

A PERTURBATION EXPANSION FOR CORRELATION FUNCTIONS VIA THE WIGNER DISTRIBUTION

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We compute the coordinate correlation $\frac{1}{2} \langle \hat{q}(t)\hat{q}(0) + \hat{q}(0)\hat{q}(t) \rangle$ via the Wigner phase space distribution, for a system with Hamiltonian $\hat{H} = \hat{H}_0 + \lambda \hat{H}'$, where the canonical ensemble Wigner distribution corresponding to \hat{H}_0 is known exactly. Perturbation expansions in powers of λ , for the correlation function and the Wigner distribution, are developed. By avoiding an expansion in powers of \hbar , we obtain results whose validity is not restricted to the near-classical regime, in contrast to the Wigner-Kirkwood approach. We illustrate our results by application to the one-dimensional anharmonic oscillator, and the relation to other perturbation methods (Lindstedt-Poincaré, Green's Function) is explored. By virtue of the fluctuation-dissipation theorem, it is anticipated that such results will also be useful for the investigation of transport problems.

I. Introduction

A wealth of information regarding the equilibrium and dynamic properties of a system may be derived from correlation functions of the form

$$C_{AA}(t) = \frac{1}{2} \langle \hat{A}(t) \hat{A}(0) + \hat{A}(0) \hat{A}(t) \rangle \quad (1)$$

where $\hat{A}(t) = e^{-i\hat{H}t/\hbar} \hat{A} e^{i\hat{H}t/\hbar}$ is a Heisenberg operator and $\langle \hat{O} \rangle = \text{Tr}(\hat{\rho} \hat{O})$, $\hat{\rho}$ being the density operator for a canonical ensemble at inverse temperature β

$$\hat{\rho} = e^{-\beta \hat{H}} / \text{Tr}[e^{-\beta \hat{H}}] \quad (2)$$

(\hat{H} is the Hamiltonian). In condensed matter physics $C_{AA}(t)$ is commonly obtained from the temperature Green's function^{1,2}

$$G(\sigma) = \langle T[\hat{A}(\sigma)\hat{A}(0)] \rangle \quad (3)$$

(where $\hat{A}(\sigma) = e^{\sigma \hat{H}} \hat{A} e^{-\sigma \hat{H}}$ and T is the time-ordering operator) via analytic continuation. An alternative method for computing correlation functions makes use of the Wigner distribution function (WDF)^{3,4}. This approach has been used to find the quantum corrections (i.e. the near-classical limit) to transport properties^{5,6,7} but does not appear to have been widely applied otherwise. In particular, the important problem of developing a perturbation theory for the WDF is largely unexplored. The purpose of this work is to present new results concerning the evaluation of correlation functions using the

WDF. An important feature of our discussion is the avoidance of the Wigner-Kirkwood expansion⁸ (i.e. in powers of \hbar) so that the validity of our results is not restricted to the near-classical regime. A brief account of our results has been published recently.⁹ In Section II we review the WDF method as applied to correlation functions, and develop a perturbation expansion for $C_{AA}(t)$. In Section III, perturbation theory for the WDF is considered, and in Section IV we illustrate some of our results by means of a simple example: corrections to the frequency and partition function of an anharmonic oscillator. We show in Appendix C that the WDF results coincide with those obtained by the usual Green's function approach.

II. Correlation Functions

In this section we examine how the WDF may be used to determine time correlation functions for a canonical ensemble. The formal solution to this problem was given some time ago by Hynes et al.¹⁰, who showed that

$$C_{AA}(t) = \int dq dp P_w(q,p;\beta) \cos\left(\frac{H_A}{2}\right) A_w(0) A_w(t) \quad (4)$$

where q and p denote classical coordinate and momentum,

$$P_w(q,p,\beta) = (\pi \hbar)^{-1} \int dy \langle q-y | \hat{\rho} | q+y \rangle e^{2ipy/\hbar} \quad (5)$$

is the normalized WDF, and

$$\Delta = \frac{\partial}{\partial p} \frac{\partial}{\partial q} - \frac{\partial}{\partial q} \frac{\partial}{\partial p} \quad (6)$$

the arrows indicating direction of operation.

(In Eq. (4) Δ operates only on the quantities within brackets.) All integrations extend from $-\infty$ to $+\infty$ unless otherwise specified. By \hat{Q} we denote the phase space equivalent of the W operator \hat{Q} ,

$$Q_W(q,p) = 2 \int dy \langle q-y | \hat{Q} | q+y \rangle e^{2ipy/\hbar}, \quad (7)$$

so that

$$\int dq dp Q_W(q,p) P_W(q,p) = \text{Tr}[\hat{\rho}\hat{Q}]. \quad (8)$$

In addition, we note from Eqs. (5) and (7), that P_W is $(2\pi\hbar)^{-1}$ times the phase space function corresponding to the density operator.

If $\hat{Q} = \hat{Q}(q)$, then $Q_W = Q(q)$, and similarly for $\hat{Q}(p)$.

The time dependence of $A_W(t) \equiv [\hat{A}(t)]_W$ is governed by^{3,4,10}

$$\frac{\partial A_W}{\partial t} = iLA_W(t) = \left\{ \frac{p}{m} \frac{\partial}{\partial q} - \frac{2}{\hbar} \sin\left(\frac{\hbar}{2} \frac{\partial}{\partial q} \frac{\partial}{\partial p}\right) V(q) \right\} A_W \quad (9)$$

so that, formally,

$$A_W(t) = e^{iLt} A_W. \quad (10)$$

In the second term of Eq. (9), the $\frac{\partial}{\partial q}$ is understood to operate only on the potential, $V(q)$.

