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Quantum Fokker–Planck equation for interacting waves

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Contents

The quantum Fokker–Planck equation for the irreversible evolution of a bath of interacting oscillators is derived with sufficient generality that both the action and angle dependence of the distribution function are maintained in the classical limit. This approach unifies Landau–Rumer processes, spontaneous phonon decay, quantum renormalization of the speed of sound, and quantum wave turbulence.

1. Introduction

Physical manifestations of the interaction between propagating waves span the classical and quantum domains. In the classical limit off-equilibrium waves interact so as to create self-similar power spectra analogous to the Kolmogorov spectrum of vortex

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turbulence. Examples are the spectrum of surface waves in a stormy sea and Alfvén waves in the solar wind. In the quantum limit a propagating wave can decay due to its interaction with a thermally excited background (Landau–Rumer processes) and for certain dispersion laws a wave can decay due to scattering from zero point motion (Slonimskii processes).

The description of these effects is generally presented in terms of a kinetic or Boltzmann type of equation for the time development of the spectral density of the excitations. In the classical limit these equations describe the dynamics of the wave action which is a function of the wave number of the interacting waves. In the quantum limit the quantity of interest is the occupation number of the given mode which corresponds to the classical action divided by Planck's constant. Since these kinetic equations determine the dynamics of the power spectrum they are limited to the square correlations of the amplitude. Higher order correlations and related effects such as intermittency and skewness are not contained in these kinetic equations. They have been swept away by some strong closure assumption such as the Stosszahl ansatz. A theory which can form the basis for an insight into these issues must start from the complete probability distribution for the interacting waves and not just from the second moment (or first moment as regards the action).

Our goal in this paper is to take a step towards developing a theory which spans quantum and classical nonlinear waves both in the turbulent and equilibrium limits and which furthermore includes independent motion for the higher moments. In this direction we develop a quantum theory of interacting waves at the Fokker–Planck level. We present no advances regarding turbulent skewness of the distribution but we do derive equations whose solutions would address the issue. At present the solutions which do exist pertain to the renormalization of the speed and attenuation of sound in a dielectric near a temperature of zero degrees and to classical equipartition and wave turbulent power spectra. The purely classical limit of the Fokker–Planck equation for interacting waves has already been published by Putterman & Roberts (1988; herein referred to as PR).

It is important to distinguish between Kolmogorov turbulence for vortex type motion and the issues of interacting propagating waves which we address in this paper. For Kolmogorov turbulence there does not exist a closed kinetic or Fokker–Planck equation. But as we shall see the case of interacting waves admits a multiple timescales approximation which leads to closure at least at the Fokker–Planck level.

The Fokker–Planck equation which we present is both closed and irreversible. Since it follows from a Hamiltonian theory of interacting waves the irreversibility must arise from some approximation. This assumption can be elucidated by considering the outline of this paper. We start from a Hamiltonian for a system which can support a three phonon (i.e. three wave) interaction. For such a system the Hamiltonian takes the general form,

$$\boldsymbol{H} = \sum_i \omega_i I_i + 8\epsilon \sum_{ijk} c_{ijk} \sqrt{I_i I_j I_k} \cos\theta_i \cos\theta_j \cos\theta_k \qquad (1.1)$$

where the ω_i are the frequencies of the interacting modes with action I_i and angle θ_i and the ϵc_{ijk} are weak coupling coefficients for the nonlinear interaction. The classical description of the motion was sought in terms of the probability distribution $P(\boldsymbol{I}, \boldsymbol{\theta}, t)$ for all the degrees of freedom. The quantum description is sought in terms of a density operator,

$$\hat{\rho}(t) = \sum_{\boldsymbol{mn}} |\boldsymbol{m}\rangle\, \rho_{\boldsymbol{mn}}(t) \langle \boldsymbol{n}|. \tag{1.2}$$

The time development is determined by the quantum mechanical von Neumann equation,

$$\frac{\partial \rho_{\boldsymbol{mn}}}{\partial t} = \frac{\mathrm{i}}{\hbar}\,[\hat{\rho}, \boldsymbol{H}]_{\boldsymbol{mn}} = \frac{\mathrm{i}}{\hbar} \sum_{\boldsymbol{p}} \left[\rho_{\boldsymbol{mp}} \boldsymbol{H}_{\boldsymbol{pn}} - \boldsymbol{H}_{\boldsymbol{mp}} \rho_{\boldsymbol{pn}}\right], \tag{1.3}$$

which is also called the quantum Liouville equation. We will solve this equation to second order in ϵ through a multiple timescale analysis.

In § 3, we discuss the transition from this Liouville theory, which describes the motion of a finite number $\mathcal{N}$ of degrees of freedom, to a continuous ($\mathcal{N} \to \infty$) system described by the irreversible Fokker–Planck equation. The irreversibility arises formally because $\mathrm{d}\hat{\rho}/\mathrm{d}t$ is given by an integral over ω that involves $(\mathrm{e}^{\mathrm{i}\omega t} - 1)/\mathrm{i}\omega$. By the method of stationary phase the effect of this term in the integrand in the limit $t \to \infty$ is identical to that resulting from the transformation,

$$\Delta^{\pm}(\omega) = \frac{e^{\pm \mathrm{i}\omega t} - 1}{\pm \mathrm{i}\omega} \to \pi\delta^{\pm}(\omega) = \pi\delta(\omega) \pm \mathcal{P}\left(\frac{1}{\omega}\right), \tag{1.4}$$

where δ is the Dirac delta function and $\mathcal{P}$ is the principal-value part of the integral over ω, see for example Benney & Newell (1969). When the limit (1.4) is imposed the resulting autonomous equations for $\partial\hat{\rho}/\partial t$ have the property that for a closed system they drive $\rho_{\boldsymbol{mn}}$ to the quantum microcanonical distribution, see § 3 *f*. The restrictions that must be obeyed before (1.4) can be applied are formally similar to the purely classical case. Namely, there should be many modes within a bandwidth $B(\omega)$ that determines the rate of change of $\rho_{\boldsymbol{mn}}$, or

$$\frac{1}{\sigma(\omega)} \ll B(\omega) \ll \omega, \tag{1.5}$$

where $\sigma(\omega)$ is the density of states. The requirement $B(\omega) \ll \omega$ has been added to (1.5) to ensure that ϵ is small enough for the perturbation expansion to be valid. In contrast to the classical problem, the quantum system is characterized by an additional independent timescale at the ϵ^2 level. It appears when the indices on $\rho_{\boldsymbol{mn}}$ correspond to far off-diagonal motions. If we introduce the Fourier mode and average action variables,

$$M_i = n_i - m_i, \tag{1.6}$$

$$N_i = \frac{n_i + m_i + 1}{2} = \frac{1}{\hbar} I_i, \tag{1.7}$$

then the new timescale is (for $M_i/N_i = \mathcal{O}(1)$)

$$B(\omega) \approx \epsilon^2 c^2 \hbar N^3 \approx \epsilon^2 c^2 I^3/\hbar^2. \tag{1.8}$$

The classical timescales apply to diffusion in action and angle space and are respectively

$$B(\omega) = \epsilon^2 c^2 \sigma I^3/\mathcal{I}^2, \tag{1.9}$$

$$B(\omega) = \epsilon^2 c^2 \sigma I M^2, \tag{1.10}$$

where I, c, N, and M are characteristic values of action, c_{ijk}, N_i, and M_i respectively, and $\mathcal{I}$ characterizes the range in action over which the probability changes. Finally the irreversible limit requires that $\rho_{\boldsymbol{mn}}$ be smooth in n_i and m_i as i varies.

The quantum timescale (1.8) can be much shorter than the corresponding classical timescale (1.10) because the classical limit corresponds to $M_i/N_i \ll 1$ or, equivalently, $\hbar M_i/I_i \ll 1$. A new procedure which shows that the classical Fokker–Planck equation follows in this limit is described in § 4 where the relation,

$$P_{\boldsymbol{M}}(\boldsymbol{I}, t) = \rho_{\boldsymbol{mn}}(t), \tag{1.11}$$

is obtained for the Fourier transform of the classical probability distrubution. This expression allows us to recover the full classical angle dependence when we take the classical limit $\hbar \to 0$, expand the classical distribution as

$$P(\boldsymbol{I}, \boldsymbol{\theta}, t) = \frac{1}{(2\pi)^{\mathcal{N}}} \sum_{\boldsymbol{M}} P_{\boldsymbol{M}}(\boldsymbol{I}, t) \mathrm{e}^{-\mathrm{i}\boldsymbol{M}\cdot\boldsymbol{\theta}}, \tag{1.12}$$

and eliminate the restrictions on the series in this equation. Here, $\mathcal{N}$ is the number of oscillators.

In §§ 3 *c*, *d* the quantum kinetic equation for interacting phonons is derived at the level of the Boltzmann equation. We find that the rate of change of the average action is given by

$$\begin{aligned}\frac{\mathrm{d}\langle N_p \rangle}{\mathrm{d}t} = 18\pi\epsilon^2\hbar \sum_{\substack{jk \\ s_p s_j s_k}} & c^2_{pjk} \delta(s_p\omega_p + s_j\omega_j + s_k\omega_k) s_p \\ & \times [s_p \langle N_j + \tfrac{1}{2}\rangle\langle N_k + \tfrac{1}{2}\rangle + s_j \langle N_p + \tfrac{1}{2}\rangle\langle N_k + \tfrac{1}{2}\rangle \\ & + s_k \langle N_p + \tfrac{1}{2}\rangle\langle N_j + \tfrac{1}{2}\rangle + \tfrac{1}{4} s_p s_j s_k],\end{aligned} \tag{1.13}$$

where $\sum_{jk}$ is an integral over the j and k indices and s_p, s_j, and s_k are summed over $+1$ and -1. This kinetic equation for interacting waves spans both the classical and quantum mechanical domains. Simulations to far off-equilibrium solutions to this equation are given by Haeri *et al.* (1993). To arrive at this closed kinetic equation the Stosszahl ansatz $\langle N_j N_k \rangle = \langle N_j \rangle \langle N_k \rangle$ must be imposed. This equation is identical to the three phonon kinetic equation (see, for example, Landau & Khalatnikov (1949*a*, *b*). It leads to the Planck distribution in equilibrium, to Landau–Rumer (Landau & Rumer 1937) and Slonimskii (1937) processes near equilibrium, and to classical and quantum wave turbulence off-equilibrium. At $T = 0$ K the quantum effects determine the attenuation of sound and equation (1.13) yields the rate of decay of the pth oscillator as being

$$\frac{\mathrm{d}\langle N_p \rangle}{\mathrm{d}t} = -36\pi\epsilon^2\hbar \left[\sum_{jk} c^2_{pjk} \delta(\omega_p - \omega_j - \omega_k) \right] \langle N_p \rangle. \tag{1.14}$$

This equation generalizes the Slonimskii result to a distribution of nonlinear interacting oscillators.

In § 5 the Fokker–Planck equation is used to calculate the renormalization of the frequencies due to nonlinear processes. This effect follows from the weak off-diagonal nature of the equilibrium density matrix or equivalently the small angle dependent terms of the probability distribution. In previous approaches such as Prigogine & Henin (1960) and Sagdeev *et al.* (1988) the irreversibility arose from either a random phase approximation or a weak-angle-dependence assumption for the initial conditions which was tied to the elimination of angle dependence from the Fokker–Planck equation. No such approximations or assumptions are needed or made in this work. In § 6 the renormalized frequency is used to calculate the shift in frequency of sound waves in low and high temperature systems for the case of small dispersion (see, for example, Khalatnikov 1965). Because the inverse temperature β and frequency ω_k appear in the combination $\beta\hbar\omega_k$, the low and high temperature limits are equivalent to high and low frequencies respectively. For low temperatures, $\beta\hbar\omega_k \gg 1$, we find

$$\Delta\omega_k \sim \frac{G^2 U\omega_k}{\rho v^2}\ln\left(\frac{1}{3.88}\frac{k_\gamma}{k}\right) + \mathcal{O}\left(\gamma + \frac{1}{(\beta\hbar v k)^2}\right), \tag{1.15}$$

where v is the speed of sound, $\beta = 1/k_{\mathrm{B}}T$, $k_\gamma = v/\gamma^{1/2}$ where γ is the coefficient of dispersion of sound, U is the total thermal energy density, ρ is the fluid density, the nonlinear Grüneison coefficient for a fluid is

$$G = 1 + \frac{\rho}{v}\frac{\partial v}{\partial \rho}, \tag{1.16}$$

and $\omega_k = vk$. For high temperatures, $\beta\hbar\omega_k \ll 1$, the frequency shift is

$$\Delta\omega_k \sim \frac{G^2 U\omega_k}{\rho v^2}\ln\left(\frac{1}{13.7}\frac{k_\gamma}{k_T}\right) + \mathcal{O}\Big(\gamma + (\beta\hbar v k)^2\Big), \tag{1.17}$$

where $k_T = 1/\beta\hbar v$. In the calculation of the nonlinear modification of the natural frequencies an infinite contribution appears. It arises from the coupling of the zero point motion to the various degrees of freedom. In § 6 *a* we discuss a means whereby this singularity can be removed by redefining the physical frequencies to include this infinite correction. This is accomplished by the introduction of a modified Hamiltonian that enables the entire Fokker–Planck development to be carried out in terms of the actual physical frequency as defined at zero temperature. Because the Planck distribution has better convergence properties than the classical Bose distribution obtained in PR, no bounded energy argument was needed here to approximate the integrals for the frequency shifts.

