]\varphi_0(x - y)\varphi_0(x + y)^*$ (we have factored out $\exp[-\beta E_0]$(at $T \to 0$), which leads us to discard any other contribution different from the ground state one to W_{eq} in the $T \to 0$ limit); (ii) any other W_{st} is necessarily proportional to W_{eq}; (iii) the initial condition, W_{in}, is proportional to W_{eq}; and (iv) W is also proportional to W_{eq} and, hence, it is equal to W_{in} and t-independent. Cases with low T will be treated later.

For V's in the second class, we choose another q_0' ($\neq$ the q_0 employed in Equation (49), in principle) and, instead of using Equation (49), the same orthogonal polynomials, $H_{Q,n}(y)$ ($n = 0, 1, 2, 3, \ldots$), will be searched for being equal to the standard Hermite polynomial, $H_n(y)$, plus another polynomial in y of a degree smaller than n. Then:

$$H_{Q,n}(y) = H_n(y) + \sum_{j=1}^{n} \sigma_{n,n-j} H_{n-j}(y) \tag{51}$$

with $n = 1, 2, 3, \ldots$ and (y-independent, but x-dependent) coefficients $\sigma_{n,n-j}$. One has: $H_{Q,n}(y) = H_n(y)$, for $n = 0, 1$ and $\sigma_{n,n-j} = 0$ for odd j. For generic q_0 and q_0' (unrelated to each other), the $H_{Q,n}(y)$'s in Equation (51) are equal to those in Equation (49) times $(2q_0/q_0')^n$, which, in general, is $\neq 1$.

5.2. One-Dimensional Quantum Harmonic Oscillator

We shall treat a quantum harmonic oscillator, with frequency $\omega(> 0)$ and $V = V(x) = m\omega^2 x^2/2$. Let the quantum oscillator be at thermal equilibrium at T with some hb. The corresponding $\langle x - y | \rho_{eq} | x + y \rangle$ in Equation (47) is well known [45], and W_{eq} reads:

$$
\begin{aligned}
W_{eq}(x, q) = & \left[\frac{1}{2(\pi\hbar)^2(1 + \cosh(\beta\hbar\omega))}\right]^{1/2} \exp\left[-\frac{m\omega(\cosh(\beta\hbar\omega) - 1)x^2}{\hbar\sinh(\beta\hbar\omega)}\right] \times \\
& \exp\left[-\frac{\sinh(\beta\hbar\omega)q^2}{m\hbar\omega(1 + \cosh(\beta\hbar\omega))}\right]
\end{aligned}
\tag{52}
$$

See [20] for the orthogonal polynomials for Equation (52). For simplicity, we shall set the ground state energy equal to zero and choose $\hbar\omega = 1$ and $m = 1$. For the harmonic oscillator $V(x)$, the series expansion of the operator, M_Q, into powers of $\hbar^2$ reduces exactly to the first term shown in Equation (41). Then, Equations (40) and (41) reduce to a quantum equation formally similar to the classical Equation (1):

$$
\frac{\partial W}{\partial t} + q\frac{\partial W}{\partial x} - x\frac{\partial W}{\partial q} = 0
\tag{53}
$$

First, let the quantum oscillator be in the ground state. The stationary Wigner function is:

$$
W_{st}(x, q) = \frac{2}{\pi}\exp[-2(x^2 + q^2)] > 0
\tag{54}
$$

The orthogonal polynomials for Equation (52) yield, as $\beta \to 0$, those for Equation (54).

Next, let the quantum oscillator be in the first excited state and let $y = 2^{1/2}q$ in the present case. The associated stationary Wigner function, of considerable interest in quantum optics, is [46]:

$$
\begin{aligned}
W_{st}(x, q) = & \frac{2}{\pi}[4(x^2 + q^2) - 1]\exp[-2(x^2 + q^2)] \\
= & \frac{2}{\pi}[\frac{1}{2}H_2(y) + 4x^2]\exp[-(2x^2 + y^2)]
\end{aligned}
\tag{55}
$$

$H_2(y)$ being the standard Hermite polynomial. One easily confirms that Equation (55) is a stationary solution of Equation (53)). $W_{st}(x, q)$ is negative in the finite domain in which $4(x^2 + q^2) < 1$ [46]. This case provides an interesting example, enabling us to justify that $W_{st}(x, q)$ in Equation (55) is indeed a quasi-definite functional regarding the y (or q) dependence for any x (except at a set of zero measure): see Appendix E. The polynomials, $H_{Q,n}(y)$ ($n = 0, 1, 2, 3, \ldots$), orthogonalized in y (for fixed x) by using W_{st} in Equation (55) as the weight function, are given in Equation (51); the low-order coefficients, $\sigma_{n,n-j}$, are given in Appendix E.

W_{eq}, given in Equation (52), is positive, and one could ask how the negativity of Equation (55) can be compensated for. To answer that question, we shall suppose that T is so low that the actual $\sum_j$ reduces

just to the contributions of the ground state and of the first excited one. Then, the corresponding Wigner function is:

$$W_{eq}(x,q) \simeq \frac{2}{\pi} \exp[-2(x^2+q^2)][1 + \exp[-\beta E_1](4(x^2+q^2)-1)]$$

$E_1 > 0$ being the energy of the first excited state. Clearly, $W_{eq}(x,q) > 0$ for any x and q, which is consistent with the positivity of Equation (52).

6. Non-Equilibrium Hierarchy

6.1. V's in the First Class

We consider only V's in the first class (all its derivatives exist and are continuous) and suppose that T is neither high nor low. We shall analyze general off-equilibrium situations by using Equations (40) and (41). We consider a generic W_{st}. The $H_{Q,n}(y)$'s in Equation (49) lead to the new moments ($n = 0, 1, 2, \ldots$):

$$W_n = W_n(x;t) = \int_{-\infty}^{+\infty} dy H_{Q,n}(y) W \tag{56}$$

The initial condition, $W_{in,n}$, for W_n is obtained by replacing W by W_{in} in Equation (56). One has the following (formal) expansion for W, which generalizes Equation (5):

$$W = W_{st}(x,q) \sum_{n=0}^{+\infty} W_n(x;t) \frac{H_{Q,n}(y)}{h_{Q,n}} \tag{57}$$

For $W = W_{st}(x,q)$, Equation (56) yields $W_{st,n} = 0$ if $n > 0$, and $W_{st,0} = h_{Q,0}$. The transformation of Equations (40) and (41) into a linear hierarchy for the new moments, W_n, for a general W_{st}, can be carried out as in the classical case. Through additional computations and cancellations, we have obtained the first five equations in that quantum hierarchy.

$$\frac{\partial W_0}{\partial t} = -\frac{q_0}{m}\frac{\partial W_1}{\partial x} \tag{58}$$

$$\frac{\partial W_1}{\partial t} = -\frac{q_0}{m}\frac{\partial W_2}{\partial x} + \frac{q_0}{m}\frac{\partial}{\partial x}[(\epsilon_{Q,2,0})W_0] - \frac{1}{q_0}\frac{\partial V}{\partial x}W_0 \tag{59}$$

$$\frac{\partial W_2}{\partial t} = -\frac{q_0}{m}\frac{\partial W_3}{\partial x} + \frac{q_0}{m}\frac{\partial}{\partial x}[(\epsilon_{Q,3,1}-\epsilon_{Q,2,0})W_1] + \frac{q_0}{m}\frac{\partial \epsilon_{Q,2,0}}{\partial x}W_1 - \frac{2}{q_0}\frac{\partial V}{\partial x}W_1 \tag{60}$$

$$\frac{\partial W_3}{\partial t} = -\frac{q_0}{m}\frac{\partial W_4}{\partial x} + \frac{q_0}{m}\frac{\partial}{\partial x}[(\epsilon_{Q,4,2}-\epsilon_{Q,3,1})W_2] + \frac{q_0}{m}\frac{\partial \epsilon_{Q,3,1}}{\partial x}W_2 - \frac{3}{q_0}\frac{\partial V}{\partial x}W_2 \tag{61}$$

$$\frac{\partial W_4}{\partial t} = -\frac{q_0}{m}\frac{\partial W_5}{\partial x} + \frac{q_0}{m}\frac{\partial}{\partial x}[(\epsilon_{Q,5,3}-\epsilon_{Q,4,2})W_3] + \frac{q_0}{m}\frac{\partial \epsilon_{Q,4,2}}{\partial x}W_3 - \frac{4}{q_0}\frac{\partial V}{\partial x}W_3 +$$

$$+\frac{\hbar^2}{2^2 q_0^3}\frac{\partial^3 V}{\partial x^3}[-6 + \frac{\epsilon_{Q,4,2}}{\epsilon_{Q,2,0}}]W_1 \tag{62}$$

The first four Equations (58)–(61) are formally identical, respectively, to those in the classical case (Equations (22)–(25)), provided that $W_{c,n}$'s are replaced by W_n's and $\epsilon_{c,n,n-j}$'s by $\epsilon_{Q,n,n-j}$'s, for $n = 0, 1, 2, 3$. On the other hand, for a general W_{st}, Equation (62) (for $n = 4$) acquires a new term

(of quantum origin) containing W_1, and so, it differs from its classical counterpart, Equation (26). The reason for the similarities for $n = 0, 1, 2, 3$ and for the difference if $n = 4$ is that the quantum corrections in Equations (40) and (41) manifest themselves only at order $\hbar^2$ and then, in turn, in the equations in the hierarchy at orders $n \geq 4$. The computation and cancellations leading to Equation (62) are very lengthy and painful, and we shall omit them. We have confirmed that $W_0 = h_{Q,0}$ and $W_n = 0$ for $n = 1, 2, 3, 4, 5$ solve the hierarchy Equations (58)–(62), with $\partial W_n / \partial t = 0$.