In all but the simplest cases (free particle, harmonic oscillator), H is such that neither $A_W(t)$ nor $P_W(q,p;\beta)$ may be evaluated exactly. We shall be interested in the case

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}' = \frac{\hat{p}^2}{2m} + V_0(\hat{q}) + \lambda \hat{H}'(\hat{q}), \quad (11)$$

where $P_W^{(0)}(q,p;\beta)$, the WDF corresponding to \hat{H}_0 , is known exactly. We shall develop an expansion for the correlation function in the coupling λ .

We shall avoid making an additional expansion in powers of \hbar . Thus the validity of our results will not be restricted to the nearly-classical regime. For simplicity we consider the coordinate correlation

$$\begin{aligned} C(t) &= \frac{1}{2} \langle \hat{q}(t)\hat{q}(0) + \hat{q}(0)\hat{q}(t) \rangle \\ &= \int dq dp P_W(q,p;\beta) q(0)q(t) \\ &= \int dq dp P_W(q,p;\beta) q e^{iLt} q. \end{aligned} \quad (12)$$

For the Hamiltonian, Eq. (11), the Liouvillian may be written

$$\begin{aligned} iL &= \frac{p}{m} \frac{\partial}{\partial q} - \frac{2}{\hbar} \sin\left(\frac{\hbar}{2} \frac{\partial}{\partial q} \frac{\partial}{\partial p}\right) [V_0(q) + \lambda H'(q)] \\ &= iL_0 + i\lambda L'. \end{aligned} \quad (13)$$

Since L_0 and L' do not commute, the expansion of e^{iLt} in powers of λ is not straightforward. In kinetic theory¹¹ this problem is circumvented by

using the "resolvent expansion", i.e. the formal identity

$$\begin{aligned} \frac{1}{s-i(L_0+\lambda L')} &= \frac{1}{s-iL_0} + \frac{1}{s-iL_0} i\lambda L' \frac{1}{s-iL_0} \\ &+ \frac{1}{s-iL_0} i\lambda L' \frac{1}{s-iL_0} i\lambda L' \frac{1}{s-iL_0} + \dots \end{aligned} \quad (14)$$

We therefore turn our attention to the Laplace transform

$$\begin{aligned} J(s) &= \int_0^\infty dt e^{-st} C(t) = \int_0^\infty dt \int dq dp P_W(q,p;\beta) q e^{iLt-st} q \\ &= \langle q \frac{1}{s-iL} q \rangle. \end{aligned} \quad (15)$$

where $\langle \rangle$ now denotes a phase space average with respect to the WDF. The perturbation expansion of $\frac{1}{s-iL}$ is furnished by Eq. (14), but in order to evaluate $J(s)$ we also require a perturbation expansion for the WDF. Anticipating the results of the following section, we use $P_n(q,p;\beta)$ to denote the WDF correct to n th order in the coupling λ , and $\langle \rangle_n$ to denote a phase space average with respect to P_n . Then we have

$$\begin{aligned} J(s) &= \langle q \frac{1}{s-iL_0} q \rangle_n + \lambda \langle q \frac{1}{s-iL_0} iL' \frac{1}{s-iL_0} q \rangle_{n-1} + \dots \\ &+ \lambda^n \langle q \frac{1}{s-iL_0} iL' \dots \frac{1}{s-iL_0} q \rangle_0 + O(\lambda^{n+1}) \\ &= \langle q \frac{1}{s-iL_0} q \rangle_n \left(1 + \lambda \frac{\langle q \frac{1}{s-iL_0} iL' \frac{1}{s-iL_0} q \rangle_{n-1}}{\langle q \frac{1}{s-iL_0} q \rangle_{n-1}} + \dots \right. \\ &\left. + \lambda^n \frac{\langle q \frac{1}{s-iL_0} iL' \dots \frac{1}{s-iL_0} q \rangle_0}{\langle q \frac{1}{s-iL_0} q \rangle_0} \right) + O(\lambda^{n+1}), \end{aligned} \quad (16)$$

which is our formal expansion for the Laplace transform of the correlation function. For some applications, the n th order correction to the quantity of interest may be obtained without evaluating the prefactor, so that the WDF is required only to order λ^{n-1} . We turn now to the evaluation of the WDF.

III. Perturbation Expansion for the WDF

For the following discussion it proves convenient to work with an unnormalized WDF

$$\Omega_W(q,p;\beta) \equiv [e^{-\beta\hat{H}}]_W. \quad (17)$$

Then

$$P_W(q,p;\beta) = \frac{\Omega_W(q,p;\beta)}{\int \int dq dp \Omega_W(q,p)} \equiv \frac{\Omega_W(q,p;\beta)}{2\pi\hbar Z(\beta)}, \quad (18)$$

where $Z(\beta)$ is the partition function. \hat{Q} satisfies the Wigner phase space equivalent of the Bloch equation.