The extended Fokker–Planck equation developed in this paper was motivated by the goal that it should span physical processes ranging from near equilibrium to turbulence. For this reason we have endeavored to generate a theory which includes not only the off-diagonal components of the density matrix, but also many degrees of freedom. The off-diagonal terms become phases or angles in the classical limit, and are therefore essential to far off-equilibrium phenomena such as turbulence where wave motion renormalizes the dynamical variables. By retaining the off-diagonal terms, our Fokker–Planck equation becomes different from various versions of the so-called ‘master equation’ (see Zwanzig 1960, 1964). The extension of the Fokker–Planck equation to include many degrees of freedom puts this theory into a form where it can be applied to the heat bath and so describe the approach of the heat bath to either an equilibrium or an off-equilibrium steady state. In this sense our analysis should be contrasted with approaches such as those of Risken (1984) aimed at studying the motion of a single degree of freedom which becomes irreversible after tracing out the heat bath and it should be contrasted with approaches such as those of Grabert (1988) and Leggett *et al.* (1987) which study the irreversibility of a single oscillator in contact with a heat bath at equilibrium. Again turbulence requires a stochastic description with many degrees of freedom. And in fact we are also interested in probing the physical issues relevant to the attainment of equilibrium by the heat bath itself as opposed to studying the decay of a single oscillator in contact with an equilibrium heat bath.

As we are dealing with second order difference equations, which are a generalization of second order differential equations, and motivated by the way de Groot & Mazur (1969) use the term, we have referred to our theory as falling into the category of Fokker–Planck equations. The quantum optics literature, as exemplified by Meystre & Sargent (1990), would refer to this second order difference equation as a master equation, but, as mentioned by Van Kampen (1981), the precise nomenclature is subject to some argument.

In addition to formulating an approach that might be useful in attacking issues related to turbulence at the interface of classical and quantum mechanics we hope that these procedures may in the future be generalized to encompass kinetic equations at order ϵ^4 as well as to include interacting systems where $\partial\omega_i/\partial I_i$ is not small or indeed vanishing.

This analysis is expounded upon in more detail in Sinclair (1992).

2. Quantum mechanical problem and notation

The Hamiltonian studied in PR was motivated by the classical analysis of the angle-dependent nonlinear interaction of sound waves. The time evolution of the corresponding nondiagonal quantum-mechanical probability density operator is developed in this section.

First, the index notation in PR is extended to the quantum mechanical formulation. In particular, the signs in PR become designations for the creation and destruction operators. After developing this notation, the problem is converted from the Heisenberg form to the interaction form. This eliminates the free Hamiltonian by incorporating time-dependent oscillations into the coefficients of the interaction Hamiltonian. Finally, we list some useful formulas, after which we will be ready to derive the master equation and its properties.

The Hamiltonian discussed in PR has the form

$$\boldsymbol{H} = \boldsymbol{H}_0 + \epsilon \boldsymbol{H}_1, \tag{2.1}$$

where the free Hamiltonian

$$\boldsymbol{H}_0 = \sum_i \omega_i I_i \tag{2.2}$$

is a bath of $\mathcal{N}$ non-interacting linear oscillators with frequencies $\omega_i > 0$ and the non-separable interaction Hamiltonian

$$\boldsymbol{H}_1 = 8 \sum_{ijk} c_{ijk} \sqrt{I_i I_j I_k} \cos\theta_i \cos\theta_j \cos\theta_k \tag{2.3}$$

models the cubic interaction of sound waves through the inertial terms of the Navier–Stokes equations, the convective term in the energy equation, and the internal energy corrections. The coupling coefficient c_{ijk} determines the relative strength of interactions between triplets of waves i, j, and k. It is symmetric with respect to its indices and is zero if an index is repeated. The fact that the interaction between the sound waves is weak is represented by $\epsilon \ll 1$ and the c_{ijk} are regarded as being $\mathcal{O}(1)$. More specifically, ϵ is taken to be dimensionless and c_{ijk} is required to be $\mathcal{O}(\omega/I^{1/2})$ where ω is a typical frequency and I is a typical action so that $\boldsymbol{H}_1$ is $\mathcal{O}(1)$.

Using standard techniques to convert the classical Hamiltonian to quantum mechanical form, the free and interaction Hamiltonians become

$$\boldsymbol{H}_0 = \frac{1}{2}\hbar \sum_i \omega_i (q_i^\dagger q_i + q_i q_i^\dagger) \tag{2.4}$$

and

$$\boldsymbol{H}_1 = \hbar^{3/2} \sum_{ijk} c_{ijk} (q_i^\dagger + q_i)(q_j^\dagger + q_j)(q_k^\dagger + q_k) \tag{2.5}$$

respectively. The quantum-mechanical creation and destruction operators, $q_i^\dagger$ and q_i respectively, obey the usual commutation rules: $[q_i, q_j^\dagger] = \delta_{ij}$ and $[q_i, q_j] = [q_i^\dagger, q_j^\dagger] = 0$.

When $\boldsymbol{H}$ is applied to an eigenstate $|\boldsymbol{n}\rangle$ of $\boldsymbol{H}_0$ to evaluate the von Neumann equation (1.3), the result is complicated because of the summand in equation (2.5). A more compact notation is achieved by associating the sign $+1$ with creation operators and the sign -1 with destruction operators. The Fock space index i and its associated sign s_i are then combined in a single symbol $I = (i, s_i)$. We now define

$$q_I = \begin{cases} q_i^\dagger & \text{if } s_i = +1 \\ q_i & \text{if } s_i = -1 \end{cases} \tag{2.6}$$

and

$$n_I = n_i + \tfrac{1}{2}(1 + s_i), \tag{2.7}$$

where n_i is an occupation number. The effects of the creation and destruction operators can now be written more succinctly as

$$q_I |\boldsymbol{n}\rangle = \sqrt{n_I} |\boldsymbol{n} + \boldsymbol{e}_I\rangle \tag{2.8}$$

where $\boldsymbol{e}_I = s_i \boldsymbol{e}_i$ is a vector of zeroes except for the ith element which has value s_i and the commutation relation becomes $[q_I, q_J] = -s_i \delta_{I,-J}$. With this notation, the expressions for the free and interaction Hamiltonians become much shorter:

$$\boldsymbol{H}_0 = \frac{1}{2}\hbar \sum_I \omega_i q_I q_{-I} \tag{2.9}$$

and

$$\boldsymbol{H}_1 = \hbar^{3/2} \sum_{IJK} c_{ijk} q_I q_J q_K, \tag{2.10}$$

where $\sum_I = \sum_i \sum_{s_i = \pm 1}$, $-I = (i, -s_i)$, $J = (j, s_j)$, and $K = (k, s_k)$. We also define

$$X_{IJK} = s_i X_i + s_j X_j + s_k X_k \tag{2.11}$$

where X_i can be $\boldsymbol{e}_i, \theta_i, \omega_i, \ldots$, but not an occupation index such as n_i or m_i. Instead, we define

$$n_{IJK} = n_I n_J n_K \tag{2.12}$$

for occupation indices.

The von Neumann equation for this Hamiltonian system can now be written in the following relatively compact form:

$$\begin{aligned} \frac{\partial \rho_{\boldsymbol{mn}}}{\partial t} &= \mathrm{i}\boldsymbol{\omega} \cdot (\boldsymbol{n} - \boldsymbol{m}) \rho_{\boldsymbol{mn}} \\ &\quad + \epsilon \mathrm{i} \hbar^{1/2} \sum_{IJK} c_{ijk} \left(\sqrt{n_{IJK}} \rho_{\boldsymbol{m}, \boldsymbol{n} + \boldsymbol{e}_{IJK}} - \sqrt{m_{-I-J-K}} \rho_{\boldsymbol{m} - \boldsymbol{e}_{IJK}, \boldsymbol{n}} \right). \end{aligned} \tag{2.13}$$

Note that, although $\rho_{\boldsymbol{m},\boldsymbol{n}+\boldsymbol{e}_{IJK}}$ and $\rho_{\boldsymbol{m}-\boldsymbol{e}_{IJK},\boldsymbol{n}}$ may have negative subscripts when an element of $\boldsymbol{m}$ or $\boldsymbol{n}$ is zero, the corresponding coefficient will be zero. For example, if $n_i = 0$ and $s_i = -1$, then $\boldsymbol{n} + \boldsymbol{e}_{IJK}$ will have -1 as its ith component. However, $n_I = 0$ in that case so that $\sqrt{n_{IJK}} = 0$ and the problematic term with negative indices is excluded by its zero coefficient.

The $\mathcal{O}(1)$ term in equation (2.13) involving the free Hamiltonian is removed by defining the interaction picture density operator $\hat{\alpha}$ by

$$\hat{\alpha} = \mathrm{e}^{\mathrm{i}\boldsymbol{H}_0 t/\hbar}\hat{\rho}\mathrm{e}^{-\mathrm{i}\boldsymbol{H}_0 t/\hbar} = \mathrm{e}^{\mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{N}t}\hat{\rho}\mathrm{e}^{-\mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{N}t}, \tag{2.14}$$

where $\boldsymbol{N}$ is the vector of counting operators N_i. Then

$$\alpha_{\boldsymbol{mn}} = \mathrm{e}^{\mathrm{i}\boldsymbol{\omega}\cdot(\boldsymbol{m}-\boldsymbol{n})t}\rho_{\boldsymbol{mn}} \tag{2.15}$$

and

$$\frac{\partial\hat{\alpha}}{\partial t} = \epsilon\frac{\mathrm{i}}{\hbar}[\hat{\alpha}, \mathrm{e}^{\mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{N}t}\boldsymbol{H}_1\mathrm{e}^{-\mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{N}t}]. \tag{2.16}$$

We expand the modified density operator and let each term depend on a hierarchy of timescales,

$$\hat{\alpha}(t;\epsilon) = \hat{\alpha}_0(\tau_0,\tau_1,\tau_2) + \epsilon\hat{\alpha}_1(\tau_0,\tau_1,\tau_2) + \epsilon^2\hat{\alpha}_2(\tau_0,\tau_1,\tau_2) + \dots, \tag{2.17}$$

where $\tau_i = \epsilon^i t$. Substituting this multiple scales expansion into the equation of motion and collecting coefficients of powers of ϵ to second order yields the three equations of motion,

$$\frac{\partial\hat{\alpha}_0}{\partial\tau_0} = 0, \tag{2.18}$$

$$\frac{\partial\hat{\alpha}_0}{\partial\tau_1} + \frac{\partial\hat{\alpha}_1}{\partial\tau_0} = \frac{\mathrm{i}}{\hbar}[\hat{\alpha}_0, \mathrm{e}^{\mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{N}t}\boldsymbol{H}_1\mathrm{e}^{-\mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{N}t}], \tag{2.19}$$

$$\frac{\partial\hat{\alpha}_0}{\partial\tau_2} + \frac{\partial\hat{\alpha}_1}{\partial\tau_1} + \frac{\partial\hat{\alpha}_2}{\partial\tau_0} = \frac{\mathrm{i}}{\hbar}[\hat{\alpha}_1, \mathrm{e}^{\mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{N}t}\boldsymbol{H}_1\mathrm{e}^{-\mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{N}t}], \tag{2.20}$$

and the initial conditions

$$\hat{\alpha}_n(0) = \begin{cases} \hat{\alpha}(0) & \text{if } n = 0 \\ 0 & \text{if } n \geqslant 1. \end{cases} \tag{2.21}$$

The thermodynamic properties of these equations are developed in the next section.