Let us now consider Equations (58)–(62) for the case $W_{st} = W_{eq}$, describing thermal equilibrium with the hb. After further analysis, the new term containing $\hbar^2 W_1$ in Equation (62) is not seen to disappear, but to be $\neq 0$ still, for generic q_0. For any W_{st} and $V \neq 0$, the equation for $\partial W_n / \partial t$ for any $n \geq 5$ contains a dependence on W_{n+1}, given below in Equation (64), but no other dependences on higher order moments. On the other hand, the fact that the full quantum equation for $n = 4$ does contain a term of order $\hbar^3$ in W_1 implies that the quantum hierarchy is not a three-term one due to moments $W_{n'}$ with $n' < n$, neither for a generic W_{st} nor for W_{eq}. The most general non-equilibrium hierarchy is:

$$\frac{\partial W_n}{\partial t} = -M_{n,n+1} W_{n+1} - \sum_{n'=1}^{n} M_{n,n-n'} W_{n'} \tag{63}$$

$$M_{n,n+1} W_{n+1} \equiv \frac{q_0}{m} \frac{\partial W_{n+1}}{\partial x} \tag{64}$$

$M_{n,n'=0} = 0$ for any n, except for $n = 1$ (with $n' = 0$). We emphasize that, in the non-equilibrium classical and quantum hierarchies (in Equations (22)–(26) for $W_{c,eq}$ and in Equations (63)–(64) for W_{eq}, respectively), the contributions from $W_{c,n+1}$ and from W_{n+1} have always the same structures $(-(q_0/m)\partial W_{c,n+1}/\partial x$ and $-(q_0/m)\partial W_{n+1}/\partial x$, with n-independent coefficients). On the other hand, the contributions from $W_{c,n-1}$ and from $W_{n'}$ ($0 < n' \leq n - 1$) do carry n-dependent coefficients, which increase with n. An example of such an n-dependence will be displayed, in the quasiclassical regime, by Equation (66). $\partial^r V / \partial x^r$ starts to contribute in Equation (63) for $n = r + 1$.

6.2. V's in the First Class: Reduction to Three-Term Hierarchy near the Classical Regime

The comments after Equations (58)–(62) imply that, in the classical case ($\hbar \to 0$), the quantum hierarchy reduces to the classical one, with $W_{st} \to W_{c,st}$.

We shall analyze the following more subtle simplification, only for $W_{st} = W_{eq}$, with $q_0 = (2m/\beta)^{1/2}$ in the quasiclassical regime at high temperature, so that both β and $\hbar(\neq 0)$ are small. W_{eq}, the orthogonal polynomials, $H_{Q,n}(y)$'s, generated by it, the non-equilibrium solutions, W, the W_n's and the dynamical equations will be considered up to and including order $\hbar^2$ (higher orders in $\hbar$ being disregarded). We shall focus on whether the exact hierarchy Equations (58)–(62), which is not a three-term one, due to the contribution, $\hbar^2 W_1$, in Equation (62), could become a three-term recurrence relation up to and including order $\hbar^2$. The analysis boils down to studying whether the coefficient multiplying $\hbar^2 W_1$ in Equation (62), namely, $-6 + \frac{\epsilon_{Q,4,2}}{\epsilon_{Q,2,0}}$, vanishes or not at the required order, which turns out to be order $\hbar^0$. In fact, as we are working to order $\hbar^2$ and there is an overall factor, $\hbar^2$, it will suffice to approximate W_{eq} and $-6 + \frac{\epsilon_{Q,4,2}}{\epsilon_{Q,2,0}}$ by $W_{c,eq}$ and $-6 + \frac{\epsilon_{c,4,2}}{\epsilon_{c,2,0}}$, respectively. Thus, in order to evaluate $\epsilon_{c,4,2}$ and $\epsilon_{c,2,0}$ through Equations (73) and (74), we use $W_{c,eq} = \exp(-y^2) \exp[-\beta V]$. A direct computation shows that $-6 + \frac{\epsilon_{c,4,2}}{\epsilon_{c,2,0}} = 0$. Then, we see that up to and including order $\hbar^2$, Equations (58)–(62) become a quasiclassical three-term

hierarchy. The simplification should hold for all higher values of $n = 5, 6, 7, ...$ (say, for Equation (63)), in general. The last paragraph in Section 6.3 leads to the same conclusion, through a different procedure.

6.3. V's in the Second Class: Examples of Quantum Hierarchies

Here, we shall use the $H_{Q,n}(y)$'s in Equation (51), which gives non-equilibrium moments equal to those in Equation (56) times $2^2(q_0/q_0')^{n+1}$ and the same formal hierarchy as in Section 6.1 (recast in terms of $\sigma_{n,n-j}$'s). See [20] for the non-equilibrium three-term hierarchy for Equation (52). The off-equilibrium three-term hierarchy for the first excited state of the harmonic oscillator is outlined in Appendix E. Let us consider a quartic anharmonic oscillator: $V = V(x) = 2^{-1}m\omega^2 x^2 + (4!)^{-1}gx^4$, $g(> 0)$ being a coupling constant. W_{eq} and the associated orthogonal polynomials (for a suitable q_0') have been constructed in [20]. The resulting hierarchy for the non-equilibrium quantum moments, W_n (for W_{eq}), has been given in [20] for $n = 0, 1, 2, 3$ and turns out to be a three-term one. However, further analysis indicates that the first quantum correction $\partial^3 V/\partial x^3$ starts to contribute in equations in the hierarchy for $n \geq 4$, so that the whole non-equilibrium hierarchy is not a three-term one.

Just to illustrate the features met upon dealing with n-term hierarchies with $n > 3$, we shall treat briefly the following four-term one, which is a simplification of the quantum ones:

$$\frac{\partial W_n}{\partial t} = -M_{n,n+1}W_{n+1} - M_{n,n-1}W_{n-1} - M_{n,n-3}W_{n-3} \tag{65}$$

where $M_{n,n+1}W_{n+1}$ could be either Equation (64) or $(q_0'/2m)(\partial W_{n+1}/\partial x)$. The essential structure of the formal solution of the four-term hierarchy Equations (64) and (65) is outlined in Appendix F.

We shall now treat the same quasiclassical regime as in Section 6.2, also up to and including order $\hbar^2$, with $q_0' = (2m/\beta)^{1/2}$. In such a regime: (i) W_{eq} is well known [6]; (ii) the $H_{Q,n}(y)$'s have been constructed explicitly in terms of Hermite polynomials [21]; and (iii) it has been shown that the W_n's (determined by the latter $H_{Q,n}(y)$) fulfill the following three-term hierarchy for all values of n, $n = 0, 1, 2, 3, ...$: $(\partial W_n/\partial t) = -(q_0'/2m)(\partial W_{n+1}/\partial x) - M_{n,n-1}W_{n-1}$ with the operators [21]:

$$M_{n,n-1}W_{n-1} = \frac{2nq_0'}{m}\frac{\partial(1+4a_2)W_{n-1}}{\partial x} + 2\left[\frac{2n}{q_0'}\frac{\partial V}{\partial x} + \frac{2q_0'n(n-1)}{m}\frac{\partial a_2}{\partial x}\right]W_{n-1} \tag{66}$$

and $a_2 = (\beta^2\hbar^2/48m)(\partial^2 V/\partial x^2)$.

The hierarchy Equation (66), with the $H_{Q,n}(y)$'s in Equation (51), also applies in the quasiclassical regime for V's in the first class [21]. This is consistent with the simplification to a three-term hierarchy studied in Section 6.2.

6.4. Long-Time Approximation in the Quantum Case: Pending Problems to Justify It

First, we treat the four-term hierarchy of Equation (65) for V's in the second class and for W_{eq}, with the initial condition $W_{in,0} \neq 0$, $W_{in,0} \neq W_{eq,0}$ and $W_{in,n} = 0$ for $n \neq 0$. We set $n = 4$ in the structure Equation (112) in Appendix F (for W_{eq}). Then:

$$\tilde{W}_4(s) = D_{Q,4}[n = 4; s]\sum_{n'=1}^{3} B_{4,n'}(s)\tilde{W}_{n'}(s) \tag{67}$$

The operators, $B_{4,n'}$, follow by comparison with Equation (112). The $\hbar$-dependent quantum corrections in Equation (41) are responsible for the fact that $B_{4,2}(s)$ and $B_{4,1}(s)$ are non-vanishing, in principle. The long-time approximation in Section 2.2 for generic $W_{c,st} = W_{c.eq}$ can be generalized formally to the present quantum case as follows. By arguing that the t-dependence of W_4 is slaved approximately by those of W_n, for $n = 0, 1, 2, 3$, one replaces $D_{Q,4}[n = 4; s]$, all $D_{Q,4}[n''; s]$ $(n'' > 4)$ and $B_{4,n'}(s)$ with $n' = 1, 2, 3$, by s-independent operators, $D_{Q,4}[4]$, $D_{Q,4}[n'']$ and $B_{4,n'}$, respectively (say, by fixing $s = \epsilon > 0$). Then, Equation (67) could be approximated as: $\tilde{W}_4(s) \simeq D_{Q,4}[4] \sum_{n'=1}^{3} B_{4,n'} \tilde{W}_{n'}(s)$. The latter, together with Equation (65), as they stand for $n = 0, 1, 2, 3$ (without setting $s = \epsilon$), would constitute a finite closed system for $\tilde{W}_n(s)$, $n = 0, 1, 2, 3, 4$, and would complete the approximation scheme. However, notice that neither Hermiticity nor non-negativity properties have been discussed nor invoked for the generalized operator continued fractions.