Our problem is to evaluate

$$\hat{Q}_W(q, p; \beta) = [e^{-\beta(\hat{H}_0 + \lambda \hat{H}')}]_W, \quad \text{where}$$

$\hat{Q}_W^{(0)}$, the WDF corresponding to \hat{H}_0 , is known. Since \hat{H}_0 and \hat{H}' do not commute, the exponential cannot readily be expanded in powers of λ . We may, however, use as our starting point an expression familiar from the temperature Green's function formalism^{1,2}

$$e^{-\beta \hat{H}} = e^{-\beta \hat{H}_0} U(\beta, 0), \quad (19)$$

where

$$U(\beta, 0) = 1 - \lambda \int_0^\beta \tilde{H}'(\sigma) d\sigma + \frac{\lambda^2}{2!} \int_0^\beta d\sigma_1 \int_0^{\sigma_1} d\sigma_2 T [\tilde{H}'(\sigma_1) \tilde{H}'(\sigma_2)] + \dots + \frac{(-\lambda)^n}{n!} \int_0^\beta d\sigma_1 \dots \int_0^{\sigma_{n-1}} d\sigma_n T [\tilde{H}'(\sigma_1) \dots \tilde{H}'(\sigma_n)] + \dots \quad (20)$$

with

$$\tilde{H}(\sigma) = e^{\sigma \hat{H}_0} \hat{H}' e^{-\sigma \hat{H}_0}, \quad (21)$$

the perturbation in the "interaction picture", and where T is the "time ordering operator."

We may now use Eqs. (19) and (20) and the well-known rule for the Wigner translation of an operator product to write

$$\hat{Q}_W(q, p; \beta) = \hat{Q}_W^{(0)}(q, p; \beta) e^{\hbar \lambda / 2i} [U(\beta, 0)]_W = \hat{Q}_W^{(0)} \left[1 - \lambda e^{\hbar \lambda / 2i} \int_0^\beta d\sigma [\tilde{H}'(\sigma)]_W + \dots \right]. \quad (22)$$

Since the perturbation \hat{H}' is a function of \hat{q} , we require $\tilde{q}(\sigma)$ for the evaluation of Eq. (22). The equation of motion for an operator $\tilde{O}(\sigma)$ in the interaction picture is

$$\frac{d\tilde{O}(\sigma)}{d\sigma} = [\hat{H}_0, \tilde{O}(\sigma)]. \quad (23)$$

For the important case where the unperturbed system is a harmonic oscillator

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2} m \omega_0^2 \hat{q}^2 \quad (24)$$

one readily finds, using Eq. (23), that

$$\tilde{q}(\sigma) = \hat{q} \cosh \sigma \hbar \omega_0 - \frac{\hat{p}}{m \omega_0} \sinh \sigma \hbar \omega_0 \quad (25)$$

while for the free particle case ($\omega_0 \rightarrow 0$)

$$\tilde{q}(\sigma) = \hat{q} - \frac{\hbar \sigma}{m} \hat{p}. \quad (26)$$

In these cases, assuming $\hat{H}'(\hat{q}) = \hat{q}^k$, it follows that

$$\tilde{H}'(\sigma) = \tilde{q}^k \equiv [a \hat{q} + b \hat{p}]^k \quad (27)$$

where a and b are given in Eqs. (25) or (26) for the appropriate case, and clearly are independent of \hat{q} and \hat{p} . The Wigner equivalent of this operator is found from the Weyl correspondence rule¹²

$$[e^{i\alpha(a\hat{q}+b\hat{p})}]_W = e^{i\alpha(aq+bp)}. \quad (28)$$

Expanding, and equating coefficients of α^n , we have

$$[(a\hat{q} + b\hat{p})^n]_W = (aq + bp)^n \quad (29)$$

so that

$$[\tilde{H}'(\sigma)]_W = (aq + bp)^k. \quad (30)$$

The Wigner distribution, Eq. (22), is now expressed in terms of c-number functions and classical phase space variables, although the remaining differentiations and integrations may be rather tedious. In Appendix A we work out the WDF to first order in λ for the quartic case, $k=4$.

In some applications the full details of the WDF are not required. For instance, in computing the phase space average of some function $F(q)$ we require:

$$\langle F(q) \rangle = \frac{\int dq \int dp [\hat{Q}_W^{(0)} e^{\hbar \lambda / 2i} [U(\beta, 0)]_W] F(q)}{\int dq \int dp \hat{Q}_W^{(0)} e^{\hbar \lambda / 2i} [U(\beta, 0)]_W}. \quad (31)$$

The numerator may be written

$$\sum_{n=0}^{\infty} \left(\frac{\hbar \lambda}{2i} \right)^n \frac{1}{n!} \sum_{s=0}^n (-1)^s \binom{n}{s} \int dq \int dp F(q) \quad (32)$$

$$\times \left(\frac{\partial^{n-s}}{\partial p^{n-s}} \frac{\partial^s}{\partial q^s} \hat{Q}_W^{(0)} \right) \left(\frac{\partial^{n-s}}{\partial q^{n-s}} \frac{\partial^s}{\partial p^s} [U(\beta, 0)]_W \right).$$

Integrating by parts, we have

$$\sum_{n=0}^{\infty} \left(\frac{\hbar \lambda}{2i} \right)^n \frac{1}{n!} \sum_{s=0}^n (-1)^s \binom{n}{s} \int dq \int dp \hat{Q}_W^{(0)} \times \frac{\partial^s}{\partial q^s} [F(q)] \frac{\partial^{n-s}}{\partial q^{n-s}} \frac{\partial^n}{\partial p^n} [U(\beta, 0)]_W = \sum_{n=0}^{\infty} \left(\frac{\hbar \lambda}{2i} \right)^n \frac{1}{n!} \sum_{s=0}^n (-1)^s \binom{n}{s} \sum_{r=0}^s \binom{s}{r} I_r, \quad (33)$$

where

$$I_r = \int dq dp \Omega_W^{(0)} \frac{\partial^r F}{\partial q^r} \frac{\partial^{n-r}}{\partial p^n} [U(\beta, \alpha)]_W \quad (34)$$