3. Thermodynamic equations of motion

The equations of motion derived in the preceding section describe the behaviour of the ensemble of oscillators to second order in the coupling coefficient. However, exact and numerical solutions of this sytem of equations are either impossible or prohibitively expensive to obtain, especially for systems with a large number of oscillators, so the immediate usefulness of this system of equations for studying physical systems is severly limited. Instead of trying to obtain exact solutions, we continue the perturbation analysis to obtain a different system of equations which, after taking the thermodynamic limit, can be used to study steady-state behaviour and the evolution to this steady state.

This thermodynamic limit of the von Neuman equation of motion, which we have called the master equation system in the introduction, is directly used to calculate an H-theorem which determines the form of the density for the steady-state bath of oscillators and the timescales to reach this steady state. We want to emphasize that, in deriving this master equation system, no assumptions are made about the initial density distribution. In particular, we show that the leading-order term of the density becomes diagonal instead of beginning with the assumption that the initial density is diagonal. We also discuss the timescales for the density to become diagonal. This situation is analogous to PR where they show that if the initial probability is not independent of angles, the leading order term for the steady-state probability will be independent of angles.

We also calculate the equation of motion for the first and second moments of the counting operator and use these results to obtain a second H-theorem. This H-theorem shows that the Planck distribution is the unique distribution for the steady-state system. Finally, microcanonical and canonical ensembles are discussed.

(*a*) *Master equation*

The notation and the interaction-picture Hamiltonian derived in the previous section simplify the computation of the master equation by placing the fast oscillations in the interaction coefficient instead of the density operator. These oscillations resonate in the $\mathcal{O}(\epsilon^2)$ equation of motion (2.20) thereby causing $\hat{\alpha}_0$ to change on the slow timescale τ_2. The resulting master equation system preserves the properties of the density operator.

The $\mathcal{O}(1)$ equation of motion (2.18) immediately tells us that $\hat{\alpha}_0$ is independent of the fast time τ_0. Neglecting the statistically insignificant accidental resonances $\omega_{IJK} = 0$ in the $\mathcal{O}(\epsilon)$ equation of motion (2.19) produces $\hat{\alpha}_0$ independent of τ_1 and

$$\alpha_{1\boldsymbol{mn}} = \mathrm{i}\hbar^{1/2}\sum_{IJK} c_{ijk}\Delta^{+}(\omega_{IJK})\left(\sqrt{n_{IJK}}\,\alpha_{0\boldsymbol{m},\boldsymbol{n}+\boldsymbol{e}_{IJK}} - \sqrt{m_{-I-J-K}}\,\alpha_{0\boldsymbol{m}-\boldsymbol{e}_{IJK},\boldsymbol{n}}\right). \tag{3.1}$$

An immediate consequence of this is that $\hat{\alpha}_1$ is independent of τ_1.

The double sum that appears when $\hat{\alpha}_1$ is substituted into the right-hand side of the $\mathcal{O}(\epsilon^2)$ equation of motion (2.20) is separated into one secular and one non-secular series by using the procedure developed in PR. Writing LMN for the second set of summation indices, the secular series consists of the essential resonances for which (L, M, N) is one of the six permutations of $(-I, -J, -K)$. Prigogine & Henin (1960) call these terms ‘cycles.’ The remaining terms on the right-hand side of the $\mathcal{O}(\epsilon^2)$ equation of motion are non-secular. Collecting the secular terms in $\partial\hat{\alpha}_0/\partial\tau_2$ and the non-secular terms in $\partial\hat{\alpha}_2/\partial\tau_0$, converting back to the Heisenberg representation, and then applying the thermodynamic limit produces the master equation

$$\begin{aligned}\frac{\mathrm{d}\rho_{0\boldsymbol{mn}}}{\mathrm{d}t} = {} & \mathrm{i}\boldsymbol{\omega}\cdot(\boldsymbol{n}-\boldsymbol{m})\rho_{0\boldsymbol{mn}} + 6\pi\epsilon^2\hbar\sum_{IJK} c_{ijk}^2\delta^{-}(\omega_{IJK})\\ & \times\left[\sqrt{m_{IJK}n_{IJK}}\,\rho_{0\boldsymbol{m}+\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{IJK}} - (m_{IJK}+n_{-I-J-K})\rho_{0\boldsymbol{mn}}\right.\\ & \left. + \sqrt{m_{-I-J-K}n_{-I-J-K}}\,\rho_{0\boldsymbol{m}-\boldsymbol{e}_{IJK},\boldsymbol{n}-\boldsymbol{e}_{IJK}}\right].\end{aligned} \tag{3.2}$$

This equation describes the thermodynamic evolution of the system. That it is dissipative and leads to an equilibrium is proven in the next section.

Some readers may question the validity of the perturbation expansion approach we have used to derive this master equation. In a separate paper (Sinclair 1997), we used a unitary transform procedure to analyse the behaviour of the bath of oscillators. There, we demonstrate that a careful analysis of the 'purely oscillatory' behaviour predicted by the unitary transform produces this same master equation in the thermodynamic limit. Therefore, rather than argue about the validity of our analysis, we derive results from it.

The first and second order corrections to the behaviour described by the master equation are

$$\rho_{1\boldsymbol{mn}} = \pi\mathrm{i}\hbar^{1/2}\sum_{IJK} c_{ijk}\Delta^-(\omega_{IJK}) \times\left(\sqrt{n_{IJK}}\,\rho_{0\boldsymbol{m},\boldsymbol{n}+\boldsymbol{e}_{IJK}} - \sqrt{m_{-I-J-K}}\,\rho_{0\boldsymbol{m}-\boldsymbol{e}_{IJK},\boldsymbol{n}}\right) \tag{3.3}$$

$$\begin{aligned}\rho_{2\boldsymbol{mn}} = -\hbar\sideset{}{'}\sum_{\substack{IJK\\LMN}} c_{ijk}c_{lmn}D(\omega_{IJK},\omega_{LMN}) &\times\Big[\sqrt{n_{LMN}}\Big(\sqrt{(\boldsymbol{n}+\boldsymbol{e}_{LMN})_{IJK}}\,\rho_{0\boldsymbol{m},\boldsymbol{n}+\boldsymbol{e}_{IJK}+\boldsymbol{e}_{LMN}} \\ &\qquad -\sqrt{m_{-I-J-K}}\,\rho_{0\boldsymbol{m}-\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{LMN}}\Big) \\ &\quad -\sqrt{m_{-L-M-N}}\Big(\sqrt{n_{IJK}}\,\rho_{0\boldsymbol{m}-\boldsymbol{e}_{LMN},\boldsymbol{n}+\boldsymbol{e}_{IJK}} \\ &\qquad -\sqrt{(\boldsymbol{m}-\boldsymbol{e}_{LMN})_{-I-J-K}}\,\rho_{0\boldsymbol{m}-\boldsymbol{e}_{IJK}-\boldsymbol{e}_{LMN},\boldsymbol{n}}\Big)\Big],\end{aligned} \tag{3.4}$$

where $D(\omega_1,\omega_2)$ is the $\mathcal{O}(1)$ thermodynamic limit of

$$\frac{\Delta^-(\omega_1+\omega_2)-\Delta^-(\omega_1)}{-\mathrm{i}\omega_2} \tag{3.5}$$

restricted to $\omega_2 \neq -\omega_1$ and $\sum'$ is the double sum with the essential resonances removed. We refer to equations (3.2)–(3.4) as the master equation system.

We observe that, as was the case with Prigogine & Henin's (1960) derivation of a master equation for the Fourier modes of the classical probability density, the equation of motion for the diagonal and non-diagonal elements only depend on other elements on the same subdiagonal. These subdiagonals are indexed by the Fourier mode $\boldsymbol{n}-\boldsymbol{m}$. The master equation for the diagonal elements of the density operator is, after changing the signs of s_i, s_j, and s_k for terms with n_{-I-J-K} and substituting $\delta^+(\omega)+\delta^-(\omega)=2\delta(\omega)$,

$$\frac{\mathrm{d}\rho_{0\boldsymbol{nn}}}{\mathrm{d}t} = 12\pi\epsilon^2\hbar\sum_{IJK} c_{ijk}^2\delta(\omega_{IJK})n_{IJK}(\rho_{0\boldsymbol{n}+\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{IJK}} - \rho_{0\boldsymbol{nn}}). \tag{3.6}$$

Thus a state $\boldsymbol{n}$ can only interact with states $\boldsymbol{n}+\boldsymbol{e}_{IJK}$ satisfying $\omega_{IJK}=0$. Also,

$$\boldsymbol{H}_{0\boldsymbol{n}+\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{IJK}} = \hbar\boldsymbol{\omega}\cdot(\boldsymbol{n}+\boldsymbol{e}_{IJK}+\tfrac{1}{2}\boldsymbol{1}) = \hbar\boldsymbol{\omega}\cdot(\boldsymbol{n}+\tfrac{1}{2}\boldsymbol{1})+\omega_{IJK} = \boldsymbol{H}_{0\boldsymbol{nn}} \tag{3.7}$$

when $\omega_{IJK}=0$ so that a state $\boldsymbol{n}$ can only interact with other states $\boldsymbol{n}+\boldsymbol{e}_{IJK}$ that have the same free energy. This shows that the master equation (3.2) preserves the free energy of the system. Here, $\boldsymbol{1}$ is a vector of ones.

The master equation preserves the following properties of the density operator: $\operatorname{tr}\hat{\rho}_0 = 1$; $\rho^*_{0\boldsymbol{mn}} = \rho_{0\boldsymbol{nm}}$; and $0 \leqslant \rho_{0\boldsymbol{nn}} \leqslant 1$. Because $\hat{\rho}_1$ can be written in terms of a commutator, $\operatorname{tr}\hat{\rho}_1 = 0$. Calculations in Sinclair (1992) show that $\operatorname{tr}\hat{\rho}_2 = 0$. Thus $\operatorname{tr}\hat{\rho} = \operatorname{tr}(\hat{\rho}_0+\epsilon\hat{\rho}_1+\epsilon^2\hat{\rho}_2+\ldots) = 1$ to $\mathcal{O}(\epsilon^2)$ as it should.

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Furthermore, we note that at $T = 0\,\mathrm{K}$ the system is in a ground state,

$$\rho_{0\boldsymbol{mn}} = \begin{cases} 0 & \text{if } \boldsymbol{m} \text{ or } \boldsymbol{n} \neq 0, \\ 1 & \text{if } \boldsymbol{m},\, \boldsymbol{n} = 0, \end{cases} \tag{3.8}$$

so that

$$\frac{\mathrm{d}\rho_{0\,\mathbf{00}}}{\mathrm{d}\tau_2} = -12\pi\hbar\epsilon^2 \sum_{ijk} c_{ijk}^2 \delta(\omega_i + \omega_j + \omega_k)\rho_{0\,\mathbf{00}} = 0 \tag{3.9}$$

and the system remains in the ground state. Thus the dissipative master equation preserves the $T = 0\,\mathrm{K}$ distribution (3.8).

(*b*) *H-theorem*

We use the master equation system to derive an H-theorem in this section. This H-theorem states that the positive quantity $\operatorname{tr}\hat{\rho}^2$ decreases and therefore the system must decay to an equilibrium state. We then discuss properties of this equilibrium state and the timescales to reach it.

Substituting the master equation system (3.2)–(3.4) into $\mathrm{d}\operatorname{tr}\hat{\rho}^2/\mathrm{d}t$ produces the H-theorem,

$$\frac{\mathrm{d}\operatorname{tr}\hat{\rho}^2}{\mathrm{d}t} = -12\pi\epsilon^2\hbar \sum_{\substack{\boldsymbol{mn}\\ IJK}} c_{ijk}^2 \delta(\omega_{IJK})$$
$$\times\left[|\sqrt{m_{IJK}} - \sqrt{n_{IJK}}|^2 |\rho_{0\boldsymbol{mn}}|^2 + \sqrt{(m_{IJK}n_{IJK})}|\rho_{0\boldsymbol{m}+\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{IJK}} - \rho_{0\boldsymbol{mn}}|^2\right], \tag{3.10}$$

from which we observe that $\mathrm{d}\operatorname{tr}\hat{\rho}^2/\mathrm{d}t \leqslant 0$ because the summand is non-negative.