Next, we turn to the three-term quasiclassical hierarchy for W_{eq} with Equation (66), considered in the preceding subsection. A long-time approximation can be formulated formally, like in Section 2.2. Due to the quantum correction at order $\hbar^2$, that hierarchy does not fulfill the requirement that $M_{n+1,n}$ be the adjoint of $-M_{n,n+1}$. We have been unable to transform such a hierarchy into another three-term one satisfying the adjointness requirement. Due to the latter difficulty, the actual counterpart of the continued fraction operator, $D[n; s]$ (Sections 2.2 and 2.4), cannot be warranted to fulfill Hermiticity and non-negativity. Then, the argument employed in the purely classical case for $W_{c,eq}$ (Section 2.2) cannot be invoked to justify the approach to thermalization in the quasiclassical regime.

For V's in the first class and W_{eq}, similar formal constructions could be generalized for Equations (63) and (64) to all orders in $\hbar$ and finite T). Criticisms for them would also apply, similar to the above ones for V's in the second class and for W_{eq}, and contrary to the classical case.

On physical grounds, and in spite of our limitations to provide justifications, we expect that, just for W_{eq} and V's in both classes, the long-time approximations outlined above for the moment approach give an approach to thermalization in the quantum regime for all hierarchies discussed in this subsection. The justification lies outside our scope here.

We shall discuss the inclusion of non-negligible dissipation due to the external hb in the quantum case. Two non-equilibrium dissipative quantum master equations for V's in the second class (quartic potentials) have been dealt with in [20]. In the first one, W_{eq} turned out to depend on dissipation, while the second was a specific, but quite interesting, subclass of Lindblad's theory [47], in which W_{eq} equals the equilibrium Wigner function for the associated dissipationless Wigner equation with the same V. In both cases, we have studied the (more difficult) construction of the $H_{Q,n}$'s and the non-equilibrium moments, W_n's, and hierarchies. The analysis in Section 2.2 (classical case) did justify that, at least, a very small (and, eventually, negligible) dissipation due to the hb was consistent with Hermiticity and non-negativity and with the long-time approximation. In the actual quantum case, the above difficulties related to Hermiticity and non-negativity will also prevent the justification of the corresponding consistency. Nevertheless, it is physically natural to expect that in the actual open quantum system at finite T, the analysis with negligible friction will not lead to inconsistencies, and that is our standpoint in Sections 4–7.

While such consistencies refer to oversimplified open one-particle systems, long-time approximate evolutions for non-equilibrium closed large systems (without external hb's) are our main goal. The

analysis in [15,16,20] and Section 3 in the present work confirmed, *a posteriori*, the reliability of letting dissipation vanish and justified the long-time approximate evolution towards thermalization for closed classical large systems, precisely through an extension of the techniques employed for open classical one-particle systems with negligible friction. The pending issues are closed large quantum systems, which are far more difficult. Then, the extraction and awareness of the consequences from the neglecting of dissipation in an open quantum one-particle system could be, at least, potentially interesting.

7. V's in the First Class: Large Thermal and de Broglie Wavelengths

We shall suppose that $V \geq 0$, $V \to 0$ as $\mid x \mid \to +\infty$ and that it is finite and continuous, except for, at worst, a finite number of finite discontinuities. Let T be suitably small, so that: (a) $k_B T \ll Max(V)$ (the absolute maximum of $V(x)$, as x varies); and (b) the thermal wavelength $\lambda_{th} = \hbar[\beta/2m]^{1/2}$ is $\gg$ the size, a, of the domain where V is appreciably different from zero. Let $q_l \equiv \hbar/\lambda_{th}$. In what follows, we shall restrict to $W(x,q;t) \simeq W_l(x,q;t) = W_l$ for $\mid x \mid /a \gg 1$ and $\mid q \mid < q_l$, which implies $\hbar/\mid q \mid$ adequately larger than a (large de Broglie wavelength). For $\mid q \mid < q_l$, the detailed structure of V should not be relevant, as a leading approximation, for W_l. Then, the expansion of M_Q in Equation (41) into successive derivatives of V, even if correct, does not seem adequate; one should take into account the integral form in Equation (41).

We shall be interested in the equilibrium Wigner function $W_{eq}(x,q) \simeq W_{l,eq}(x,q)$, given by Equations (39) and (47) and describing thermal equilibrium with the hb, in the actual low-T regime characterized by the above Conditions (a) and (b). This is exemplified for the case of a finite repulsive square well in Appendix D. See Appendix G for the derivation of an approximate representation for $W_{eq}(x,q)$ for the above general V. To leading order (orders $(a/\lambda_{th})^0$ and $((\beta Max(V))^{-1/2})^0$), the underlying physics appears to correspond to total reflection and zero transmission of the quantum particle by the potential $V(x)$ concentrated in a region of very small size, a. This picture is qualitatively consistent with the general features of quantum bosonic many-particle systems at very low T [48]. ¿From Appendices G and D, one gets:

$$W_{eq}(x,q) \simeq W_{l,eq}(x,q) \simeq \int_0^{\lambda_{th}^{-1}} \frac{dk_1}{\pi\hbar} \exp[-\beta(\hbar k_1)^2/2m][-2\cos 2k_1 x \frac{\sin 2(q/\hbar)x}{q/\hbar} + \frac{\sin 2(k_1+q/\hbar)x}{k_1+q/\hbar} + \frac{\sin 2(-k_1+q/\hbar)x}{-k_1+q/\hbar}] \tag{68}$$

This $W_{l,eq}(x,q)$ can be < 0 in some region, while, on the other hand, $\int_{|q|<q_l} dq W_{l,eq}(x,q) > 0$. One has:

$$a^2 q \frac{\partial W_{l,eq}(x,q)}{\partial x} \simeq \int_0^{\lambda_{th}^{-1}} \frac{dk_1}{\pi\hbar} \exp[-\beta(\hbar k_1)^2/2m][4(k_1 a)(qa)\sin 2k_1 x \frac{\sin 2(q/\hbar)x}{q/\hbar}] \tag{69}$$

which is negligible to leading order. Then, under the above Conditions (a) and (b) and the approximations yielding Equation (68), it would appear that, to leading order, M_Q in Equation (43) could be neglected. Moreover, M_Q can be also neglected to leading order in the non-equilibrium Equation (41). In fact, in the integral form of $M_Q W$, we set $\exp[i2(q-q')y/\hbar] \simeq 1$, under the above approximations, and notice that $\int_{-\infty}^{+\infty} dy[V(x+y) - V(x-y)] = 0$. Then, one gets the quantum non-equilibrium equation:

$$\frac{\partial W_l(x,q;t)}{\partial t} \simeq -\frac{q}{m}\frac{\partial W_l(x,q;t)}{\partial x} \tag{70}$$

which is formally similar to the one encountered in the classical case, for $V = 0$. We shall introduce the polynomials $H_{Q,l,n} = H_{Q,l,n}(y)$ ($n = 0, 1, 2, 3, \dots$), orthogonalized in $y = q/q_l$ with weight function $W_{l,eq}(x, q)$ using Equation (49), by integrating in $| y | \leq +1$. New non-equilibrium moments, $W_{l,n}$ ($n = 0, 1, 2, \dots$), are introduced through the analogue of Equation (56), also by integrating in $| y | \leq +1$. With the corresponding replacements ($\epsilon_{Q,n,n-j} \to \epsilon_{Q,l,n,n-j}$ and $W_n \to W_{l,n}$), Equations (58)–(62) now become a linear hierarchy for the new moments, $W_{l,n}$, in which all successive derivatives of V are neglected to leading order. Moreover, further computation, also with $M_Q = 0$, gives another three-term equation:

$$\frac{\partial W_{l,5}}{\partial t} = -\frac{q_0}{m}\frac{\partial W_{l,6}}{\partial x} + \frac{q_0}{m}\frac{\partial}{\partial x}[(\epsilon_{Q,l,6,4} - \epsilon_{Q,l,5,3})W_{l,4}] + \frac{q_0}{m}\frac{\partial \epsilon_{Q,l,5,3}}{\partial x}W_{l,4} \tag{71}$$

See Appendix G. It is plausible that the equations for all $\partial W_{l,n}/\partial t$ could constitute an infinite three-term hierarchy for any n and $V = 0$, namely:

$$\frac{\partial W_{l,n}}{\partial t} = -\frac{q_0}{m}\frac{\partial W_{l,n+1}}{\partial x} + \frac{q_0}{m}\frac{\partial}{\partial x}[(\epsilon_{Q,l,n+1,n-1} - \epsilon_{Q,l,n,n-2})W_{l,n-1}] + \frac{q_0}{m}[\frac{\partial \epsilon_{Q,l,n,n-2}}{\partial x}]W_{l,n-1} \tag{72}$$

for a generic W_{st}, but a proof lies outside our scope here.

For the approximate hierarchy Equation (72) in the actual quantum system, under the above Conditions (a) and (b) and approximations, a long-time approximation can also be formulated formally, by following the procedure in Section 2.4. Approximate estimates in Appendix G suggest that those $H_{Q,l,n}$ are not radically different (or differ little, eventually) from those determined by the Gaussian $\exp[-\frac{\beta q^2}{2m}]$, for very large β and $| q | < q_l$. The Gaussian $\exp[-\frac{\beta q^2}{2m}]$ (for any $| q | < +\infty$) determines a three-term non-equilibrium hierarchy similar to the one for g_n's in Equation (6) with $V = 0$, which displays D's with Hermiticity and non-negativity and, so, thermalization under the long-time approximation. The latter D's could possibly not differ much from those for Equation (72). Then, for the approximate hierarchy Equation (72), an approximate long-time thermalization with the hb could possibly be justified. Detailed computations lie outside our scope.