Note that

$$\sum_{s=0}^n (-1)^s \binom{n}{s} \sum_{r=0}^s \binom{s}{r} I_r$$

$$\sum_{r=0}^n I_r \sum_{s=r}^n (-1)^s \frac{n!}{(n-s)!(s-r)!r!}$$

$$= \sum_{r=0}^n (-1)^r \binom{n}{r} I_r \sum_{s=0}^{n-r} (-1)^s \binom{n-r}{s} \quad (35)$$

The second sum is zero unless $n=r$. Hence

$$\int dq dp \Omega_W^{(0)} e^{\beta H_W/2i} [U(\beta, \alpha)]_W F(q)$$

$$= \sum_{n=0}^{\infty} \left(\frac{\beta}{2i}\right)^n \frac{1}{n!} \int dq dp \Omega_W^{(0)} \frac{\partial^n F}{\partial q^n} \frac{\partial^n [U(\beta, \alpha)]_W}{\partial p^n} \quad (36)$$

The partition function is obtained by setting $F=1$ in Eq. (36):

$$Z(\beta) = (2\pi\hbar)^{-1} \int dq dp \Omega_W$$

$$= (2\pi\hbar)^{-1} \int dq dp \Omega_W^{(0)} [U(\beta, \alpha)]_W \quad (37)$$

IV. Application to Anharmonic Oscillators

We now illustrate the results of the preceding sections by computing the frequency shift and partition function of a one-dimensional anharmonic oscillator. H_0 is given by Eq. (24), so that^{3,4}

$$\Omega_W^{(0)} = \text{sech}(\beta\hbar\omega_0/2) \exp \left[-\frac{2}{\hbar\omega_0} \tanh \left(\frac{\beta\hbar\omega_0}{2} \right) H_0(q, p) \right] \quad (38)$$

We consider

$$H' = q^{2n} \quad (39)$$

(If H' is odd in q , the first order corrections vanish.) A quantity of great interest in the study of nonlinear oscillators is the frequency shift due to anharmonicity. We compute the first order frequency shift as follows. From Eq. (16) we have

$$J(s) = \langle q \frac{1}{s-iL_0} q \rangle_1 (1+\lambda) \frac{\langle q \frac{1}{s-iL_0} iL' \frac{1}{s-iL_0} q \rangle_0}{\langle q \frac{1}{s-iL_0} q \rangle_0}$$

$$+ O(\lambda^2). \quad (40)$$

Note that for H_0 given by Eq. (24), we have from Eq. (9) that

$$iL_0 = \frac{p}{m} \frac{\partial}{\partial q} - m\omega_0^2 q \frac{\partial}{\partial p} \quad (41)$$

so that

$$iL_0 q = \frac{p}{m} \quad (42)$$

and

$$iL_0 p = m\omega_0^2 q \quad (43)$$

Then

$$\frac{1}{s-iL_0} q = \frac{1}{s} \sum_{n=0}^{\infty} \left(\frac{iL_0}{s} \right)^n q$$

$$= \frac{1}{s} \left(\sum_{n=0}^{\infty} \left(\frac{\omega_0}{s} \right)^{2n} (-1)^n q + \sum_{n=0}^{\infty} \left(\frac{1}{s} \right)^{2n+1} \omega_0^{2n} (-1)^n \frac{p}{m} \right)$$

$$= q \frac{s}{s^2 + \omega_0^2} + \frac{p}{m} \frac{1}{s^2 + \omega_0^2} \quad (44)$$

i.e. just the Laplace transform of $q(t)$ for the initial conditions $q(0)=q$, $p(0)=p$. Thus, since $\langle qp \rangle = 0$,

$$\langle q \frac{1}{s-iL_0} q \rangle = \langle q^2 \rangle \frac{s}{s^2 + \omega_0^2} \quad (45)$$

Writing $H' = U(q)$, we have for the perturbing Liouvillian

$$iL' = -\frac{2}{\hbar} \sin \left(\frac{\hbar}{2} \frac{\partial}{\partial q} \frac{\partial}{\partial p} \right) U = -U' \frac{\partial}{\partial p} + \dots \quad (46)$$

where $U' = \partial U / \partial q$ and the subsequent terms involve higher (odd) p -derivatives. Using Eqs. (44) and (46) we have

$$\langle q \frac{1}{s-iL_0} iL' \frac{1}{s-iL_0} q \rangle = -\frac{1}{m} \frac{1}{s^2 + \omega_0^2} \langle q \frac{1}{s-iL_0} U' \rangle$$

$$= -\frac{1}{m} \frac{1}{s^2 + \omega_0^2} \langle U' \frac{1}{s+iL_0} q \rangle$$

$$= -\frac{1}{m} \frac{s}{(s^2 + \omega_0^2)^2} \langle U' q \rangle \quad (47)$$

The second line is obtained through an integration by parts and the third line by use of Eq. (44). Inserting this result in Eq. (40), and using Eq. (45), we have

$$J(s) = \langle q^2 \rangle_1 \frac{s}{s^2 + \omega_0^2} \left[1 - \frac{\lambda}{ms \langle q^2 \rangle_0} \langle q U'(q) \rangle_0 \right] + O(\lambda^2) \quad (48)$$