If we compute the time derivative of the trace before we take the thermodynamic limit we obtain $\mathrm{d}\operatorname{tr}\hat{\rho}^2/\mathrm{d}t = 0$. However, if we compute the same derivative after we take the thermodynamic limit, we obtain the negative semi-definite expression (3.10) for the evolution of the positive quantity $\operatorname{tr}\hat{\rho}^2$. This illustrates the difference between the reversible pre-thermodynamic limit and the irreversible thermodynamic limit.

To determine the equilibrium state, we examine the terms on the right-hand side of equation (3.10). The first summand under $\sum_{\boldsymbol{mn}}$, namely

$$\left\{\sum_{IJK} c_{ijk}^2 \delta(\omega_{IJK}) |\sqrt{n_{IJK}} - \sqrt{m_{IJK}}|^2\right\} |\rho_{0\boldsymbol{mn}}|^2, \tag{3.11}$$

will be zero only if either the term in braces is zero or $\rho_{0\boldsymbol{mn}}$ is zero. If $\boldsymbol{m} \neq \boldsymbol{n}$ then, because the interaction Hamiltonian is not separable as described in § 2, because $\delta(\omega)$ is non-negative, and because $\sum_{IJK}$ is really an integral, the term in braces is non-zero. Thus, in order to be at equilibrium we must have $\rho_{0\boldsymbol{mn}} = 0$ when $\boldsymbol{m} \neq \boldsymbol{n}$ so that one condition for equilibrium is that $\hat{\rho}_0$ is diagonal:

$$\rho_{0\boldsymbol{mn}} = 0 \quad \text{if} \quad \boldsymbol{m} \neq \boldsymbol{n}. \tag{3.12}$$

The second term in the summand of $\sum_{IJK}\sum_{\boldsymbol{mn}}$ in equation (3.10) is

$$c_{ijk}^2 \delta(\omega_{IJK}) \sqrt{(m_{IJK}n_{IJK})} |\rho_{0\boldsymbol{m}+\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{IJK}} - \rho_{0\boldsymbol{mn}}|^2. \tag{3.13}$$

The square root can be zero only if one of m_i, m_j, m_k, n_i, n_j, or n_k is zero and the corresponding sign, s_i, s_j, or s_k, is -1. Since these correspond to non-physical situations, i.e. a negative occupation number in $\rho_{0\boldsymbol{m}+\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{IJK}}$, the zero coefficient excludes these terms from the summation. Since c_{ijk}^2 and the remaining square root terms are non-zero, a second condition for equilibrium is that the diagonal elements obey

$$\delta(\omega_{IJK})|\rho_{0\boldsymbol{n}+\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{IJK}} - \rho_{0\boldsymbol{n}\boldsymbol{n}}|^2 = 0. \tag{3.14}$$

Thus, not only is $\hat{\rho}_0$ diagonal, but also the diagonal matrix elements obey

$$\rho_{0\boldsymbol{n}+\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{IJK}} - \rho_{0\boldsymbol{n},\boldsymbol{n}} \propto \omega_{IJK}. \tag{3.15}$$

As was the case in the classical calculation, if $\hat{\rho}_0 = \rho(\boldsymbol{H}_0)$, then this condition will be satisfied. The equilibrium value of $\hat{\rho}_0$ will be investigated further in § 3 *e* by deriving the Planck distribution and in § 3 *f* when we discuss the microcanonical and canonical ensembles.

Because the equilibrium density operator $\hat{\rho}_0$ is diagonal, the equilibrium values of $\hat{\rho}_1$ and $\hat{\rho}_2$ are zero along the diagonal.

The timescale for $\hat{\rho}_0$ to reach equilibrium depends on the timescale for it to become diagonal and on the timescale for the energy along the diagonal to be distributed. The first of these timescales is determined by the coefficient of $|\rho_{0\boldsymbol{mn}}|^2$ in the H-theorem (3.10), namely

$$-12\pi\epsilon^2\hbar \sum_{IJK} c_{ijk}^2 \delta(\omega_{IJK})|\sqrt{m_{IJK}} - \sqrt{n_{IJK}}|^2. \tag{3.16}$$

The second timescale is determined by the remaining term in the H-theorem,

$$-12\pi\epsilon^2\hbar \sum_{IJK} c_{ijk}^2 \delta(\omega_{IJK}) n_{IJK} |\rho_{0\boldsymbol{n}+\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{IJK}} - \rho_{0\boldsymbol{n}\boldsymbol{n}}|^2. \tag{3.17}$$

The timescale to reach equilibrium must also be discussed for two classes of systems: classical systems in which the occupation numbers of interest are $\mathcal{O}(\hbar^{-1})$ and strongly quantum mechanical systems in which the occupation numbers are $\mathcal{O}(1)$ in $\hbar$.

We have three timescales for the system to reach equilibrium. In increasing order of magnitude they are (1) $\mathcal{O}(\epsilon^{-2}\hbar^2)$ for far off-diagonal Fourier mode indices, $\boldsymbol{n}-\boldsymbol{m} = \mathcal{O}(\hbar^{-1})$, (2) $\mathcal{O}(\epsilon^{-2})$ for near-diagonal, $\boldsymbol{n}-\boldsymbol{m} = o(\hbar^{-1})$, and (3) $\mathcal{O}(\epsilon^{-2}\hbar^{-1})$. The first two timescales apply to classical systems, $I = \mathcal{O}(1)$, while the last one applies to strongly quantum mechanical systems, $I = \mathcal{O}(\hbar)$. In particular, the first timescale produces equation (1.8) and the second produces equations (1.9) and (1.10) for $M = \mathcal{O}(1)$. Because the first timescale is associated with extremely short wavelengths in the classical regime, we call it the noise timescale. The second timescale is associated with smooth classical behaviour and, because it agrees with the timescale for dissipation in the classical limit, we call it the classical timescale. Finally, the third timescale, which is the only timescale in the quantum mechanical limit, is called the quantum timescale. Because classical systems have more observable variables than quantum mechanical systems (i.e. angles), it is not surprising that they exhibit a richer variety of timescales than quantum mechanical systems.

These systems display irreversibility on different timescales. The classical system displays irreversibility immediately because the noise disappears $\mathcal{O}(\hbar^2)$ faster than the classical Fourier modes. As the energy of strongly quantum mechanical systems increases, the low-frequency quantum Fourier modes become classical modes while the high frequency modes become noise.

In terms of the density of modes introduced in equation (1.5), the timescales for dissipation are

$$t \gg \frac{1}{\epsilon^2 f(\omega)\sigma(\omega)} \tag{3.18}$$

for the classical system and

$$t \gg \frac{1}{\epsilon^2 \hbar f(\omega)\sigma(\omega)} \tag{3.19}$$

for the strongly quantum mechanical system. In both cases, $f(\omega)$ is an $\mathcal{O}(1)$ scaling parameter depending on the coefficients (3.16) and (3.17). In conjunction with the asymptotic relations (1.4) and (1.5) for the thermodynamic limit, these limits place a lower bound on the coupling coefficient:

$$\epsilon \gg \frac{1}{\sigma(\omega) f(\omega)^{1/2}} \tag{3.20}$$

for classical systems and

$$\epsilon \gg \frac{1}{\hbar^{1/2}\sigma(\omega) f(\omega)^{1/2}} \tag{3.21}$$

for strongly quantum mechanical systems. The $\hbar^{1/2}$ in the denominator of the second asymptotic relation means that the quantum mechanical system must have a relatively strong interaction compared with the classical system in order for dissipation to be observed. This gives us a new criterion for the validity of the master equation, namely that when there is more energy in the system, the interaction can be weaker and more time allowed to observe the decay to a steady state.

(*c*) *Moment equations*

The master equation (3.2), contains information about all moments of the density operator $\hat{\rho}_0$. The first and second moments of the counting operator are examined here. The problem of closure is examined in the next section.

The general formula for the expected value of a function of the number operator is

$$\langle f(\boldsymbol{N})\rangle_0 = \mathrm{tr}[\hat{\rho}_0 f(\boldsymbol{N})], \tag{3.22}$$

where the subscript '0' is used to emphasize that the expectation is with respect to the leading order density operator $\hat{\rho}_0$. Since $\boldsymbol{N}$ is a diagonal operator, $f(\boldsymbol{N})$ is also diagonal and

$$\frac{\mathrm{d}\langle f(\boldsymbol{N})\rangle_0}{\mathrm{d}t} = \sum_{\boldsymbol{n}} f(\boldsymbol{n}) \frac{\mathrm{d}\rho_{0\boldsymbol{n}\boldsymbol{n}}}{\mathrm{d}t}. \tag{3.23}$$

Substituting the diagonalized version (3.6) of the master equation into this equation produces

$$\frac{\mathrm{d}\langle f(\boldsymbol{N})\rangle_0}{\mathrm{d}t} = 12\pi\epsilon^2\hbar \sum_{IJK} c_{ijk}^2 \delta(\omega_{IJK}) \langle N_{IJK}(f(\boldsymbol{N}+\boldsymbol{e}_{IJK}) - f(\boldsymbol{N}))\rangle_0, \tag{3.24}$$

or

$$\frac{\mathrm{d}\langle f(\boldsymbol{N})\rangle_0}{\mathrm{d}t} = 6\pi\epsilon^2\hbar \sum_{IJK} c_{ijk}^2 \delta(\omega_{IJK}) \langle D_{IJK}^*(N_{IJK} D_{IJK} f(\boldsymbol{N}))\rangle_0, \tag{3.25}$$

where the difference operators D_{IJK} and D_{IJK}^* are defined by

$$D_{IJK}\, g(\boldsymbol{n}) = g(\boldsymbol{n}+\boldsymbol{e}_{IJK}) - g(\boldsymbol{n}) \tag{3.26}$$

and

$$D_{IJK}^*\, g(\boldsymbol{n}) = g(\boldsymbol{n}) - g(\boldsymbol{n}-\boldsymbol{e}_{IJK}). \tag{3.27}$$

Note that only the terms with even powers of products of s_i, s_j, and s_k are retained when computing moments of $\boldsymbol{N}$.

The first and second order moments are calculated using this general formula by first noting that $D_{IJK}N_p = 0$ if $p \notin \{i, j, k\}$ and then by counting multiplicities. The first and second order moments are

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle N_p + \tfrac{1}{2}\rangle_0 = 18\pi\epsilon^2\hbar \sum_{s_p JK} c^2_{pjk}\delta(\omega_{PJK})s_p\langle M_{PJK}\rangle_0, \tag{3.28}$$

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle (N_p + \tfrac{1}{2})^2\rangle_0 = 36\pi\epsilon^2\hbar \sum_{s_p JK} c^2_{pjk}\delta(\omega_{PJK})s_p \\ \times\langle 2s_p(N_p+\tfrac{1}{2})(N_j+\tfrac{1}{2})(N_k+\tfrac{1}{2}) + s_j(N_p+\tfrac{1}{2})^2(N_k+\tfrac{1}{2}) \\ + s_k(N_p+\tfrac{1}{2})^2(N_j+\tfrac{1}{2}) + \tfrac{1}{4}s_j(N_k+\tfrac{1}{2}) + \tfrac{1}{4}s_k(N_j+\tfrac{1}{2}) \\ + \tfrac{1}{4}2s_p s_j s_k(N_p+\tfrac{1}{2})\rangle_0,\end{aligned} \tag{3.29}$$

and for $p \neq q$

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle (N_p + \tfrac{1}{2})(N_q + \tfrac{1}{2})\rangle_0 = 18\pi\epsilon^2\hbar \sum_{s_p JK} c^2_{pjk}\delta(\omega_{PJK})s_p\langle M_{PJK}(N_q+\tfrac{1}{2})\rangle_0 \\ +36\pi\epsilon^2\hbar \sum_{s_p s_q K} c^2_{pqk}\delta(\omega_{PQK})s_p\langle s_q(N_p+\tfrac{1}{2})(N_q+\tfrac{1}{2})(N_k+\tfrac{1}{2}) \\ + \tfrac{1}{4}2s_p s_q s_k(N_q+\tfrac{1}{2}) + \tfrac{1}{4}s_p(N_k+\tfrac{1}{2})\rangle_0 \\ +(p \leftrightarrow q),\end{aligned} \tag{3.30}$$

where

$$M_{PJK} = D^*_{PJK}N_{PJK} \tag{3.31}$$

$$\begin{aligned} = s_p(N_j+\tfrac{1}{2})(N_k+\tfrac{1}{2}) + s_j(N_p+\tfrac{1}{2})(N_k+\tfrac{1}{2}) \\ + s_k(N_p+\tfrac{1}{2})(N_j+\tfrac{1}{2}) + \tfrac{1}{4}s_p s_j s_k\end{aligned} \tag{3.32}$$

and $(p \leftrightarrow q)$ means to exchange p and q in the expression to its left. According to the model used in § 6, the second series in equation (3.30) is $\mathcal{O}(V^{-1})$ smaller than the first series as the volume $V \to \infty$. Thus it can be ignored in the thermodynamic limit. We return to this equation in the next section.