8. Conclusions and Discussion

The existence of approximate long-time thermalization or the absence thereof for open one-dimensional systems subject to a potential V and to a hb (with negligible external dissipation) has been studied, in the framework of hierarchies for non-equilibrium moments ($W_{c,n}$ and W_n). The conceptual issues involved in treating an open system subject to a hb with negligible dissipation have been discussed (Sections 2.3 and 6.4). The universal dependences of the non-equilibrium Liouville and Wigner equations on momenta imply that the equations for $W_{c,n}$ and W_n have universal dependences on one unique moment of higher order ($W_{c,n+1}$ and W_{n+1}, respectively), while in different cases, there are various dependences on moments of lower orders.

In the classical case, the non-equilibrium moments, $W_{c,n}$, for the canonical distribution, $W_{c,eq}$, are obtained in terms of operator continued fractions, D's, which are Hermitian and have non-negative eigenvalues (non-negativity): these properties, in a suitable long-time approximation, justify thermalization. In this work, we deal with a general stationary $W_{c,st}$ ($\neq W_{c,eq}$), which is not Gaussian in momenta and fails, on physical grounds, to lead to approximate long-time thermalization, and the

moment method displays this failure. In fact, hierarchies for the non-equilibrium moments, $W_{c,n}$'s, determined by $W_{c,st}$ are obtained for $n \leq 4$, but they lead to several unsolved difficulties (Section 2.4). Then, the formal construction through non-equilibrium moments provides one additional partial support to the selection of the Boltzmann equilibrium distribution, $W_{c,eq}$, out of the set of all $W_{c,st}$, on a dynamical basis (although not a proof of it). From the outset, $W_{c,eq}$ and $W_{c,st}$ correspond to different situations, and the moment method emphasizes, *a posteriori*, the differences. The microcanonical $W_{c,st}$ and its special features are discussed briefly. The above analysis is one novelty of the present paper. The formal structure of the non-equilibrium hierarchies for $n \leq 4$ so obtained is very useful for the quantum case.

For closed classical interacting non-relativistic many-particle systems, without external hb's and for the canonical equilibrium distribution, $W_{c,eq}$, non-equilibrium three-term hierarchies for moments with Hermiticity have enabled us to justify approximate long-time thermalization [15,16,20]. Here, we have pointed out an interpretation in terms of interacting random walkers and an approximate Lyapunov function yielding an arrow of time, as novelties. Our proposal, based directly on moment approaches to classical non-equilibrium statistical mechanics and selecting approximately a time direction in the evolution, fails to give a non-equilibrium entropy. It could possibly be regarded as partially complementary to the proposals by other authors. The latter do not appear to be based directly on moment methods in classical non-equilibrium statistical mechanics, but, on the other hand, they do provide non-equilibrium entropies and other ways to select a time arrow, in different settings.

We have concentrated on a non-equilibrium open quantum one-dimensional particle, in the presence of a hb at thermal equilibrium at T with negligible external dissipation and subject to suitable repulsive $V(x)$'s (characterized in Section 4.1). We have used non-equilibrium Wigner functions $W(x, q; t)$, to all orders in Planck's constant.

The following developments and results are reported in this work (and are new, to the best of the author's knowledge).

The exact equilibrium canonical Wigner function, $W_{eq}(x, q)$, for a repulsive finite square potential is presented.

We have shown that $W_{eq}(x, q) > 0$ for small T, x and q and have obtained two exact relationships for any non-equilibrium, W.

We have assumed that, for rather general repulsive V's, any W and any stationary Wigner functions, W_{st} (even if < 0 in some region), determine quasi-definite functionals [26] regarding their dependences on the momentum, q. The assumption is confirmed for the W_{st} (< 0 in some domain) corresponding to the first excited state of the quantum harmonic oscillator. That general assumption implies the existence of orthogonal polynomials, $H_{Q,n}$, in q's, having W_{st}'s as weight functions, and leads to non-equilibrium moments, W_n, of W.

Non-equilibrium quantum hierarchies for the W_n's have been obtained. As an illustration, we treat the $H_{Q,n}$'s and the hierarchy for the first excited state of the harmonic oscillator. In general, with $V \neq 0$, the hierarchies for each W_n are not three-term ones, due to moments $W_{n'}$ with $n' < n$, neither for a generic W_{st} nor for W_{eq}, due to the quantum corrections. As another illustration, we have studied a non-equilibrium four-term hierarchy and have outlined its solution in terms of generalized operator continued fractions.

As an interesting new check for $W_{st} = W_{eq}$, we have found consistency between the present non-equilibrium quantum hierarchies and the three-term ones derived previously [21] in the quasiclassical regime at high temperature (up to and including order $\hbar^2$).

In the non-equilibrium hierarchies for the corresponding W_{eq}'s (both in the full quantum case and in the quasiclassical regime, up to and including order $\hbar^2$), we have formulated a long-time approximation. One expects physically that such an approximation should yield thermalization with the hb. However, we have been unable to display properties like Hermiticity and non-negativity and, hence, to justify thermalization with the hb, so far.

In the regime of large thermal and de Broglie wavelengths and to leading order, we have obtained an approximate W_{eq} and an approximate non-equilibrium Wigner equation (Equations (68) and (70)) with $V \simeq 0$. To leading order, the underlying physics corresponds to total reflection and zero transmission of the quantum particle by the potential $V(x')$ concentrated in a region of very small size. Further computations with $V \simeq 0$ show that the equation for the non-equilibrium moment W_5 contains a three-term structure. That and the hierarchy for $n \leq 4$ obtained in Section 6.1 suggest that, for $V \simeq 0$, the non-equilibrium quantum hierarchy could plausibly be a three-term one for any n. An approximate long-time evolution towards thermalization through moment methods can also be formulated. Based upon that, we have argued that, in such a regime, an approximate long-time thermalization could possibly hold.

Among other pending problems, we quote the following ones. In the classical case: (i) mathematical studies of the operator continued fractions, D's, in the three-term hierarchies for $W_{c,eq}$, for one and N particles; (ii) connections of the non-equilibrium hierarchy for N particles, in the long-time approximation, with non-equilibrium thermodynamics and fluid dynamics. There is no attempt here to replace the latter by moment methods: rather, non-equilibrium moments emphasize Brownian motion features and approximate long-time thermalization, and it could be interesting to relate those (eventually, complementary) standpoints. In the quantum case: (iii) for one particle, studies of the non-equilibrium hierarchies, which are not three-term ones, and of the generalized operator continued fractions; (iv) generalizations to closed quantum (at least, bosonic) many-particle systems, without external hb's, which are far more difficult and, hopefully, could receive some qualitative partial hints from the analysis in the present paper.

Acknowledgments

Conflicts of Interest

The authors declare no conflicts of interest.

Appendix

A. $\epsilon_{c,n,n-j}$'s for any $W_{c,st}$ and for $W_{c,st} = W_{c,mc}$

We shall give the nonvanishing $\epsilon_{c,n,n-j}$ for low order $n = 2, 3, 4, 5$ (j even), by using Equations (2) and (20). After some algebra, one finds:

$$\epsilon_{c,2,0} = - <y^2> \ , \ \epsilon_{c,3,1} = -\frac{<y^4>}{<y^2>} \tag{73}$$

$$\epsilon_{c,4,2} = \frac{<y^2><y^4> - <y^6>}{<y^4> - <y^2>^2} \ , \ \epsilon_{c,4,0} = \frac{<y^2><y^6> - <y^4>^2}{<y^4> - <y^2>^2} \tag{74}$$

$$\epsilon_{c,5,3} = \frac{<y^4><y^6> - <y^2><y^8>}{<y^2><y^6> - <y^4>^2} \ , \ \epsilon_{c,5,1} = \frac{<y^4><y^8> - <y^6>^2}{<y^6><y^2> - <y^4>^2} \tag{75}$$

$$<y^n> = \frac{\int_{-\infty}^{+\infty} dy W_{c,st}(x,q) y^n}{\int_{-\infty}^{+\infty} dy W_{c,st}(x,q)} \tag{76}$$

Equations (73)–(76) imply the following identities:

$$\epsilon_{c,4,0} + \epsilon_{c,2,0}(-\epsilon_{c,4,2} + \epsilon_{c,3.1}) = 0 \tag{77}$$

$$\epsilon_{c,5,1} - \epsilon_{c,4,0} + \epsilon_{c,3,1}(-\epsilon_{c,5,3} + \epsilon_{c,4,2}) = 0 \tag{78}$$

$$-\epsilon_{c,2,0}\frac{\partial \epsilon_{c,3,1}}{\partial x} + (3\epsilon_{c,2,0} - \epsilon_{c,3,1})\frac{m}{q_0^2}\frac{\partial V}{\partial x} = 0 \tag{79}$$

$$\frac{\partial \epsilon_{c,4,0}}{\partial x} - \epsilon_{c,3,1}\frac{\partial \epsilon_{c,4,2}}{\partial x} + (4\epsilon_{c,3,1} - 2\epsilon_{c,4,2})\frac{m}{q_0^2}\frac{\partial V}{\partial x} = 0 \tag{80}$$