Note that

$$\langle q^{2n} \rangle_0 = \frac{\int dq dp \Omega_W^{(0)} q^{2n}}{\int dq dp \Omega_W^{(0)}} = \frac{(2n-1)!!}{(m\omega_0^2)^n} \quad (49)$$

where

$$A = \frac{2}{\hbar\omega_0} \tanh \frac{\beta\hbar\omega_0}{2} \quad (50)$$

Thus, for $U(q) = q^{2n}$,

$$J(s) = \langle q^2 \rangle_1 \frac{s}{s^2 + \omega_0^2} \left[1 - \frac{2n(2n-1)!!\lambda}{(s^2 + \omega_0^2)^n (m\omega_0^2 A)^{n-1}} \right] + O(\lambda^2) \quad (51)$$

Now, in the direct Laplace inversion of this expression, the term $-\lambda$ is secular

($\propto t \sin \omega t$). To avoid the appearance of a secular term, we interpret the correction term as leading to a renormalized frequency ω_R . That is, we write

$$J(s) = \langle q^2 \rangle_1 \frac{s}{s^2 + \omega_0^2} \frac{1}{1 + \frac{2n(2n-1)!!\lambda}{n(m\omega_0^2 A)^{n-1}(s^2 + \omega_0^2)}} + O(\lambda^2) \\ = \langle q^2 \rangle_1 \frac{s}{s^2 + \omega_R^2} + O(\lambda^2) \quad (52)$$

where

$$\omega_R^2 = \omega_0^2 + \frac{2n(2n-1)!!\lambda}{n(m\omega_0^2 A)^{n-1}} + O(\lambda^2) \quad (53)$$

The first-order frequency shift is thus

$$\Delta = \omega_R - \omega_0 = \frac{n(2n-1)!!\lambda}{m\omega_0} \left[\frac{\hbar}{2m\omega_0} \coth \frac{\beta\hbar\omega_0}{2} \right]^{n-1} \quad (54)$$

It should be noted that, whereas there are an infinite number of functions which reduce to first order to Eq. (51), the choice given in Eq. (52) is unique in the sense that it satisfies the demand that it has exactly the same form as the $\lambda=0$ result except that ω_0 is replaced by ω_R .

Secondly, it should be further emphasized that the technique we have outlined is not confined to the example shown. In all cases the secular term (which grows with increasing t no matter how small λ is) must be re-interpreted and, of course, this is physically reasonable since one expects that the frequencies associated with a particular motion will be changed when one superimposes an interaction. While we cannot give a general proof that frequency renormalization can always get rid of divergencies due to secular terms, we have not been able to find a contrary example.

Thirdly, the question might be asked as to whether it might be possible to modify the expansion in Eq. (16) so as to obtain the above results more directly. The answer is that a modification of Eq. (16) does not simplify the problem in general. The choice of absorbing the correction term in Eq. (51) into a renormalized frequency is analogous to the Poincaré-Lindstedt approach⁴ in nonlinear mechanics. In the latter method the frequency is chosen so as to avoid a secular term in the motion. In Appendix B we

show how Liouville perturbation theory may be used to reproduce the usual frequency correction for a nonlinear oscillator. The manipulations leading to Eq. (52) are also reminiscent of the introduction of the self energy in the Green's function method.^{1,2} In Appendix C we show that our result is in accord with the Green's function prediction.

Finally, we consider the first order correction to the partition function for the anharmonic oscillator. Combining Eq's (22), (25), (30), and (37), we have (with $k=2n$)

$$Z = (2n!)^{-1} \int dq dp \Omega_w^{(0)} (1-\lambda)^\beta \int d\alpha (a q + b p)^{2n} + O(\lambda^2) \\ = Z_0 - (2n!)^{-1} \lambda \int d\alpha \int dq dp \Omega_w^{(0)} (a q + b p)^{2n} + O(\lambda^2) \quad (55)$$

where $a = \cosh \beta\hbar\omega_0$, $b = -\frac{i}{m\omega_0} \sinh \beta\hbar\omega_0$, and

$$Z = [2 \sinh(\beta\hbar\omega_0/2)]^{-1} \quad (56)$$

Note that

$$(2n!)^{-1} \int dq dp \Omega_w^{(0)} (a q + b p)^{2n} \\ = Z_0 \sum_{s=0}^{2n} \binom{2n}{s} a^{2n-s} b^s \langle q^{2n-2s} p^{2s} \rangle_0 \\ = Z_0 \sum_{s=0}^n \binom{2n}{2s} a^{2(n-s)} b^{2s} \frac{(2(n-s)-1)!!}{(m\omega_0^2 A)^{n-s}} \frac{(2s-1)!!}{(A/m)^s} \\ = \frac{Z_0}{(m\omega_0^2 A)^n} \sum_{s=0}^n (-)^s \frac{(2n)!}{[2(n-s)]!(2s)!} \frac{[2(n-s)]!}{2^{n-s}(n-s)!} \\ \times \frac{(2s)!}{2^s s!} \cosh^{2(n-s)} \beta\hbar\omega_0 \sinh^{2s} \beta\hbar\omega_0 \\ = \frac{Z_0}{(m\omega_0^2 A)^n} \frac{(2n)!}{2^n n!} \sum_{s=0}^n (-)^s \binom{n}{s} \cosh^{2(n-s)} \beta\hbar\omega_0 \\ \times \sinh^{2s} \beta\hbar\omega_0 \\ = \frac{(2n-1)!! Z_0}{(m\omega_0^2 A)^n} \quad (57)$$

Then Eq. (55) becomes

$$Z = Z_0 \left[1 - \frac{\beta\lambda(2n-1)!!}{(m\omega_0^2 A)^n} + O(\lambda^2) \right] \quad (58)$$

The same result may be obtained via the Green's function approach, as shown in Appendix C.