Substituting the equation of motion for first order moments, equation (3.28), into $\mathrm{d}\langle \boldsymbol{H}_0\rangle/\mathrm{d}t$ shows that the mean free energy is preserved.

This equation of motion for first order moments also describes the correct behaviour for an oscillator interacting with a bath at $T = 0$ K. We demonstrate this by imposing the initial conditions $\langle N_p\rangle > 0$ where p is the index of the excited oscillator and $\langle N_q\rangle = 0$ for all $q \neq p$. Then, at $t = 0$, the excited oscillator obeys

$$\begin{aligned}\left.\frac{\mathrm{d}\langle N_p\rangle_0}{\mathrm{d}t}\right|_{t=0} = 18\pi\epsilon^2\hbar \sum_{s_p JK} c^2_{pjk}\delta(\omega_{PJK}) \\ \times\{\tfrac{1}{4}(1+s_p s_j)(1+s_p s_k) + \tfrac{1}{2}s_p(s_j+s_k)\langle N_p\rangle_0\}\end{aligned} \tag{3.33}$$

$$= -36\pi\epsilon^2\hbar\left[\sum_{jk} c^2_{pjk}\delta(\omega_p - \omega_j - \omega_k)\right]\langle N_p\rangle_0 \tag{3.34}$$

$$< 0 \tag{3.35}$$

and the $T = 0$ K oscillators obey

$$\left.\frac{\mathrm{d}\,\langle N_q\rangle_0}{\mathrm{d}t}\right|_{t=0} = 72\pi\epsilon^2\hbar\left[\sum_k c_{pqk}^2\delta(\omega_p-\omega_q-\omega_k)\right]\langle N_p\rangle_0 \geqslant 0. \tag{3.36}$$

Thus energy is immediately lost by the excited oscillator and any oscillator which interacts directly with the excited oscillator is immediately excited. Because frequencies are positive, the coefficient $\delta(\omega_p-\omega_j-\omega_k)$ in equations (3.34) and (3.36) tells us that energy is initially removed from frequency ω_p to lower frequencies ω_q and that $\mathrm{d}\langle N_q\rangle_0/\mathrm{d}t|_{t=0} = 0$ for all $\omega_q > \omega_p$. This cascade of energy is only downward at $t = 0$. Higher frequencies may be excited on a slower timescale depending on the second order moments discussed in the next section. Equations (3.34) and (3.36) generalize Slonimskii's result (1937) to a distribution of nonlinear interacting oscillators.

This behaviour is markedly different than the classical moment equation (5.4) in PR:

$$\frac{\mathrm{d}\,\langle I_p\rangle}{\mathrm{d}t} = 18\pi\epsilon^2\sum_{s_pJK}\delta(\omega_{PJK})c_{pjk}^2 s_p[s_p\langle I_jI_k\rangle + s_j\langle I_pI_k\rangle + s_k\langle I_pI_j\rangle]. \tag{3.37}$$

In this equation, if $\langle I_q\rangle = 0$ for all $q \neq p$ then $\mathrm{d}\,\langle I_j\rangle/\mathrm{d}t = 0$ for the excited and $T = 0$ K oscillators no matter how large $\langle I_p\rangle$ is. The quantum mechanical zero-point action must be incorporated into the classical equation to restore the decay of the excited oscillator with the $T = 0$ K bath.

(d) Closure and the Stosszahl ansatz

The main problem with the moment equations (3.28)–(3.30) is that the order n equations depend on order $n+1$ moments. This problem has no completely satisfactory answer, but by using the same procedure as PR, we show that under certain conditions, second order moments can be approximated by first order moments during the timescale for dissipation:

$$\langle(N_p+\tfrac{1}{2})(N_q+\tfrac{1}{2})\rangle_0 \sim \langle N_p+\tfrac{1}{2}\rangle_0\langle N_q+\tfrac{1}{2}\rangle_0. \tag{3.38}$$

This lack of correlation and the underlying assumption is called the Stosszahl ansatz.

When we substitute this factorization of the second order moments into the equation of motion for the first-order moments (3.28), we obtain the closed form for the equation of motion. This can be written as equation (1.13) or, for the subsequent analysis, as

$$\begin{aligned}\frac{\mathrm{d}\langle N_p\rangle_0}{\mathrm{d}t} = 36\pi\epsilon^2\hbar\sum_{jk} c_{pjk}^2\langle N_p\rangle_0\langle N_j\rangle_0\langle N_k\rangle_0 \\ \times[\delta(\omega_p-\omega_j-\omega_k)(\gamma_p-\gamma_j\gamma_k) \\ -\delta(\omega_j-\omega_p-\omega_k)(\gamma_j-\gamma_p\gamma_k) \\ -\delta(\omega_k-\omega_p-\omega_j)(\gamma_k-\gamma_p\gamma_j)],\end{aligned} \tag{3.39}$$

where

$$\gamma_i = \frac{1}{\langle N_i\rangle_0} + 1. \tag{3.40}$$

Note that the system will be in a steady state, $\mathrm{d}\langle N_p\rangle/\mathrm{d}t = 0$, if $\gamma_p - \gamma_j\gamma_k = 0$ for any triplet p, j, k satisfying $\omega_p - \omega_j - \omega_k = 0$. Thus the Planck distribution $\ln\gamma_p \propto \omega_p$

will produce a steady state. In the next section we prove that the Planck distribution is the unique distribution for a steady state.

(*e*) *Planck distribution*

We have derived conditions for equilibrium in § 3 *b*, but not the equilibrium distribution. In this section, the entropy

$$S = \sum_P s_p \langle N_P \rangle_0 \ln \langle N_P \rangle_0 \tag{3.41}$$

is used to derive a second H-theorem and show that the steady-state first-order moments satisfy the Planck distribution

$$\langle N_p \rangle_0 = \frac{1}{\mathrm{e}^{\beta\hbar\omega_p} - 1}, \tag{3.42}$$

where β is the inverse temperature.

Substituting the factorization (3.39) for the equation of motion for first-order moments into $\mathrm{d}S/\mathrm{d}t$ yields

$$\begin{aligned}\frac{\mathrm{d}S}{\mathrm{d}t} = 36\pi\epsilon^2\hbar \sum_{pjk} c_{pjk}^2 \delta(\omega_p - \omega_j - \omega_k)\, \langle N_p\rangle_0 \langle N_j\rangle_0 \langle N_k\rangle_0\ \gamma_p \\ \times(\gamma_j\gamma_k/\gamma_p - 1)\ln(\gamma_j\gamma_k/\gamma_p).\end{aligned} \tag{3.43}$$

Since $(x-1)\ln x \geqslant 0$ for $x > 0$, the summand is non-negative. Thus, the second H-theorem is that the entropy S increases until $\gamma_j\gamma_k = \gamma_p$ whenever $\omega_j + \omega_k = \omega_p$ and $c_{pjk} \neq 0$. Equivalently, $\ln\gamma_j + \ln\gamma_k = \ln\gamma_p$ whenever $\omega_j + \omega_k = \omega_p$ and $c_{pjk} \neq 0$. Since the Hamiltonian $\boldsymbol{H}$ is not separable, $\ln\gamma_p = \beta\hbar\omega_p$ for all p and some positive constant β called the inverse temperature. Solving for $\langle N_p\rangle_0$ produces the Planck distribution (3.42).

(*f*) *Microcanonical and canonical ensembles*

The preceding calculations have demonstrated some of the properties of the equilibrium solutions to the master equation (3.2), but we have not calculated explicit expressions for the equilibrium density operator. In this section, we derive the equilibrium distribution for two cases, the microcanonical and canonical distributions. In order to examine these solutions, we must derive a third H-theorem. Two equilibrium solutions to this H-theorem produce the microcanonical and canonical distributions.

The H-theorem examined in § 3 *b* involved the time derivative of the square norm $\mathrm{tr}\,\hat{\rho}^2$ of the density operator. We observed that this positive-definite quantity decreases until a steady state satisfying equations (3.12) and (3.14) is reached. We use the diagonality of the steady-state density operator $\hat{\rho}_0$ to create an entropy from which we calculate more explicit solutions to equation (3.14). We want to emphasize again that this diagonality is a result of our earlier analysis. It is not a result of assuming that the initial density is diagonal.

Since the equilibrium density operator is diagonal, we will use the standard form of entropy from statistical mechanics defined by

$$S = \mathrm{tr}(\hat{\rho}_0 \ln \hat{\rho}_0) = \sum_{\boldsymbol{n}} \rho_{0\boldsymbol{nn}} \ln \rho_{0\boldsymbol{nn}}. \tag{3.44}$$

Substituting the master equation (3.2) into $\mathrm{d}S/\mathrm{d}t$ produces

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -6\pi\epsilon^2\hbar \sum_{\substack{\boldsymbol{n}\\ IJK}} c_{ijk}^2 \delta(\omega_{IJK}) n_{IJK}\, \rho_{0\boldsymbol{nn}} \times \left(\frac{\rho_{0\boldsymbol{n}+\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{IJK}}}{\rho_{0\boldsymbol{nn}}} - 1\right) \ln\left(\frac{\rho_{0\boldsymbol{n}+\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{IJK}}}{\rho_{0\boldsymbol{nn}}}\right). \tag{3.45}$$

Since $(x-1)\ln x \geqslant 0$ for $x > 0$, we observe that the negative semi-definite quantity S decreases until

$$\delta(\omega_{IJK})\,(\rho_{0\boldsymbol{n}+\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{IJK}} - \rho_{0\boldsymbol{nn}})\,(\ln \rho_{0\boldsymbol{n}+\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{IJK}} - \ln \rho_{0\boldsymbol{nn}}) = 0. \tag{3.46}$$

The microcanonical and canonical distributions describe two kinds of solutions to this condition for equilibrium.

The microcanonical ensemble is a distribution initially concentrated on a specified value of energy, that is,

$$\rho_{0\boldsymbol{nn}}(0) = 0 \quad \text{if} \quad \boldsymbol{H}_{0\boldsymbol{nn}} \neq E. \tag{3.47}$$

From the discussion following equation (3.6), we know that the distribution will satisfy this condition for all $t > 0$. The equilibrium condition (3.46) is then satisfied if the states $\boldsymbol{n}$ and $\boldsymbol{n} + \boldsymbol{e}_{IJK}$ do not have energy E since $\rho_{0\boldsymbol{nn}}$ and $\rho_{0\boldsymbol{n}+\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{IJK}}$ are both zero. It is also satisfied if one of the two states has energy E and the other does not because

$$\omega_{IJK} = \frac{\boldsymbol{H}_{0\boldsymbol{n}+\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{IJK}} - \boldsymbol{H}_{0\boldsymbol{nn}}}{\hbar} \neq 0 \tag{3.48}$$

means that $\delta(\omega_{IJK}) = 0$. Finally, if the states $\boldsymbol{n}$ and $\boldsymbol{n} + \boldsymbol{e}_{IJK}$ both have energy E, then $\omega_{IJK} = 0$ and we must have $\rho_{0\boldsymbol{nn}} = \rho_{0\boldsymbol{n}+\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{IJK}}$. Since the interaction Hamiltonian is not separable, this means that

$$\rho_{0\boldsymbol{nn}} = \begin{cases} 1/N_E & \text{if } \boldsymbol{H}_{0\boldsymbol{nn}} = E, \\ 0 & \text{otherwise,} \end{cases} \tag{3.49}$$

where N_E is the number of states with energy E. The Stosszahl ansatz and Planck distribution will only be satisfied if N_E is large so that the energy represented by the occupation number in one state is small compared with the total energy.