B. Classical Microcanonical Distribution $W_{c,mc}$

We consider two possible values for the total energy: $E(>0)$ and $E + \Delta(>0)$, with $E \gg \Delta > 0$. First, we shall treat an open classical one particle system. The stationary microcanonical distribution describing equal probability for the particle, provided that $E \leq H_c \leq E + \Delta$, is:

$$W_{c,mc} = \int_{E}^{E+\Delta} dE' \delta(H_c - E') = \theta(H_c - E)\theta(E + \Delta - H_c) \tag{81}$$

δ and θ denote, respectively, the Dirac delta and the step functions. We introduce some fixed (x-independent) momentum, q_0. In order to have a finite weight function, $W_{c,mc}$, and a well-defined family of orthogonal polynomials $H_{c,n}(y) = H_{c,mc}(y)$ (in $y = q/q_0$), it is necessary that $\Delta \neq 0$. The coefficients, $\epsilon_{c,mc,n,n-j}$, in Equation (20) for $H_{c,mc}(y)$ are given by the above formulas in Appendix A, in terms of the corresponding $<y^n> = <y^n>_{mc}$ evaluated, in turn, with $W_c = W_{c,mc}$. One gets:

$$\int_{-\infty}^{+\infty} dy W_{c,mc}(x,q) = \frac{4(2m)^{1/2}(E - V(x))^{1/2}[(1 + \Delta_{mc})^{1/2} - 1]}{q_0} \tag{82}$$

$$\int_{-\infty}^{+\infty} dy W_{c,mc}(x,q) y^n = \frac{4(2m)^{(n+1)/2}(E - V(x))^{(n+1)/2}[(1 + \Delta_{mc})^{(n+1)/2} - 1]}{(n+1)q_0^{n+1}} \tag{83}$$

$n = 2, 4, 6, ...$, with $\Delta_{mc} = \Delta/(E - V(x))$. The lowest nontrivial coefficients $C_{c,n} = C_{c,,mc,n}$ in the counterpart of the fundamental recurrence relation Equation (21) for $H_{c,mc,n}(y)$ are:

$$C_{c,mc,2} = \frac{\epsilon_{c,mc,2,0} - \epsilon_{c,mc,3,1}}{q_0^2} \ , \ C_{c,mc,3} = \frac{\epsilon_{c,mc,3,1} - \epsilon_{c,mc,4,2}}{q_0^2} \ , \ C_{c,mc,4} = \frac{\epsilon_{c,mc,4,2} - \epsilon_{c,mc,5,3}}{q_0^2} \tag{84}$$

The general theorem [26] requires that $C_{c,,mc,n} > 0$. This general requirement is warranted, provided that $\Delta > 0$. Since Δ is small, by expanding into powers of Δ_{mc}, one finds, for instance:

$$\epsilon_{c,mc,2,0} - \epsilon_{c,mc,3,1} = 2m(E - V)\frac{37\Delta_{mc}^2}{48} \ , \ \epsilon_{c,mc,3,1} - \epsilon_{c,mc,4,2} = 2m(E - V)(1 + \frac{\Delta_{mc}}{2}) \tag{85}$$

The first Equation (85) clearly shows that the fundamental recurrence relation and, hence, the very family of $H_{c,mc,n}(y)$'s become ill-defined if $\Delta = 0$. The non-equilibrium hierarchy for the moments determined by the family, $H_{c,mc}(y)$, could face the problems discussed in Section 2.4.

One now turns briefly to N particles. The stationary classical microcanonical distribution and orthogonal polynomials can be obtained directly, by generalizing Equations (81)–(83), by using the Hamiltonian, $H_{c,N}$, in Section 3. The most interesting situation occurs when the number of degrees of freedom is very large (in the thermodynamical limit) and the classical microcanonical and canonical distributions yield the same equilibrium thermodynamics. The (rather delicate) analysis, based upon the equilibrium partition functions, requires that the system be divided into two subsystems, one being much smaller than the other (which behaves as a *hb*); see [48,49]. A study of the equilibrium distributions themselves (and their orthogonal polynomials) and of the off-equilibrium evolutions, in the transition from the microcanonical ensemble to the canonical one (under those thermodynamical limit conditions), lies outside our scope here. Since both ensembles give the same equilibrium thermodynamics, one pragmatic standpoint could be to concentrate primarily on the off-equilibrium evolution in the canonical ensemble; that is the point of view adopted here.

C. Behavior of W_{eq} for Large q

Here, we shall check the behavior of W_{eq} as $\mid q \mid \to$, assumed in Section 4.1. A quick decrease of W_{eq}'s is necessary for constructing the orthogonal polynomials, $H_{Q,n}(y)$'s. We shall always start from $\int_{-\infty}^{+\infty} dq q^n W_{eq}(x, q)$ for $n = 0, 1, 2, 3, ...$, and use Equations (39) and (47). First, we shall treat the case of harmonic/anharmonic oscillators (V's in second class), for which all $\varphi_j(y)$'s and all $[d^n\varphi_j(y)/dy^n]$ are continuous and finite. By exchanging $\int_{-\infty}^{+\infty} dq$ and $\int_{-\infty}^{+\infty} dy$ and by performing first $\int_{-\infty}^{+\infty} dq$, we get:

$$\int_{-\infty}^{+\infty} dq q^n W(x, q) = [\frac{-i\hbar}{2}]^n \sum_j \exp[-\beta E_j] \int_{-\infty}^{+\infty} dy[\varphi_j(x - y)\varphi_j(x + y)^*][\frac{\partial}{\partial y}]^n\delta(y) \tag{86}$$

$\delta(y)$ being the Dirac delta function. One can integrate directly by using $\delta(y)$:

$$\int_{-\infty}^{+\infty} dq q^n W(x, q) = [\frac{i\hbar}{2}]^n \sum_j \exp[-\beta E_j][d^n(\varphi_j(x - y)\varphi_j(x + y)^*)/dy^n]_{y=0} \tag{87}$$

$\sum_j$ denoting an infinite sum. $\exp[-\beta E_j]$ in Equation (87) decreases quickly with j. Then, the infinite series Equation (87) converges and $\int_{-\infty}^{+\infty} dq q^n W_{eq}(x, q)$ is finite for any x and any $n = 1, 2, 3....$ Next, we

consider V's in the first class and study two possibilities: (a) Let $V(x)$ and all $d^n V(x)/dx^n$, $n = 1, 2, 3...$, be continuous for any x, so that all $\varphi_j(y)$'s and all $[d^n \varphi_j(y)/dy^n]$ are continuous. Then, by operating like for V's in the second class above, we get:

$$\int_{-\infty}^{+\infty} dq q^n W(x, q) = [\frac{i\hbar}{2}]^n \sum_j \exp[-\beta E_j][d^n(\varphi_j(x-y)\varphi_j(x+y)^*)/dy^n]_{y=0} \tag{88}$$

However, now, $\sum_j \equiv \int_{-\infty}^{+\infty} dj$, and E_j sweeps the continuous positive real half-line: $0 \le E_j < +\infty$, with a double degeneracy, associated with two different asymptotic conditions (incoming plane waves) at $x \to \pm\infty$, with the same energy, E_j. Then, Equation (87) also converges and renders $\int_{-\infty}^{+\infty} dq q^n W_{eq}(x, q)$ finite for any x and any $n = 1, 2, 3...$. (b) Let V and all $d^n V(x)/dx^n$, $n = 1, 2, 3...$, be continuous for almost any x, except for a finite number of points $x = a_l$, $l = 1, ..., l_{max} < \infty$, at which V has finite discontinuities. Then, one also arrives to the same convergent result in Equation (88) for any $n = 1, 2, 3...$, provided that $x \ne a_l$. The finiteness of $\int_{-\infty}^{+\infty} dq q^n W_{eq}(x, q)$ for any $n = 1, 2, 3...$ is not warranted at $x = a_l$, due to the discontinuities of V and, hence, of derivatives of φ_j's (of orders ≥ 2) at the latter points.

D. W_{eq} for a Finite Repulsive Square Well

We shall consider the finite repulsive square well: $V(x) = +V_0 > 0$, for $| x | < a/2$ and $V(x) = 0$, for $| x | > a/2$, with $V_0 < +\infty$ and $0 < a < +\infty$. We shall give the eigenfunctions of H, Equation (37). The first set of eigenfunctions is ($j = k_1 \ge 0$, $E_j = (\hbar k_1)^2/2m$, $A = (2\pi)^{-1/2}$):

$$\varphi_{+,k_1}(x) = A[\exp ik_1 x + A_1(k_1)\exp(-ik_1 x)], x < -a/2 \tag{89}$$

$$\varphi_{+,k_1}(x) = A[A_2(k_1)\exp ik_2 x + A_3(k_1)\exp(-ik_2 x)], -a/2 < x < +a/2 \tag{90}$$

$$\varphi_{+,k_1}(x) = AA_4(k_1)\exp ik_1 x, x > a/2 \tag{91}$$

with $k_2 = k_2(E) = [2m(E - V_0)]^{1/2}/\hbar$. If $E - V_0 > 0$, then $k_2 > 0$, while, if $E - V_0 < 0$, then $k_2 = +i\kappa_2$, with $\kappa_2 > 0$. The amplitudes $A_l = A_l(k_1)$, $l = 1, ..., 4$, are:

$$A_1 = \frac{(k_2^2 - k_1^2)\exp(-ik_1 a)(\exp(ik_2 a) - \exp(-ik_2 a))}{D} \tag{92}$$

$$A_2 = \frac{2k_1(k_1 + k_2)\exp[-i(k_1 + k_2)(a/2)]}{D}, A_3 = \frac{2k_1(-k_1 + k_2)\exp[i(-k_1 + k_2)(a/2)]}{D} \tag{93}$$

$$A_4 = \frac{4k_1 k_2 \exp(-ik_1 a)}{D}, D = (k_1 + k_2)^2 \exp(-ik_2 a) - (-k_1 + k_2)^2 \exp ik_2 a \tag{94}$$