Conclusions

The MDF has been shown to provide an alternative method for evaluating correlation functions, one which may in certain instances prove simpler than the Green's function approach. We have shown how to express the MDF, and the Laplace transform of the correlation

function, in powers of a perturbing potential, without resorting to an expansion in powers of \hbar . It is anticipated, by virtue of the fluctuation-dissipation theorem, that such results will also be useful for the investigation of transport properties. Explicit evaluation of the correction terms may be tedious, but for many applications the full details of the WDF are not required.

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Appendix A. Wigner Distribution for an Anharmonic Oscillator

We consider the Hamiltonian $\hat{H} = \hat{H}_0 + \lambda \hat{q}^4$ with \hat{H}_0 given by Eq. (24). From Eqs. (25) and (30) we have

$$[\hat{H}^{(1)}(\sigma)]_W = [q \cosh \sigma \hbar \omega_0 - \frac{i p}{m \omega_0} \sinh \sigma \hbar \omega_0]^4 \quad (A1)$$

According to Eq. (22) the first order correction to the WDF is

$$-\lambda \Omega_W^{(1)} e^{\hbar A / 2i} \int_0^\beta d\sigma [\hat{H}^{(1)}(\sigma)]_W \quad (A2)$$

with $\Omega_W^{(0)}$ given by Eq. (38). We note that

$$\begin{aligned} \Omega_W^{(0)} e^{\hbar A / 2i} q^4 &= q^4 \Omega_W^{(0)} - 2i \hbar q^3 \frac{\partial \Omega_W^{(0)}}{\partial p} - \frac{3}{2} \hbar^2 q^2 \frac{\partial^2 \Omega_W^{(0)}}{\partial p^2} \\ &+ \frac{i \hbar^3}{2} q \frac{\partial^3 \Omega_W^{(0)}}{\partial p^3} + \frac{\hbar^4}{16} \frac{\partial^4 \Omega_W^{(0)}}{\partial p^4} \end{aligned} \quad (A3)$$

and similar results for $\Omega_W^{(0)} e^{\hbar A / 2i} q^3, \dots$, etc. Substituting these results in Eq. (A2), evaluating the derivatives, performing the σ integration, and collecting terms, one eventually finds

$$\begin{aligned} \Omega_W &= \Omega_W^{(0)} \left[1 - \lambda \left(\frac{3\beta \hbar^4 A^2}{16m^2} - \frac{3\hbar^2}{4m^3 \omega_0^2} (A^2 - \frac{\beta A}{1+z^2}) p^2 \right) \right. \\ &+ \frac{3\hbar^2}{4m} (A^2 + \frac{\beta A}{1+z^2}) q^2 + \frac{1}{8} \left(A \frac{2z^2+5}{z^2+1} + \frac{3\beta}{(1+z^2)^2} \right) q^4 \\ &+ \frac{1}{8m^4 \omega_0^4} \left(A \frac{2z^2-3}{1+z^2} + \frac{3\beta}{(1+z^2)^2} \right) p^4 \\ &\left. - \frac{3}{4m^2 \omega_0^2} \left(A \frac{2z^2+1}{1+z^2} - \frac{\beta}{(1+z^2)^2} \right) q^2 p^2 \right] + O(\lambda^2), \end{aligned} \quad (A4)$$

where A is given by Eq. (50) and

$$z = \sinh \frac{\beta \hbar \omega_0}{2} \quad (A5)$$

As a check on our result, we compare it with the first order Wigner-Kirkwood expansion. Expanding Eq. (A4) to first order in \hbar^2 , we find

$$\begin{aligned} \Omega_W &= e^{-\beta H_0} \left[1 - \beta \lambda q^4 + \beta^2 \hbar^2 \left(\left(-\frac{3\omega_0 p^2}{24m} + \frac{\beta m \omega_0^4 q^2}{24} \right) \right. \right. \\ &\times \frac{\omega_0}{8} (1 - \beta \lambda q^4) \\ &\left. \left. - \lambda \left(\frac{3}{2m} q^2 - \frac{3\omega_0^2}{3} q^4 - \frac{\beta}{2m^2} q^2 p^2 \right) \right) \right] + O(\lambda \hbar^4) \end{aligned} \quad (A6)$$

which agrees, to first order in λ and \hbar^2 , with the result of the direct application of the Wigner-Kirkwood expansion.

Appendix B: Liouville Perturbation Theory for an Anharmonic Oscillator

Consider the classical system with Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 q^2 + \lambda q^4 \quad (B1)$$

The naive solution of the equation of motion

$$\frac{d^2 q}{dt^2} + \omega_0^2 q + \frac{4\lambda}{m} q^3 = 0 \quad (B2)$$

by successive approximations (i.e.

$q(t) = q^{(0)}(t) + \lambda q^{(1)}(t) + \lambda^2 q^{(2)}(t) + \dots$) generates a solution with secular terms. A well-behaved solution may be obtained by rearranging the terms, by defining a renormalized frequency ω_R so as to eliminate secular terms

(see Ref. (13) for details). The result, to first order in λ , for the initial condition $q(t=0) = q_0, p(t=0) = 0$ is

$$q(t) = \left(q_0 - \frac{\lambda q_0^3}{8m\omega_0^2} \right) \cos \omega_R t + \frac{\lambda q_0^3}{8m\omega_0^2} \cos 3\omega_R t \quad (B3)$$

where

$$\omega_R = \omega_0 + \frac{3q_0^2 \lambda}{2m\omega_0} + O(\lambda^2) \quad (B4)$$

We now show how this result may be obtained in a manner analogous to the approach of Section IV.