To obtain the canonical distribution, we observe that

$$\ln \rho_{0\boldsymbol{n}+\boldsymbol{e}_{IJK},\boldsymbol{n}+\boldsymbol{e}_{IJK}} - \ln \rho_{0\boldsymbol{nn}} = -\beta\hbar\omega_{IJK}, \tag{3.50}$$

or

$$\hat{\rho}_0 = K\mathrm{e}^{-\beta \boldsymbol{H}_0}, \tag{3.51}$$

is also a solution of the equilibrium condition (3.46) where

$$K = \frac{1}{\mathrm{tr}\, \mathrm{e}^{-\beta \boldsymbol{H}_0}} \tag{3.52}$$

is the renormalizing coefficient and $\beta \geqslant 0$. Because the free Hamiltonian is separable, we can write the canonical distribution as a product of independent distributions,

$$\rho_{0\boldsymbol{nn}} = \prod_i (1 - \mathrm{e}^{-\beta\hbar\omega_i})\mathrm{e}^{-\beta\hbar\omega_i n_i}, \tag{3.53}$$

so that the Stosszahl ansatz (3.38) is satisfied and the Planck distribution (3.42) is easily rederived.

4. Classical limit

In this section, we demonstrate a new technique to obtain the classical limit of the quantum mechanical equations of motion. We have applied this method to equations (2.13), (3.2), (3.10), and (3.25) which are the quantum mechanical analogs of the classical Liouville equation, Fokker–Planck equation, H-theorem, and moment equations given in PR. The results we obtained are the same as the results of the classical analysis to $\mathcal{O}(1)$ in $\hbar$. After presenting a discussion of the method, we demonstrate it by applying it to the quantum Liouville equation.

While others have noticed the similarity between the occupation number representation used in the quantum mechanical calculations and Fourier modes (see, for example, Resibois 1961), the relationship has not been developed as completely as we have developed here. Also, the limiting procedure presented here has the advantage that it preserves the positive semi-definiteness of the density operator. Other methods, such as Wigner's transform, in general do not (see, for example, Tatarskii 1987, § 4).

(*a*) *Preliminary considerations*

Before presenting the method we discuss a simple example. Consider the classical function $I^{1/2}\mathrm{e}^{\mathrm{i}\theta}$ which is converted to the creation operator, $\hbar^{1/2}q^{\dagger}$. If we examine the matrix form of this operator we find that

$$\sqrt{\hbar}q^{\dagger}_{mn} = \sqrt{\tfrac{1}{2}\hbar(n+m+1)}\delta_{n-m,-1}, \tag{4.1}$$

where $q^{\dagger}_{mn} = \langle m|q^{\dagger}|n\rangle$ is the usual matrix notation for quantum mechanical operators. If we change our notation by defining the action

$$I = \tfrac{1}{2}\hbar(m+n+1) \tag{4.2}$$

and Fourier mode index

$$M = n - m \tag{4.3}$$

and write $q^{\dagger}_{M}(I)$ instead of the matrix form $q^{\dagger}_{mn}$ we obtain

$$\sqrt{\hbar}q^{\dagger}_{M}(I) = \sqrt{\hbar}q^{\dagger}_{mn} = \sqrt{I}\delta_{M,-1}. \tag{4.4}$$

Before discussing the details of this change of notation, we note that removing the bound on M and applying the inverse Fourier transform (1.12) to $q^{\dagger}_{M}(I)$ produces

$$\sqrt{\hbar}q^{\dagger}(I,\theta) = \sum_{M}\mathrm{e}^{-\mathrm{i}M\theta}\sqrt{\hbar}q^{\dagger}_{M}(I) = \sqrt{I}\mathrm{e}^{\mathrm{i}\theta}, \tag{4.5}$$

where $q^{\dagger}(I,\theta)$ is the creation operator expressed in terms of the action-angle variables I and θ. This is the classical function with which we started our analysis! We demonstrate that this simple procedure works for more complicated expressions below.

For our first comment about the change of notation, observe that the definition (4.2) of action reflects the fact that the minimum action of a quantum mechanical oscillator is $\hbar/2$. Secondly, because the quantum mechanical matrix indices m and n are non-negative, they are bound for a fixed value of action:

$$n, m \leqslant \frac{I-\hbar/2}{\hbar/2}. \tag{4.6}$$

This and the non-negativity of n and m also impose a bound on the Fourier mode index M:

$$|M| \leqslant \frac{I}{\hbar/2} - 1. \tag{4.7}$$

We also note that when I is an odd multiple of $\hbar/2$, M must be even and when I is an even multiple of $\hbar/2$, M must be odd.

These bounds and restrictions would seem to prohibit the application of the inverse Fourier transform. They do not because in the classical limit we are interested in non-quantum mechanical actions, $I \gg \hbar$, and in functions which display oscillations on large scales compared to the quantum mechanical regime. That is, the quantum mechanical operator $f_M(I) = f_{mn}$ is large only for $M = \mathcal{O}(1)$ and $f_M(I)$ is smooth for fixed M. The first of the asymptotic relations, $I \gg \hbar$, removes the bound on M in the classical limit $\hbar \rightarrow 0$. The second relation guarantees that the removal of the bound on M does not affect the value of the inverse Fourier transform.

Finally, the restriction of the range of M in the quantum mechanical system is expected. If the range is not restricted, then

$$\theta_M(I) = \frac{1}{2\pi}\int_{-\pi}^{\pi} \theta e^{\mathrm{i}M\theta}\, \mathrm{d}\theta = \begin{cases} 0 & \text{if } M = 0, \\ (-1)^M/\mathrm{i}M & \text{if } M \neq 0, \end{cases} \tag{4.8}$$

would be the angle operator taking values on $(-\pi, \pi)$. However, as Peierls points out (1979), there is no quantum mechanical angle operator, so the range of M must be restricted. Since angles exist in the classical limit $I \gg \hbar$, the range of M becomes unbound in the classical limit.

(*b*) *Method*

Our procedure is to use the ideas developed in the preceding section to write the quantum mechanical density operator $\hat{\rho}$ in a form that relates the matrix indices of $\rho_{\boldsymbol{mn}}$ to action and Fourier index variables, and then to take the classical limit $\hbar \rightarrow 0$ with the action and Fourier index fixed.

Let $P_{\boldsymbol{M}}(\boldsymbol{I}) = \rho_{\boldsymbol{mn}}$ be the new density operator where the action vector $\boldsymbol{I}$ is defined by

$$\boldsymbol{I} = \tfrac{1}{2}\hbar(\boldsymbol{m} + \boldsymbol{n} + \boldsymbol{1}), \tag{4.9}$$

the Fourier index vector $\boldsymbol{M}$ is defined by

$$\boldsymbol{M} = \boldsymbol{n} - \boldsymbol{m}, \tag{4.10}$$

and where $\boldsymbol{1}$ is a vector of ones. To take the classical limit, we rewrite the quantum mechanical equations to $\mathcal{O}(1)$ in $\hbar$ while treating $\hbar M_i/I_i$ and $\hbar\partial/\partial I_i$ as small terms wherever they appear. The $\mathcal{O}(\hbar)$ term would be the difference between the quantum and classical behaviours. The full classical angle dependence is finally recovered by applying the inverse Fourier transform (1.12).

(*c*) *Results*

In this section, we summarize the steps to compute the classical Liouville equation from the von Neumann equation. More detailed calculations for this limit and the other classical evolution equations are performed in Sinclair (1992).

Referring to the von Neumann equation (2.13), we first need to apply the $\hbar$ expansion to $\sqrt{n_{IJK}}$, $\rho_{\boldsymbol{m},\boldsymbol{n}+\boldsymbol{e}_{IJK}}$, $\sqrt{m_{-I-J-K}}$, and $\rho_{\boldsymbol{m}-\boldsymbol{e}_{IJK},\boldsymbol{n}}$. We obtain

$$\sqrt{n_{IJK}} \sim \frac{1}{\hbar^{3/2}}\sqrt{I_i I_j I_k}\left[1 + \tfrac{1}{2}\hbar\left(\frac{M_i + s_i}{2I_i} + \frac{M_j + s_j}{2I_j} + \frac{M_k + s_k}{2I_k}\right) + \mathcal{O}(\hbar^2)\right] \tag{4.11}$$

and

$$\rho_{\boldsymbol{m},\boldsymbol{n}+\boldsymbol{e}_{IJK}} \sim P_{\boldsymbol{M}+\boldsymbol{e}_{IJK}}(\boldsymbol{I}) + \tfrac{1}{2}\hbar\nabla_{ijk}P_{\boldsymbol{M}+\boldsymbol{e}_{IJK}}(\boldsymbol{I}) + \mathcal{O}(\hbar^2), \tag{4.12}$$

where

$$\nabla_{ijk} = s_i\frac{\partial}{\partial I_i} + s_j\frac{\partial}{\partial I_j} + s_k\frac{\partial}{\partial I_k}. \tag{4.13}$$

The calculations for $\sqrt{m_{-I-J-K}}$ and $\rho_{\boldsymbol{m}-\boldsymbol{e}_{IJK},\boldsymbol{n}}$ are similar and produce the same results respectively with the opposite signs for the $\mathcal{O}(\hbar)$ terms. Substituting these expressions into the von Neumann equation (2.13) produces

$$\frac{\partial P_{\boldsymbol{M}}(\boldsymbol{I})}{\partial t} \sim \mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{M}P_{\boldsymbol{M}}(\boldsymbol{I}) + \epsilon\mathrm{i}\sum_{IJK} c_{ijk}\sqrt{I_i I_j I_k}$$
$$\times\left[\left(\frac{M_i + s_i}{2I_i} + \frac{M_j + s_j}{2I_j} + \frac{M_k + s_k}{2I_k}\right)P_{\boldsymbol{M}+\boldsymbol{e}_{IJK}}(\boldsymbol{I}) + \nabla_{ijk}P_{\boldsymbol{M}+\boldsymbol{e}_{IJK}}(\boldsymbol{I})\right] \tag{4.14}$$

to $\mathcal{O}(1)$ in $\hbar$. Since $M_i P_{\boldsymbol{M}}(\boldsymbol{I})$ is the Fourier transform of $\mathrm{i}\partial P(\boldsymbol{I},\boldsymbol{\theta})/\partial\theta_i$,

$$\left(\frac{M_i}{2I_i} + \frac{M_j}{2I_j} + \frac{M_k}{2I_k}\right)\bar{P}_{\boldsymbol{M}}(\boldsymbol{I}) \tag{4.15}$$

is the Fourier transform of

$$\left(\frac{\mathrm{i}}{2I_i}\frac{\partial}{\partial\theta_i} + \frac{\mathrm{i}}{2I_j}\frac{\partial}{\partial\theta_j} + \frac{\mathrm{i}}{2I_k}\frac{\partial}{\partial\theta_k}\right)\bar{P}(\boldsymbol{I},\boldsymbol{\theta}). \tag{4.16}$$

After applying the inverse Fourier transform (1.12) we obtain the classical Liouville equation of PR:

$$\frac{\partial P(\boldsymbol{I},\boldsymbol{\theta})}{\partial t} + \sum_i \omega_i\frac{\partial P(\boldsymbol{I},\boldsymbol{\theta})}{\partial\theta_i} = \epsilon\mathrm{i}\sum_{IJK} c_{ijk}\sqrt{I_i I_j I_k}\,\mathrm{e}^{\mathrm{i}\theta_{IJK}}\,\nabla_{IJK}P(\boldsymbol{I},\boldsymbol{\theta}), \tag{4.17}$$

where

$$\nabla_{IJK} = s_i\nabla_I + s_j\nabla_J + s_k\nabla_K \tag{4.18}$$

and

$$\nabla_I = \frac{\partial}{\partial I_i} + \frac{\mathrm{i}s_i}{2I_i}\frac{\partial}{\partial\theta_i}. \tag{4.19}$$

5. Frequency renormalization

The nonlinearities in the interaction Hamiltonian change the equilibrium frequency of the linear oscillators. This is demonstrated by converting Hamilton's equation for the angular rate into its quantum mechanical form and computing its expected value. Two expressions for the renormalized frequency are obtained, one is a function of the first moments of the counting operator and the second is a function of differences along the diagonal of the density matrix. These results will be used in the next section for an example sound-wave interaction.