The second set of eigenfunctions is ($j = -k_1 \le 0$, $E_j = (\hbar k_1)^2/2m$:

$$\varphi_{-,k_1}(x) = A[\exp(-ik_1 x) + B_1(k_1)\exp ik_1 x], x > a/2 \tag{95}$$

$$\varphi_{-,k_1}(x) = A[B_2(k_1)\exp(-ik_2 x) + B_3(k_1)\exp ik_2 x], -a/2 < x < +a/2 \tag{96}$$

$$\varphi_{-,k_1}(x) = AB_4(k_1)\exp(-ik_1 x), x < -a/2 \tag{97}$$

with the same A and the same $k_2 = k_2(E)$ as for the first set. One gets: $B_l(k_1) = A_l(k_1)$. The equilibrium Wigner function in Equations (39)–(47) becomes:

$$W_{eq}(x, q) = \frac{1}{\pi\hbar} \int_{-\infty}^{+\infty} dy \exp[\frac{i2qy}{\hbar}] \int_0^{+\infty} dk_1 \exp[-\beta(\hbar k_1)^2/2m][\varphi_{+,k_1}(x-y)\varphi_{+,k_1}(x+y)^* + \varphi_{-,k_1}(x-y)\varphi_{-,k_1}(x+y)^*] \tag{98}$$

By using Equations (92)–(94) and their counterparts for $B_l(k_1)$, one finds important exact cancellations. It will suffice to display the resulting exact $W_{eq}(x, q)$ for $x \geq 0$:

$$W_{eq}(x, q) = \frac{1}{\pi\hbar} \int_0^{+\infty} dk_1 \exp[-\beta(\hbar k_1)^2/2m][\int_{-(a/2)-x}^{(a/2)+2x} dy \exp[\frac{i2qy}{\hbar}][\varphi_{+,k_1}(x-y)\varphi_{+,k_1}(x+y)^* +$$

$$\varphi_{-,k_1}(x-y)\varphi_{-,k_1}(x+y)^*] + \int_{-\infty}^{-(a/2)-x} dy \exp[\frac{i2qy}{\hbar}][B_4(k_1)^* \exp(2ik_1y) + A_4(k_1) \exp(-2ik_1y] +$$

$$\int_{a/2)+2x}^{+\infty} dy \exp[\frac{i2qy}{\hbar}][B_4(k_1) \exp(2ik_1y) + A_4(k_1)^* \exp(-2ik_1y]] \tag{99}$$

In agreement with Appendix C, $\int_{-\infty}^{+\infty} dq q^n W_{eq}(x, q)$ is finite for any $n = 1, 2, 3...$ and any $x \neq \pm a/2$. Let us consider the regime of large thermal and de Broglie wavelengths: $\lambda_{th} = \hbar(\beta/2m)^{1/2}$, $q_l = \hbar/\lambda_{th}$, $\mid q \mid a \ll \hbar$, $\mid q \mid < q_l$ ($\lambda_{th} \gg a$), $V_0 \gg \beta^{-1}$ and $\mid x \mid /a \gg 1$. Let $\kappa_{2,0} = [2mV_0]^{1/2}/\hbar$. Then, the dominant contributions to $\int_0^{+\infty} dk_1$ in Equation (99) come from $k_1\lambda_{th} < 1$. We shall start by keeping terms only up to and including orders a/λ_{th} and $(\beta V_0)^{-1/2}$ and indicate later at which stage they are dropped, so as to have a record of them and to handle, and at the end, manageable expressions at leading order. Then: $A_1 \simeq -1 + i[k_1a + 2(k_1/\kappa_{2,0}) \coth(a\kappa_{2,0})]$, while $A_2 \simeq (k_1/\kappa_{2,0})(\exp(a\kappa_{2,0}/2)/\sinh(a\kappa_{2,0}))$, $A_3 \simeq (k_1/\kappa_{2,0})(\exp(-a\kappa_{2,0}/2)/\sinh(a\kappa_{2,0}))$ and $A_4 \simeq (k_1/\kappa_{2,0})(2/\sinh(a\kappa_{2,0}))$. By starting from Equation (99): (i) the contributions from A_4, A_4^*, B_4 and B_4^* (second and third integrals over y) are of order $k_1/\kappa_{2,0}$, as is that from $\int_{(a/2)+x}^{(a/2)+2x} dy$; (ii) $\int_{-(a/2)-x}^{(a/2)+x} dy$ is dominated by $\int_{-x}^{+x} dy\varphi_{-,k_1}\varphi_{-,k_1}^*$ (dropping terms of order $(k_1/\kappa_{2,0})^2$ and $\int_{-(a/2)-x}^{-x} dy$ and $\int_x^{(a/2)+x} dy$); (iii) in $\int_{-x}^{+x} dy\varphi_{-,k_1}\varphi_{-,k_1}^*$, we discard the two contributions of orders $k_1/\kappa_{2,0}$ and k_1a and the one quadratic in them (all coming from $B_1 + 1$ and $B_1^* + 1$). Then:

$$W_{eq}(x, q) \simeq W_{l,eq}(x, q) \simeq \int_0^{\lambda_{th}^{-1}} \frac{dk_1}{\pi\hbar}$$

$$\times \exp[-\frac{\beta(\hbar k_1)^2}{2m}][-2\cos 2k_1 x \frac{\sin 2(q/\hbar)x}{q/\hbar} + \frac{\sin 2(k_1 + q/\hbar)x}{k_1 + q/\hbar} + \frac{\sin 2(-k_1 + q/\hbar)x}{-k_1 + q/\hbar}] \tag{100}$$

which corresponds to dominant reflection and small transmission of the quantum particle by the repulsive finite square well, at leading order (orders $(a/\lambda_{th})^0$ and $((\beta V_0)^{-1/2})^0$). One gets: $\int_{|q|<q_l} dq q^{2n+1} W_{l,eq}(x, q) = 0$, for $n = 0, 1, 2, 3, ...$ These results will be helpful in Section 7 and Appendix G.

E. First Excited State of Harmonic Oscillator: Orthogonal Polynomials and Hierarchy

First, we shall study whether W_{st}, given in Equation (55), provides a quasi-definite functional regarding the y dependence. We have computed the actual μ_n's, the $(S+1) \times (S+1)$ matrices M_S and their determinants: $Det[M_S]$. One finds that $Det[M_S]$ bears the structure $\exp[-(S+1)(2x^2)]d_{S+1}$, where d_{S+1} is a polynomial in x^2 of degree $S+1$, which can vanish only at a finite set of x values. It follows from a theorem in [26] that W_{st} is a quasi-definite functional regarding the y dependence for any x, except at a set of x-values having zero measure (formed by all zeroes of all d_{S+1}'s). Consequently,

except for the latter set, the orthogonal polynomials, $H_{Q,n}$, exist for the quasi-definite functional, W_{st}. We shall give the lowest non-vanishing $\sigma_{n,n-j}$ (j being even) in those $H_{Q,n}$'s (Equation (51)):

$$\sigma_{2,0} = -\frac{1}{x^2} \ , \ \sigma_{3,1} = -\frac{3!}{2x^2 + 1} \tag{101}$$

$$\sigma_{4,2} = -x^2\sigma_{4,0} \ , \ \sigma_{4,0} = -\frac{4!}{4x^2 + 4 - (1/2x^2)} \tag{102}$$

Consistently with a general theorem in [26], the $H_{Q,n}$'s fulfill the recurrence relation:

$$2yH_{Q,n}(y) = H_{Q,n+1}(y) + C_n H_{Q,n-1}(y) \tag{103}$$

for $n = 0, 1, 2, \ldots$, with $C_0 \equiv 0$. C_n are y-independent (but x-dependent). The lowest C_n's are:

$$C_1 = 2 - \sigma_{2,0} \ , \ C_2 = 4 + \sigma_{2,0} - \sigma_{3,1} \tag{104}$$

$$C_3 = 6 + \sigma_{3,1} - \sigma_{4,2} \tag{105}$$

That general theorem in [26] does not warrant that all C_n's be positive; in fact, $C_2 < 0$ for small x^2.

We now consider the quantum Equation (53) for a non-equilibrium, W, and define its off-equilibrium moments, W_n, by using the actual counterpart of Equation (56) with the polynomials, $H_{Q,n}$, constructed in this Appendix. Through computations similar to those in Section 6.1, one gets the following off-equilibrium three-term hierarchy for the W_n, for low n's:

$$\frac{\partial W_0}{\partial t} = -\frac{1}{2^{3/2}} \frac{\partial W_1}{\partial x} \tag{106}$$

$$\frac{\partial W_1}{\partial t} = -\frac{1}{2^{3/2}} \frac{\partial W_2}{\partial x} + \frac{1}{2^{3/2}} \frac{\partial}{\partial x}[(\sigma_{2,0} - 2]W_0] - 2^{1/2}2xW_0 \tag{107}$$

$$\frac{\partial W_2}{\partial t} = -\frac{1}{2^{3/2}} \frac{\partial W_3}{\partial x} + \frac{1}{2^{3/2}} \frac{\partial}{\partial x}[\sigma_{3,1} - 4)W_1] - \frac{\sigma_{2,0}}{2^{3/2}} \frac{\partial W_1}{\partial x} - 2^{1/2}4xW_1 \tag{108}$$

$$\frac{\partial W_3}{\partial t} = -\frac{1}{2^{3/2}} \frac{\partial W_4}{\partial x} + \frac{1}{2^{3/2}} \frac{\partial}{\partial x}[(\sigma_{4,2} - 6)W_2] - \frac{\sigma_{3,1}}{2^{3/2}} \frac{\partial W_2}{\partial x} - 2^{1/2}6xW_2 \tag{109}$$

and so on for W_n, $n > 3$, with suitable initial conditions $W_{in,n}$. The computations for $n = 3, 4, 5, \ldots$ become more difficult. The hierarchy in Equations (106)–(109) is satisfied by the t-independent moments determined by W_{st} in Equation (55). The actual hierarchy falls into the class given in Equation (27), for which $M_{st,n,n+1}$ is not the adjoint of $-M_{st,n+1,n}$. Then, the corresponding operator continued fractions (counterparts of Equation (28)) are not expected to fulfill Hermiticity and non-negativity properties; recall Section 2.4.