For any phase space function $F(q,p)$ we have

$$F(q(t), p(t)) = e^{iLt} F(q,p) \Big|_{\substack{q=q_0 \\ p=p_0}} \quad (B5)$$

where

$$\begin{aligned} iL &= \frac{p}{m} \frac{\partial}{\partial q} - \frac{\partial V}{\partial q} \frac{\partial}{\partial p} \\ &= \frac{p}{m} \frac{\partial}{\partial q} - m\omega_0^2 q \frac{\partial}{\partial p} - 4\lambda q^3 \frac{\partial}{\partial p} \\ &= iL_0 + i\lambda L' \end{aligned} \quad (B6)$$

For the initial conditions q_0, p_0 , we have

$$\begin{aligned} \int_0^\infty e^{-st} q(t) dt &= \int_0^\infty dt e^{-st} e^{iLt} q \Big|_{\substack{q=q_0 \\ p=p_0}} \\ &= \frac{1}{s-iL} q \Big|_{\substack{q=q_0 \\ p=p_0}} \end{aligned} \quad (B7)$$

Using Eq's (14) and (44), we have, for $p_0 = 0$

$$\frac{1}{s-iL} q = \frac{1}{s-iL_0} q + \frac{1}{s-iL_0} i\lambda L' \frac{1}{s-iL_0} q + O(\lambda^2)$$

$$= q \frac{s}{s^2+\omega_0^2} - \frac{4\lambda}{m} \frac{1}{s^2+\omega_0^2} \frac{1}{s-iL_0} q^3 + O(\lambda^2) \quad (B8)$$

Now $\frac{1}{s-iL_0} q^3$ is just the Laplace transform of $q^3(t)$, where $q(t)$ is the unperturbed harmonic oscillator solution for $q_0(t=0)=q_0$, $\dot{p}(t=0)=0$, i.e.

$$\frac{1}{s-iL_0} q^3 = \int_0^\infty dt e^{-st} q^3(t) \cos^3 \omega_0 t$$

$$= \frac{q_0^3}{4} \left\{ \frac{s}{s^2+\omega_0^2} + \frac{3s}{s^2+9\omega_0^2} \right\} \quad (B9)$$

Hence

$$\frac{1}{s-iL} q = q_0 \frac{s}{s^2+\omega_0^2} \left[1 - \frac{\lambda q_0^2}{m} \left\{ \frac{3}{s^2+\omega_0^2} + \frac{1}{s^2+9\omega_0^2} \right\} \right] + O(\lambda^2) \quad (B10)$$

According to Eq. (B7), $q(t)$ is given by the inverse transform of Eq. (B10). However, the inverse transform of the term $\sim \lambda$ is secular, having a contribution proportional to $t \sin \omega_0 t$. We therefore attempt to write the RHS of Eq. (B10) in the form

$$(q_0 - \lambda \alpha) \frac{s}{s^2+\omega_R^2} + \lambda \alpha \frac{s}{s^2+9\omega_R^2} + O(\lambda^2) \quad (B11)$$

where $\omega_R^2 = \omega_0^2 + \zeta$.

$$\omega_R^2 = \omega_0^2 + \zeta \quad (B12)$$

Substituting this in Eq. (B11), and equating real and imaginary coefficients of λ , we find

$$\zeta = \frac{3q_0^2}{m} \quad (B13)$$

and

$$a = \frac{q_0^3}{3m\omega_0^2} \quad (B14)$$

which, combined with Eq's. (B11) and (B12), yields the first order solution, Eq. (B3).

Appendix C. Green's Function for Anharmonic Oscillator

A natural object for study in this case is the Fourier transform of the correlation

$$B(\omega) = \int dt e^{i\omega t} \langle \hat{q}(t) \hat{q}(0) \rangle \quad (C1)$$

If we define the temperature Green's function

$$G(u) = \langle T \hat{q}(u) \hat{q}(0) \rangle \quad (C2)$$

then

$$B(\omega) = \frac{2\pi\beta\hbar}{1-e^{-\beta\hbar\omega}} \lim_{\epsilon \rightarrow 0^+} \frac{a(\omega+i\epsilon) - a(\omega-i\epsilon)}{2\pi i} \quad (C3)$$

where $a(\omega)$ is obtained by analytical continuation ($2\pi i/2\beta\hbar + \omega$) of

$$a_\lambda = \frac{1}{\beta} \int_0^\beta G(u) e^{-2\pi i \omega u/\beta} du \quad (C4)$$

The Green's function has the well-known expansion

$$G(u) = \sum_{n=0}^\infty \frac{(-1)^n}{n!} \int_0^\beta d\sigma_1 \dots \int_0^\beta d\sigma_n \langle T \tilde{q}(n) \tilde{q}(0) \tilde{H}'(\sigma_1) \dots \tilde{H}'(\sigma_n) \rangle_{0,c}$$

$$(C5)$$

where

$$\langle \hat{O} \rangle_0 = Z_0^{-1} \text{Tr} [e^{-\beta \hat{H}_0} \hat{O}] \quad (C6)$$

and the subscript "c" indicates that only connected terms in the Wick expansion are retained. To evaluate Eq. (C5) via Wick's theorem, we require

$$g(u) = \langle T \tilde{q}(u) \tilde{q}(0) \rangle_0 \quad (C7)$$

A short calculation reveals that

$$g(u) = \frac{\hbar}{2m\omega_0} \left[\bar{n} e^{|u|\hbar\omega_0} + (\bar{n}+1) e^{-|u|\hbar\omega_0} \right] \quad (C8)$$

where

$$\bar{n} = \frac{1}{e^{\beta\hbar\omega_0} - 1} \quad (C9)$$

$$g(0) = \frac{\hbar}{2m\omega_0} \coth \frac{\beta\hbar\omega_0}{2} \quad (C10)$$