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Applying Hamilton's equations to the Hamiltonian introduced in equation (2.1) produces

$$\dot{\theta}_p = \omega_p + \tfrac{3}{2}\epsilon \sum_{s_p JK} c_{pjk} \sqrt{\frac{I_j I_k}{I_p}}\, \mathrm{e}^{\mathrm{i}\theta_{PJK}}. \tag{5.1}$$

This equation is easily converted to its quantum mechanical form by using the notation developed in § 2. Substituting $\sqrt{\hbar} q_I$ for $I_i^{1/2}\mathrm{e}^{\mathrm{i}s_i\theta_i}$ and defining $\widehat{\omega}_p'$ to be the resulting frequency operator in place of the classical frequency $\dot{\theta}_p$ produces

$$\widehat{\omega}_p' = \omega_p + \tfrac{3}{2}\hbar^{1/2}\epsilon \sum_{s_p JK} c_{pjk} \frac{q_J q_K}{q_{-P}}, \tag{5.2}$$

where the $1/q_P$ operator is defined by

$$\frac{1}{q_P} q_P = q_P \frac{1}{q_P} = I. \tag{5.3}$$

Calculating the expected value of the renormalized frequency for the equilibrium distribution produces the equivalent expressions

$$\langle \widehat{\omega}_p' \rangle = \omega_p - 9\hbar\epsilon^2 \sum_{s_p JK} c_{pjk}^2 \mathcal{P}\left(\frac{1}{\omega_{PJK}}\right)\left(s_j\langle N_k + \tfrac{1}{2}\rangle_0 + s_k\langle N_j + \tfrac{1}{2}\rangle_0\right) \tag{5.4}$$

and

$$\langle \widehat{\omega}_p' \rangle = \omega_p - 9\hbar\epsilon^2 \sum_{\substack{\boldsymbol{n} \\ s_p JK}} c_{pjk}^2 \mathcal{P}\left(\frac{1}{\omega_{PJK}}\right) n_J n_K \left(\rho_{0\boldsymbol{n}\boldsymbol{n}} - \rho_{0\boldsymbol{n}+\boldsymbol{e}_{PJK},\boldsymbol{n}+\boldsymbol{e}_{PJK}}\right). \tag{5.5}$$

Taking the classical limits of these expressions reproduce the two results in PR.

PR also present a second method for computing $\langle\dot{\theta}\rangle$ where the angles in the probability density are allowed to range over the entire real line and $\langle\dot{\theta}\rangle$ is computed by integrating $\theta\,\mathrm{d}P/\mathrm{d}t$. Their method cannot be used here because there is no angle operator in quantum mechanics.

6. Sound-wave interaction

In this section we use the model Hamiltonian presented in PR for a semi-dispersive barotropic material to calculate the frequency shift due to nonlinear wave interaction. First, we reformulate the model so as to eliminate their problem with double-counting. The model produces an infinite frequency shift due to zero-point action. We resolve this by incorporating the unmeasurable frequency shift into the free Hamiltonian. We then calculate the frequency shift for low and high temperatures. The high temperature frequency shift is the same as that derived in PR except for the numerical coefficient. This occurs because we do not need to approximate the integral because of the non-convergent classical Bose distribution.

The Hamiltonian for sound-wave interaction is written in terms of the Fourier transforms of the velocity potential Φ and the departure ρ' from the equilibrium density ρ. We use the Fourier components of the departure and the velocity potential, $\rho_{\boldsymbol{k}}$ and $\Phi_{\boldsymbol{k}}$, to write the Hamiltonian in the form introduced in the beginning of § 2.

The total Hamiltonian is written as $\boldsymbol{H} = \boldsymbol{H}_0 + \epsilon \boldsymbol{H}_1$ where the free Hamiltonian is

$$\boldsymbol{H}_0 = \tfrac{1}{2} V \sum_{\boldsymbol{k}} \left\{ \frac{v^2}{\rho} |\rho_{\boldsymbol{k}}|^2 + \rho |\boldsymbol{k} \varPhi_{\boldsymbol{k}}|^2 \right\}, \tag{6.1}$$

the interaction Hamiltonian is

$$\epsilon \boldsymbol{H}_1 = \tfrac{1}{6} V \sum_{\boldsymbol{ijk}} \left\{ \frac{v^2}{\rho^2} \left(\frac{2\rho}{v} \frac{\mathrm{d}v}{\mathrm{d}\rho} - 1 \right) \rho_{\boldsymbol{i}} \rho_{\boldsymbol{j}} \rho_{\boldsymbol{k}} \right.$$
$$\left. - \rho_{\boldsymbol{i}} (\boldsymbol{j} \cdot \boldsymbol{k}) \varPhi_{\boldsymbol{j}} \varPhi_{\boldsymbol{k}} - \rho_{\boldsymbol{j}} (\boldsymbol{i} \cdot \boldsymbol{k}) \varPhi_{\boldsymbol{i}} \varPhi_{\boldsymbol{k}} - \rho_{\boldsymbol{k}} (\boldsymbol{i} \cdot \boldsymbol{j}) \varPhi_{\boldsymbol{i}} \varPhi_{\boldsymbol{j}} \right\} \delta_{\boldsymbol{i}+\boldsymbol{j}+\boldsymbol{k}}, \tag{6.2}$$

V is the volume of the system, v is the unperturbed speed of sound, and the Kronecker delta function for a 3-vector is $\delta_{\boldsymbol{k}} = \prod_{i=1}^{3} \delta_{k_i,0}$.

We transform to action-angle coordinates by writing the Fourier components in terms of waves traveling in antiparallel directions:

$$\rho_{\boldsymbol{k}} = \left(\frac{\rho \omega_{\boldsymbol{k}}}{2Vv^2} \right)^{1/2} \sum_{s_k} I_{s_k \boldsymbol{k}}^{1/2} \exp(\mathrm{i} s_k \theta_{s_k \boldsymbol{k}}), \tag{6.3}$$

$$\varPhi_{\boldsymbol{k}} = \left(\frac{\omega_{\boldsymbol{k}}}{2V\rho k^2} \right)^{1/2} \sum_{s_k} \mathrm{i} s_k I_{s_k \boldsymbol{k}}^{1/2} \exp(\mathrm{i} s_k \theta_{s_k \boldsymbol{k}}). \tag{6.4}$$

In these equations, we have abbreviated $s_{\boldsymbol{k}}$ by s_k to improve the readability of the equations.

We then change the summation indices from $\boldsymbol{i}$, $\boldsymbol{j}$, and $\boldsymbol{k}$ to $s_i \boldsymbol{i}$, $s_j \boldsymbol{j}$, and $s_k \boldsymbol{k}$ and observe that $\omega_{s_k \boldsymbol{k}} = \omega_{\boldsymbol{k}}$ because the fluid is isotropic. The notation developed in § 2 can now be used and the Hamiltonian becomes

$$\boldsymbol{H}_0 = \sum_{\boldsymbol{k}} \omega_{\boldsymbol{k}} I_{\boldsymbol{k}}, \tag{6.5}$$

$$\boldsymbol{H}_1 = \sum_{IJK} c_{IJK} I_{ijk}^{1/2} \mathrm{e}^{\mathrm{i}\theta_{IJK}}, \tag{6.6}$$

where

$$\epsilon c_{IJK} = \frac{1}{6} \left(\frac{\omega_{\boldsymbol{i}}\, \omega_{\boldsymbol{j}}\, \omega_{\boldsymbol{k}}}{8V\rho v^2} \right)^{1/2} \left(\frac{2\rho}{v} \frac{\mathrm{d}v}{\mathrm{d}\rho} - 1 + \hat{\imath} \cdot \hat{\jmath} + \hat{\imath} \cdot \hat{k} + \hat{\jmath} \cdot \hat{k} \right) \delta_{s_i \boldsymbol{i} + s_j \boldsymbol{j} + s_k \boldsymbol{k}}, \tag{6.7}$$

$\omega_{\boldsymbol{k}} = \rho k / v$, and $I_{ijk} = I_{\boldsymbol{i}} I_{\boldsymbol{j}} I_{\boldsymbol{k}}$.

To simplify this system we anticipate that $s_i \omega_{\boldsymbol{i}} + s_j \omega_{\boldsymbol{j}} + s_k \omega_{\boldsymbol{k}} = o(1)$ is the region of interest. In the semidispersive case, $s_i \omega_{\boldsymbol{i}} + s_j \omega_{\boldsymbol{j}} + s_k \omega_{\boldsymbol{k}} = 0$, which, with the condition $s_i \boldsymbol{i} + s_j \boldsymbol{j} + s_k \boldsymbol{k} = 0$ from the Kronecker delta in equation (6.7), produces

$$\epsilon c_{IJK} = \frac{G}{3} \left(\frac{\omega_{\boldsymbol{i}}\, \omega_{\boldsymbol{j}}\, \omega_{\boldsymbol{k}}}{8V\rho v^2} \right)^{1/2} \delta_{s_i \boldsymbol{i} + s_j \boldsymbol{j} + s_k \boldsymbol{k}}, \tag{6.8}$$

where G is defined in equation (1.16). We can now separate the sign-dependent term from c_{IJK} by defining

$$\epsilon c_{ijk} = \frac{G}{3} \left(\frac{\omega_{\boldsymbol{i}}\, \omega_{\boldsymbol{j}}\, \omega_{\boldsymbol{k}}}{8V\rho v^2} \right)^{1/2} \tag{6.9}$$

so that

$$c_{IJK} = c_{ijk} \delta_{s_i \boldsymbol{i} + s_j \boldsymbol{j} + s_k \boldsymbol{k}}. \tag{6.10}$$

We now have the Hamiltonian stated in a form similar to the form introduced in § 2.

The interaction Hamiltonian introduced in the beginning of § 2 involves the angles through a product of three cosines. This Hamiltonian does not have that feature because c_{IJK} also depends on the signs s_i, s_j, and s_k through $\delta_{s_i\boldsymbol{i}+s_j\boldsymbol{j}+s_k\boldsymbol{k}}$. Thus, instead of substituting $\frac{1}{2}\hbar^{1/2}(q^\dagger + q)$ for $I^{1/2}\cos\theta$, we must substitute $\hbar^{1/2}q^\dagger$ and $\hbar^{1/2}q$ for $I^{1/2}\mathrm{e}^{\mathrm{i}\theta}$ and $I^{1/2}\mathrm{e}^{-\mathrm{i}\theta}$ respectively.

The difference between the two interaction models only causes problems when selecting the essential resonances to compute $\partial\hat{\alpha}_0/\partial\tau_2$. However, since (L, M, N) is one of the six permutations of $(-I, -J, -K)$ for resonance and since $c_{-I-J-K} = c_{IJK}$, we can write c_{IJK} for c_{ijk} in the results from the previous sections.

(*a*) *Zero temperature renormalization*

In this section we calculate an explicit expression for the zero temperature renormalization, that is, the change in frequency due to background zero-point action. At $T = 0\,\mathrm{K}$, $\langle N_j\rangle = 0$ for all j so that equation (5.4) becomes

$$\langle\widehat{\omega}_p'\rangle = \omega_p - \frac{G^2\hbar\omega_p}{8V\rho v^2}\sum_{s_p J} s_j\omega_j\omega_{s_p\boldsymbol{p}+s_j\boldsymbol{j}}\ \mathcal{P}\left(\frac{1}{s_p\omega_p + s_j(\omega_j + \omega_{s_p\boldsymbol{p}+s_j\boldsymbol{j}})}\right). \tag{6.11}$$

Writing the integral explicitly,

$$\sum_{\boldsymbol{j}}\cdot = \frac{V}{(2\pi)^3}\int\cdot\,\mathrm{d}\boldsymbol{j}, \tag{6.12}$$

produces the volume-independent expression

$$\langle\widehat{\omega}_p'\rangle = \omega_p - \frac{G^2\hbar\omega_p}{4\rho v^2}\frac{1}{(2\pi)^3}\,\mathrm{p.v.}\int\omega_j\left[\frac{\omega_{\boldsymbol{p}+\boldsymbol{j}}}{\omega_p + \omega_j + \omega_{\boldsymbol{p}+\boldsymbol{j}}} - \frac{\omega_{\boldsymbol{p}-\boldsymbol{j}}}{\omega_p - \omega_j - \omega_{\boldsymbol{p}-\boldsymbol{j}}}\right]\mathrm{d}\boldsymbol{j}. \tag{6.13}$$

Note that the integrand grows like j^3 as $|\boldsymbol{j}| \to \infty$ and that unlike PR, we do not have a bounded quantity such as the free-energy, $\int\omega_j\langle I_j\rangle\,\mathrm{d}\boldsymbol{j}$, to bound the integral. One method to bound this integral would be to limit the wavenumber $\boldsymbol{j}$ by the inverse of the inter-molecular spacing, ℓ. This would produce a frequency shift of order $G^2\hbar\omega_p/\rho v\ell^4$; however, the magnitude of this number is much larger than the unperturbed frequency ω_p so this method is useless for computing the frequency shift. We note that this problem does not occur in the classical analysis because $\hbar = 0$ removes the infinite integral.