F. Formal Solution of Equation (65) through Generalized Operator Continued Fractions

The procedure for solving formally the four-term hierarchy Equation (65) (for any n) in terms of generalized operator continued fractions extends directly to the strategy employed for the three-term one, at the expense of working with more complicated expressions. For simplicity, we shall assume the initial condition $W_{in,0} \neq 0$, $W_{in,0} \neq W_{eq,0}$ and $W_{in,n} = 0$ for $n \neq 0$. We perform the Laplace transform, which leads from Equation (65) to:

$$s\tilde{W}_n(s) = W_{in,n} - M_{n,n+1}\tilde{W}_{n+1}(s) - M_{n,n-1}\tilde{W}_{n-1}(s) - M_{n,n-3}\tilde{W}_{n-3}(s)_{n-3} \tag{110}$$

The solution of Equation (110) is given in terms of products of the s-dependent generalized operator continued fractions, $D_{Q,4}[n; s]$. The latter are defined recurrently, for $n = 1, 2, ...$, through the following generalization of Equation (9):

$$
\begin{aligned}
D_{Q,4}[n; s] &= [sI - M_{n,n+1}D_{Q,4}[n+1; s]][M_{n+1,n} + M_{n+1,n+2}D_{Q,4}[n+2; s]M_{n+2,n+3} \times \\
&\quad D_{Q,4}[n+3; s]M_{n+3,n}]]^{-1}
\end{aligned} \tag{111}
$$

I is the unit operator. By iteration of Equation (111), $D_{Q,4}[n; s]$ becomes a formal generalized infinite continued fraction of nonconmuting operators. Omitting calculational details, one gets for $n = 1, 2, ...$:

$$
\begin{aligned}
\tilde{W}_n(s) &= D_{Q,4}[n; s][[-M_{n,n+1}D_{Q,4}[n+1; s]M_{n+1,n+2}D_{Q,4}[n+2; s]M_{n+2,n-1} - M_{n,n-1}]\tilde{W}_{n-1}(s) + \\
&\quad M_{n,n+1}D_{Q,4}[n+1; s]M_{n+1,n-2}\tilde{W}_{n-2}(s) - M_{n,n-3}\tilde{W}_{n-3}(s)]
\end{aligned} \tag{112}
$$

G. Approximate $W_{eq}(x, q)$ for Large Thermal and de Broglie Wavelengths

We shall get an approximate representation for $W_{l,eq}(x, q)$ with V's in the first class, to leading order in the low-T regime characterized by the Conditions (a) and (b) in Section 7. The exact $W_{eq}(x, q)$ (Equations (39) and (47)) is given, alternatively, by Equation (98), in which $\varphi_{+,k_1}(x)$ is now the exact solution of the following inhomogeneous linear integral equation for one-dimensional scattering in $-\infty < x < +\infty$, with the incoming plane wave as $x \to -\infty$:

$$
\varphi_{+,k_1}(x) = \exp ik_1 x - \frac{mi}{\hbar^2 k_1} \int_{-a/2}^{+a/2} dx' \exp ik_1 \mid x - x' \mid V(x')\varphi_{+,k_1}(x') \tag{113}
$$

In Equation (113) for simplicity, we set firstly $V(x') \neq 0$ only in $-a/2 < x' < +a/2$ (finite range potential). We shall study the approximate solution of Equation (113) for $-a/2 < x < +a/2$ and very small k_1. That approximate solution cannot come from Equation (113) as it stands, due to the explicit singularity, k_1^{-1}, in the integral. The problem will be solved by extending to scattering a technique used in [50] for bound states. For that purpose, we set $\exp ik_1 \mid x - x' \mid = 1 + C(k_1 \mid x - x' \mid)$ (thereby defining $C(k_1 \mid x - x' \mid)$), multiply the resulting Equation (113) by $V(x)$, integrate in $-a/2 < x < +a/2$ and solve for $\int_{-a/2}^{+a/2} dx V(x)\varphi_{+,k_1}(x)$. By reshuffling the latter into Equation (113), we get for $-a/2 < x < +a/2$:

$$
\begin{aligned}
\varphi_{+,k_1}(x) &= \exp ik_1 x - \frac{1}{(\hbar^2 k_1/im) + \int_{-a/2}^{+a/2} dx'' V(x'')}[\int_{-a/2}^{+a/2} dx' \exp ik_1 x' V(x') \\
&\quad - \int_{-a/2}^{+a/2} dx' \frac{mi V(x')}{\hbar^2 k_1} \times \int_{-a/2}^{+a/2} dx'' C(k_1 \mid x' - x'' \mid)V(x'')\varphi_{+,k_1}(x'')] \\
&\quad - \int_{-a/2}^{+a/2} dx' \frac{mi C(k_1 \mid x - x' \mid)}{\hbar^2 k_1} V(x')\varphi_{+,k_1}(x')
\end{aligned} \tag{114}
$$

Equation (115) has no singularity at $k_1 = 0$ (since $C(k_1 \mid x - x' \mid)/k_1$ is finite as $k_1 \to 0$). Even if the iterations of Equation (115) provide $\varphi_{+,k_1}(x)$, the full corrections of order k_1 require one to solve a (singularity-free) linear integral equation, so that we shall limit ourselves to leading order $((k_1)^0)$, which is simpler. We come back to Equation (113) for $x < -a/2$, set $\exp(-ik_1 x') \simeq +1$ for $-a/2 < x' < $

$+a/2$, use the above $\int_{-a/2}^{+a/2} dx V(x)\varphi_{+,k_1}(x)$ and see that the singularity in k_1^{-1} cancels out, consistently with the study yielding Equation (115). In the resulting expression, we neglect the terms in $V(x')V(x'')$. For small k_1, the leading contribution for $x < -a/2$ is: $\varphi_{+,k_1}(x) \simeq \exp ik_1x - \exp(-ik_1x)$, to order $(k_1)^0$ (the total reflection of the quantum particle by $V(x')$). A similar analysis for $x > a/2$ gives: $\varphi_{+,k_1}(x) \simeq 0$, to order $(k_1)^0$ (zero transmission). There is a similar analysis for $\varphi_{-,k_1}(x)$ with the incoming plane wave as $x \to +\infty$. The same results hold for V's in the first class without finite range.

The above leading order approximations (to order $(k_1)^0$) apply in the low-T regime characterized by the Conditions (a) and (b) in Section 7. Then, through Equation (98), the exact $W_{eq}(x,q)$ can be approximated like in the derivation of Equation (100) in Appendix D. The resulting expression is given in Equation (68). The new coefficients, $\epsilon_{Q,l,n,n-j}$, in the polynomials, $H_{Q,l,n}$, in Equation (49) are given formally by the right-hand sides of Equations (73)–(76) for low n and j, with the above $W_{l,eq}(x,q)$. Equation (71) employed the new identities $\epsilon_{Q,l,6,2} - \epsilon_{Q,l,5,1} + \epsilon_{Q,l,4,2}(-\epsilon_{Q,l,6,4} + \epsilon_{Q,l,5.3}) = 0$, $\partial \epsilon_{Q,l,5.3}/\partial x = 0$ and $\partial \epsilon_{Q,l,5.1}/\partial x = 0$, which extend Equations (77)–(80).

For very large x, one can approximate Equation (68) by:

$$W_{l,eq}(x,q) \simeq \int_0^{\lambda_{th}^{-1}} \frac{dk_1}{\hbar} \exp[-\beta(\hbar k_1)^2/2m][-2\cos 2k_1 x.\hbar\delta(q) + \delta(k_1 + q/\hbar) +$$

$$\delta(-k_1 + q/\hbar)] = -\delta(q) \int_0^{\lambda_{th}^{-1}} dk_1 \exp[-\frac{\beta(\hbar k_1)^2}{2m}]\cos 2k_1 x + \frac{1}{\hbar}\exp[-\frac{\beta q^2}{2m}] \tag{115}$$

δ being the Dirac delta function. By using Equation (115):

$$\int_{|q|<q_l} dq W_{l,eq}(x,q) = -\int_0^{\lambda_{th}^{-1}} dk_1 \exp[-\frac{\beta(\hbar k_1)^2}{2m}]\cos 2k_1 x + \int_{-\lambda_{th}^{-1}}^{\lambda_{th}^{-1}} \frac{dq}{\hbar}\exp[-\frac{\beta q^2}{2m}] > 0 \tag{116}$$

Then, for very large x and $\mid q \mid \leq q_l$ (except at $q = 0$), $W_{eq}(x,q)$ equals roughly a Gaussian minus the $\delta(q)$ contribution. Even if $W_{l,eq}(x,q)$ in Equation (68) can be < 0 in some region, a glance at it (and at the approximation for it in Equation (115)) would suggest that, in some sense and for $\mid q \mid \leq q_l$ and adequately large x, $W_{l,eq}(x,q)$ could have properties not radically different from those a Gaussian has in q (in the same range). We use Equation (115)) below. Certain $\epsilon_{Q,l,n,n-j}$ ($\epsilon_{Q,l,3,1}$, $\epsilon_{Q,l,5.3}$, $\epsilon_{Q,l,5.1}$,....) are x-independent and rather similar to those for the Gaussian case (say, to the classical case): the main difference is that, in the actual quantum case, one has structures like $\int_{-\lambda_{th}^{-1}}^{\lambda_{th}^{-1}}(dq/\hbar)\exp[-(\beta q^2/2m)]$, instead of the classical $\int_{-\infty}^{+\infty}(dq/\hbar)\exp[-(\beta q^2/2m)]$. Other $\epsilon_{Q,l,n,n-j}$ ($\epsilon_{Q,l,2,0}$, $\epsilon_{Q,l,4,2}$, $\epsilon_{Q,l,4,0}$,....) are x-dependent: then one finds structures like $\int_0^{\lambda_{th}^{-1}} dk_1 \exp[-(\beta q^2/2m)][-\cos 2k_1 x + 2] > 0$, in which the x-dependent contributions are dominated by constant Gaussian-like ones.