The Fourier components are given by

$$a_\lambda(0) = \frac{1}{\beta} \int_0^\beta du e^{-2\pi i \lambda u/\beta} g(u) = \frac{1}{\beta m(\omega_0^2 + \omega_\lambda^2)} \quad (C11)$$

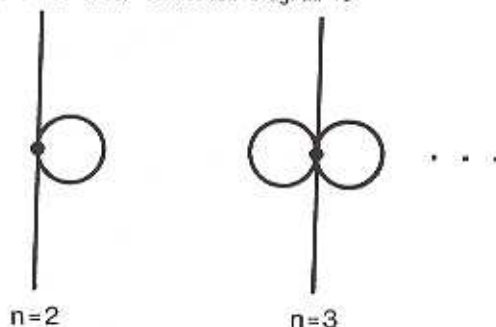
where

$$\omega_\lambda = 2\pi\lambda/\beta\hbar \quad (C12)$$

If $\hat{H}' = \lambda \hat{q}^{2n}$ then

$$G(u) = g(u) - \lambda \int_0^\beta d\sigma \langle T \tilde{q}(u) \tilde{q}(0) [\tilde{q}(\sigma)]^{2n} \rangle_0 + O(\lambda^2) \quad (C13)$$

The first order connected diagram is



i.e. two of the $\tilde{q}(o)$'s are contracted with the external lines, and the remaining $2(n-1)$ are paired off together. There are $2n(2n-1)$ ways of

pairing the operators in \tilde{H}' with the external lines, and the remaining operators may be paired in

$$\frac{(2n-2)!}{2^{n-1}(n-1)!} = (2n-3)!!$$

ways. Hence

$$\langle T \tilde{q}(u) \tilde{q}(o) [\tilde{q}(o)]^{2n} \rangle_{o,c}$$

$$= 2n(2n-1)!! g(u-o)g(o) [g(o)]^{n-1}, \quad (C14)$$

and

$$\int_0^{\beta} d\sigma \langle T \tilde{q}(u) \tilde{q}(o) [\tilde{q}(o)]^{2n} \rangle_{o,c}$$

$$= 2n(2n-1)!! \int_0^{\beta} d\sigma e^{2\pi i \lambda u / \beta} a_{\lambda}^{(o)} [g(o)]^{n-1} a_{\lambda}^{(o)}, \quad (C15)$$

Thus, to first order in λ , the Fourier component of G is

$$a_{\lambda} = a_{\lambda}^{(o)} - 2n(2n-1)!! \beta \lambda a_{\lambda}^{(o)} [g(o)]^{n-1} a_{\lambda}^{(o)}, \quad (C16)$$

and the self-energy, defined through

$$a_{\lambda} = [(a_{\lambda}^{(o)})^{-1} - \Sigma_{\lambda}]^{-1}$$

$$\Sigma_{\lambda} = -2n(2n-1)!! \beta \lambda [g^{(o)}]^{n-1} + O(\lambda^2) \quad (C17)$$

Now performing the analytic continuation $i\omega_{\lambda} \rightarrow \omega$, we have

$$a(\omega) = \frac{1}{2m\omega_0\beta} \left[\frac{1}{\omega + i\omega_0 - \varepsilon/2\beta m\omega_0} - \frac{1}{\omega - (i\omega_0 - \varepsilon/2\beta m\omega_0)} \right] + O(\lambda^2), \quad (C18)$$

The first order frequency shift is then

$$\Delta = -\frac{\Sigma}{2\beta m\omega_0} = \frac{2n(2n-1)!!}{m\omega_0} \left[\frac{\hbar}{2m\omega_0} \coth \frac{\beta\hbar\omega_0}{2} \right]^{n-1}, \quad (C19)$$

in accord with the WDF result, Eq. (54).

The first order correction to the partition function is found as follows. We have, from Eq. (19),

$$Z = \text{Tr} [e^{-\beta \hat{H}} U(\beta, 0)]$$

$$= Z_0 [1 - \lambda \int_0^{\beta} d\sigma \langle \tilde{H}'(\sigma) \rangle_0 + O(\lambda^2)] \quad (C20)$$

The Wick expansion of $\langle [\tilde{q}(o)]^{2n} \rangle_0$ yields the diagram



$n=2$

$n=3$

(n loops). There are $(2n-1)!!$ distinct pairings. Thus

$$\int_0^{\beta} d\sigma \langle \tilde{H}'(\sigma) \rangle_0 = (2n-1)!! \beta \lambda [g(o)]^n = \frac{(2n-1)!! \beta \lambda}{(m\omega_0^2 \lambda)^n}, \quad (C21)$$

so that

$$Z = Z_0 (1 - \beta \lambda \frac{(2n-1)!!}{(m\omega_0^2 \lambda)^n} + O(\lambda^2)) \quad (C22)$$

in agreement with Eq. (58).

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