References

1. Wallace, D. Reading list for advanced philosophy of physics: The philosophy of statistical mechanics. Available online: http://www.osti.gov/eprints/topicpages/documents/record/366/4717199.html (accessed on 20 Febraury 2014).
2. Kreuzer, H. J. *Nonequilibrium Thermodynamics and its Statistical Foundations*; Clarendon Press: Oxford, UK, 1981.

3. Balescu, R. *Equilibrium and Nonequilibrium Statistical Mechanics*; John Wiley and Sons: New York, NY, USA, 1975.

4. Liboff, R.L. *Kinetic Theory*, 2nd ed.; John Wiley (Interscience): New York, NY, USA, 1998.

5. Zubarev, D.; Morozov V.G.; Röpke, G. *Statistical Mechanics of Nonequilibrium Processes*; Akademie Verlag: Berlin, Germany, 1996; Volume I.

6. Wigner, E.P. On the quantum correction for thermodynamic equilibrium. *Phys. Rev.* **1932**, *40*, 749–759.

7. Hillery, M.; O'Connell, R.F.; Scully, M.O.; Wigner, E.P. Distribution functions in physics: Fundamentals. *Phys. Rep.* **1984**, *106*, 121–167.

8. Zakos, C.K.; Fairlie, D.B.; Curtwright, T.L. *Quantum Mechanics in Phase Space. An Overview with Selected Papers*; World Scientific Publication: Singapore, Singapore, 2005.

9. Callender, C. Thermodynamic Asymmetry in Time. In *Stanford Encyclopedia of Philosophy*, Fall 2011 ed.; Zalta, E.N., Ed.; Stanford University: Stanford, CA, USA, 2011. Available online: http://plato. stanford.edu/entries/time-thermo/ (accessed on 23 February 2014).

10. Penrose, O. Foundations of statistical mechanics. *Rep. Progr. Phys.* **1979**, *42*, 1937–2006.

11. Brinkman, H.C. Brownian motion in a field of force and the diffusion theory of chemical reactions. *Physica* **1956**, *22*, 29–34.

12. Risken, H. *The Fokker-Planck Equation*, 2nd ed.; Springer: Berlin, Germany, 1989.

13. Coffey, W.T.; Kalmykov, Y.P. *The Langevin Equation*, 3rd ed.; World Scientific: Singapore, Singapore, 2012.

14. Coffey, W.T.; Kalmykov, Y.P.; Titov, S.V.; Mulligan, B.P. Wigner function approach to the quantum Brownian motion of a particle in a potential. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3361–3382.

15. Alvarez-Estrada, R.F. New hierarchy for the Liouville equation, irreversibility and Fokker-Planck-like structures. *Ann. Phys.* **2002**, *11*, 357–385.

16. Alvarez-Estrada, R.F. Liouville and Fokker-Planck dynamics for classical plasmas and radiation. *Ann. Phys.* **2006**, *15*, 379–415.

17. Alvarez-Estrada, R.F. Nonequilibrium quasi-classical effective meson gas: Thermalization. *Eur. Phys. J. A* **2007**, *31*, 761–765.

18. Alvarez-Estrada, R.F. Nonequilibrium quantum anharmonic oscillator and scalar field: High temperature approximations. *Ann. Phys.* **2009**, *18*, 391–409.

19. Alvarez-Estrada, R.F. Classical systems: Moments, continued fractions, long-time approximations and irreversibility. *AIP Con. Proc.* **2011**, *1332*, 261–264.

20. Alvarez-Estrada, R.F. Classical and quantum models in nonequilibrium statistical mechanics: Moment methods and long-time approximations. *Entropy* **2012**, *14*, 291–322.

21. Alvarez-Estrada, R.F. Brownian motion, quantum corrections and a generalization of the Hermite polynomials. *J. Comput. Appl. Math.* **2010**, *233*, 1453–1461.

22. Alvarez-Estrada, R.F. Quantum Brownian motion and generalizations of the Hermite polynomials. *J. Comput. Appl. Math.* **2011**, *236*, 7–18.

23. Hochstrasser, U.W. Orthogonal Polynomials. In *Handbook of Mathematical Functions*; Abramowitz, M., Stegun, I.A., Eds.; Dover: New York, NY, USA, 1965.

24. Barreiro, L.A., Campanha, J.R.; Lagos, R.E. The thermohydrodynamical picture of Brownian motion via a generalized Smoluchowski equation. *Physica A* **2000**, *283*, 160–165.

25. Doi, M; Edwards, S.F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, UK, 1988.

26. Chihara, T.S. *An Introduction to Orthogonal Polynomials*; Gordon and Breach: New York, NY, USA, 1978.

27. Penrose, O.; Coveney, P.V. Is there a "canonical" non-equilibrium ensemble? *Proc. R. Soc. Lond.* **1994**, *A447*, 631–646.

28. Beretta, G.P. Modeling non-Equilibrium dynamics of a discrete probability distribution: General rate equation for maximal entropy generation in a maximum-entropy landscape with time-dependent constraints. *Entropy* **2008**, *10*, 160–182.

29. Lebon, G.; Jou, D.; Casas-Vazquez, J. *Understanding Non-Equilibrium Thermodynamics*; Oxford University Press: Oxford, UK, 2008.

30. Rubi, J.M. The non-equilibrium thermodynamics approach to the dynamics of mesoscopic systems. *J. Non-Equilib. Thermodyn.* **2004**, *29*, 315–326.

31. Reguera, D. Mesoscopic nonequilibrium kinetics of nucleation processes. *J. Non-Equilib. Thermodyn.* **2004**, *29*, 327–344.

32. Maes, C. Nonequilibrium entropies. *Phys. Scr.* **2012**, *86*, 058509.

33. Gyftopoulos, E.P.; Beretta, G.P. *Thermodynamics. Foundations and Applications*; Dover: New York, NY, USA, 2005.

34. Van Kampen, N.G. *Stochastic Processes in Physics and Chemistry*; Elsevier: Amsterdam, The Netherlands, 2001.

35. Gardiner, C.W.; Zoller, P. *Quantum Noise*, 3rd ed.; Springer: Berlin, Germany, 2004.

36. Weiss, U. *Quantum Dissipative Systems*, 4th ed.; World Scientific: Singapore, Singapore, 2012.

37. Breuer, H.-P.; Petruccione, F. *The Theory of Open Quantum Systems*; Oxford University Press: Oxford, UK, 2006.

38. Rivas, A.; Huelga, S.F. *Open Quantum Systems. An Introduction*; Springer: Heidelberg, Germany, 2011.

39. Hudson, R.L. When is the Wigner quasi-probability density non-negative? *Rep. Math. Phys.* **1974**, *6*, 249–252.

40. Piquet, C. Fonctions du type positif associees a deux operateurs hermitiens. *C. R. Acad. Sci. Paris* **1974**, *279A*, 107–109. (in French)

41. Schleich, W.P. *Quantum Optics in Phase Space*; Wiley VCH: Berlin, Germany, 2001.

42. Dahl, J.P. Springborg. The Morse oscillator in position space, momentum space and phase space. *J. Chem. Phys.* **1988**, *88*, 4535–4547.

43. Bund, G.W.; Tijero, M.C. Mapping the Wigner distribution function of the Morse oscillator into a semi-classical distribution function. **2003**, arXiv:quant-ph/0304092v1.

44. Hug, M.; Menke, C.; Schleich, W.P. How to calculate the Wigner function from phase space. *J. Phys. Math. Gen.* **1998**, *31*, L217–L224.

45. Louisell, W.H. *Quantum Statistical Properties of Radiation*; John Wiley and Sons: New York, NY, USA, 1973.

46. Haroche, S.; Raimond, J.-M. *Exploring the Quantum*; Oxford University Press: Oxford, UK, 2008.

47. Lindblad, G. On the generators of quantum dynamical semigroups. *Commun. Math. Phys.* **1976**, *48*, 119–130.

48. Huang, K. *Statistical Mechanics*, 2nd ed.; John Wiley and Sons: New York, NY, USA, 1987.

49. Munster, A. *Statistical Thermodynamics*; Springer: Berlin, Germany, 1969; Volume I.

50. Simon, B. The bound states of weakly coupled Schrödinger operators in one and two dimensions. *Ann. Phys.* **1976**, *97*, 279–288.