The problem with the unbounded magnitude of this integral is not caused by the bounds on the integral. It is caused by the formulation of the original problem. We began with a set of equations which were valid for the classical problem with a bounded free energy or for the quantum mechanical problem for a small ω. The bounded free energy in the classical problem prevented the non-physical values of c_{ijk} for large ω from contributing to the integral for the frequency shift. We lost this feature of the classical analysis when we transformed the classical problem to a quantum mechanical problem. Thus, we cannot calculate the frequency shift at $T = 0\,\mathrm{K}$ without reformulating the interaction model. Instead, we incorporate the $T = 0\,\mathrm{K}$ frequency shift into the unrenormalized frequency. We do this by reformulating the Hamiltonian and regarding the right-hand side of equation (6.13) as a finite, unmeasurable quantity.

In short, the physical speed of sound differs from the parameter v by a function which depends upon the nonlinear interactions even at 0 K. This difference is not a small parameter, in contrast with Gurevich & Laikhtman (1979), and we now recast the theory in terms of physically measurable parameters.

In order to incorporate the $T = 0$ K frequency shift into the free Hamiltonian, we need a diagonal operator, $\epsilon^2 \boldsymbol{H}_\omega$, such that

$$\boldsymbol{H}_{\omega \boldsymbol{n}+\boldsymbol{e}_p, \boldsymbol{n}+\boldsymbol{e}_p} - \boldsymbol{H}_{\omega \boldsymbol{n}\boldsymbol{n}} = \hbar \omega^{(2)}_{p,\boldsymbol{0}}, \tag{6.14}$$

where

$$\omega^{(2)}_{p,\boldsymbol{0}} = -\tfrac{9}{2}\hbar \sum_{s_p JK} c^2_{PJK} \mathcal{P}\left(\frac{1}{\omega_{PJK}}\right)(s_j + s_k) \tag{6.15}$$

is the $T = 0$ K shift from the right-hand side of equation (6.11). Note that

$$\boldsymbol{H}_\omega = -\tfrac{9}{2}\hbar^2 \sum_{IJK} c^2_{IJK} \mathcal{P}\left(\frac{1}{\omega_{PJK}}\right)(N_i + \tfrac{1}{2})(s_j + s_k) \tag{6.16}$$

satisfies this criterion where N_i is the counting operator for state i. We now write the total Hamiltonian as

$$\boldsymbol{H} = \boldsymbol{H}'_0 + \epsilon \boldsymbol{H}_1 - \epsilon^2 \boldsymbol{H}_\omega, \tag{6.17}$$

where

$$\boldsymbol{H}'_0 = \hbar \boldsymbol{\omega}^0 \cdot (\boldsymbol{N} + \tfrac{1}{2}\boldsymbol{1}) \tag{6.18}$$

is the perturbed free Hamiltonian and $\omega^0_p = \omega_p + \epsilon^2 \omega^{(2)}_{p,\boldsymbol{0}}$ is the $T = 0$ K frequency.

If we repeat the analysis in § 6 *a* and use a superscript '0' to designate the $T = 0$ K frequency, we obtain equation (3.1) with $\Delta^+(\omega_{IJK})$ replaced by $\Delta^+(\omega^0_{IJK})$ for the $\mathcal{O}(\epsilon)$ correction. The $\mathcal{O}(\epsilon^2)$ equation of motion must also be modified by the $\mathcal{O}(\epsilon^2)$ perturbation in equation (6.17). The non-secular terms reproduce equation (3.4) for $\hat{\rho}_2$ with ω_{IJK} and ω_{LMN} replaced by ω^0_{IJK} and ω^0_{LMN} respectively. Instead of equation (3.2), the secular terms produce

$$\begin{aligned}\frac{\mathrm{d}\rho_{0\boldsymbol{m}\boldsymbol{n}}}{\mathrm{d}t} &= \mathrm{i}\boldsymbol{\omega}^0 \cdot (\boldsymbol{n} - \boldsymbol{m})\rho_{0\boldsymbol{m}\boldsymbol{n}} \\ &\quad + 6\hbar \sum_{IJK} c^2_{IJK}\delta(\omega^0_{IJK})[\sqrt{m_{IJK} n_{IJK}}\, \rho_{0\boldsymbol{m}+\boldsymbol{e}_{IJK}, \boldsymbol{n}+\boldsymbol{e}_{IJK}} \\ &\quad - (m_{IJK} + n_{-I-J-K})\rho_{0\boldsymbol{m}\boldsymbol{n}} + \sqrt{m_{-I-J-K} n_{-I-J-K}}\, \rho_{0\boldsymbol{m}-\boldsymbol{e}_{IJK}, \boldsymbol{n}-\boldsymbol{e}_{IJK}}] \\ &\quad - \left[9\mathrm{i}\hbar \sum_{IJK} c^2_{IJK} \mathcal{P}\left(\frac{1}{\omega^0_{IJK}}\right) s_i (n_j n_k - m_j m_k)\right]\rho_{0\boldsymbol{m}\boldsymbol{n}}\end{aligned} \tag{6.19}$$

for the master equation. We recognize the last term on the right-hand side of this equation as the frequency shift due to the interaction. The modifications to the first and second order corrections (3.3) and (3.4) are similar.

(*b*) *The* $T > 0$ K *frequency shift*

Now that we have a finite frequency, we are ready to use the Planck distribution derived in § 3 *e* to calculate the contribution to the frequency shift due to occupied states in the case of small dispersion. We perform asymptotic analyses to evaluate the shift for low and high temperatures. The form of the high-temperature shift agrees with the calculations performed in PR. Details of the calculation are summarized in the appendix.

Using the definition for ω_p^0 following equation (6.18) enables us to rewrite equation (5.4) as $\langle\omega_p'\rangle = \omega_p^0 + \Delta\omega_p$ where

$$\Delta\omega_p = -18\hbar\epsilon^2 \sum_{s_pJK} c_{PJK}^2 \mathcal{P}\left(\frac{1}{\omega_{PJK}}\right) s_j\langle N_k\rangle_0. \tag{6.20}$$

We define the mean free energy U by its difference from the zero-point energy:

$$U = \frac{1}{V}\sum_{\boldsymbol{k}} \hbar\omega_k\langle N_{\boldsymbol{k}}\rangle \sim \frac{24\pi\zeta(4)\hbar v}{(2\pi)^3(\beta\hbar v)^4}, \tag{6.21}$$

where $\zeta(s)$ is the Riemann zeta function and $\zeta(4) = \pi^4/90 \approx 1.08$.

Then the low temperature limit $\beta\hbar vp \gg 1$ is

$$\Delta\omega_p \sim \frac{G^2U\omega_p}{2\rho v^2}\left[\ln\left(\frac{4v^2}{3|\gamma|p^2}\right) - 3\right] + \mathcal{O}\left(\gamma + \frac{1}{(\beta\hbar vp)^2}\right), \tag{6.22}$$

which is equivalent to equation (1.15). Note that the group velocity $\mathrm{d}\langle\omega_p'\rangle/\mathrm{d}p$ diverges as $\ln p$ as $p \to 0$ provided $\beta\hbar vp$ remains large. That is, the group velocity diverges in the limit of long wavelengths provided that the energy β^{-1} of the system is small compared with the energy $\hbar vp$ of the wave.

The high temperature limit $\beta\hbar vp \ll 1$ is

$$\Delta\omega_p \sim \frac{G^2U\omega_p}{2\rho v^2}\left[\ln\left(\frac{4(\beta\hbar)^2v^4}{3|\gamma|}\right) - 3 - \frac{(\Gamma(4)\zeta(4))'}{3\zeta(4)}\right] + \mathcal{O}\left(\gamma + (\beta\hbar vp)^2\right). \tag{6.23}$$

If we define $k_\gamma = v/|\gamma|^{1/2}$ to be the characteristic wavenumber separating the regimes of weak and strong dispersion and define $k_T = 1/\beta\hbar v$ to be the characteristic wavenumber for thermal waves, equation (6.23) reduces to equation (1.17). The condition that $\gamma k^2/v^2 \ll 1$ for wavenumbers contributing significantly to the integral in equation (A 5) means that $k_T \ll k_\gamma$. Note that the group velocity does not diverge as $p \to 0$ in the high temperature limit.

Thus, in the high temperature limit, we see a large, $\mathcal{O}(\ln(k_T/k_\gamma))$, positive frequency shift which has a relative magnitude, $\Delta\omega_p/\omega_p$, independent of the wavenumber of the affected wave. This is significantly different from the low temperature limit for which the relative magnitude of the frequency shift is $\mathcal{O}(\ln(v^2/|\gamma|p^2))$, that is, it is proportional to the logarithm of the relative dispersion for the affected wave.

7. Conclusion

In this paper we set out to develop a theory spanning both quantum and classical theory for the nonlinear interaction of waves at the Fokker–Planck level. We have developed a quantum mechanical theory which complements the classical analysis performed in PR. We demonstrated this through a new method to calculate the classical limit from the quantum mechanical results. The reverse transformation has not been achieved. In particular, the high-temperature frequency shift we calculated here is based on a convergent integral as opposed to the non-convergent classical Bose distribution used in PR.

As part of this theory we have presented an alternative to classical limit procedures such as Wigner's transform. We demonstrated that our classical limit procedure does not have some of the problems inherent in other classical limit procedures. This procedure merits further study, particularly to extend it to free Hamiltonians producing a different space of eigenfunctions than the Fourier transform eigenfunctions produced by a system of independent linear oscillators.

The master equation was derived here using a multiple timescale analysis. Because the canonical transform and unitary transform methods predict oscillatory solutions instead of dissipative solutions, we had to demonstrate that the oscillatory solutions are actually dissipative in the thermodynamic limit. That analysis is performed in Sinclair (1992) and Sinclair (1997). In addition to calculating the thermodynamic limits of the transform solutions, we show that the transform solutions can also be obtained from the results of our multiple timescale analysis.

We have also investigated black body radiation by an atom in an electromagnetic field by performing this multiple timescale analysis on a nonlinear oscillator interacting weakly with a bath of linear oscillators. This problem proved to be intractable at the Fokker–Planck level because of secular terms caused by the derivative of the frequency of the nonlinear oscillator. In addition to the problems encountered in this analysis, Sinclair (1992) asserts that $\mathcal{O}(\epsilon^n t^{n-1})$ secularities are encountered when the free Hamiltonian only consists of linear oscillators and higher-order regular perturbation analysis is attempted. Thus, the extension of the multiple timescales analysis to $\mathcal{O}(\epsilon^3)$ and higher appears to be an open issue.

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Appendix A. $T > 0\,$K frequency shift calculation

This appendix summarizes the details of the calculations for the $T > 0\,$K frequency shift in § 6 *b*.

First, we substitute the Planck distribution (3.42) and the coupling coefficient c_{PJK} defined by equations (6.9) and (6.10), multiply the numerator and denominator by s_p and replace $s_p s_j$ and $s_p s_k$ by s_j and s_k respectively. We then eliminate the sum over s_p by multiplying the series by 2 so that

$$\Delta\omega_p = \frac{G^2\hbar\omega_p}{(2\pi)^3\rho v^2}\,\text{p.v.}\int \omega_k \left[\frac{\omega^2_{\boldsymbol{p}+\boldsymbol{k}}}{(\omega_p+\omega_k)^2-\omega^2_{\boldsymbol{p}+\boldsymbol{k}}} + \frac{\omega^2_{\boldsymbol{p}-\boldsymbol{k}}}{(\omega_p-\omega_k)^2-\omega^2_{\boldsymbol{p}-\boldsymbol{k}}}\right]\frac{1}{\mathrm{e}^{\beta\hbar\omega_k}-1}\,\mathrm{d}\boldsymbol{k}. \tag{A 1}$$

We now select the coordinate system for $\boldsymbol{k}$ so that $\boldsymbol{p}\cdot\boldsymbol{k} = pk\mu$ where $-1 \leqslant \mu \leqslant 1$ and

$$\int \cdot\,\mathrm{d}\boldsymbol{k} = \int_0^\infty \int_{-1}^1 \int_0^{2\pi} \cdot\, k^2\,\mathrm{d}\phi\,\mathrm{d}\mu\,\mathrm{d}k. \tag{A 2}$$

We also introduce small dispersion for ω_k by using equation (8.20) of PR: $\omega_k^2 = v^2k^2 + \gamma k^4$ for $\gamma k^2/v^2 \ll 1$. This means that

$$(\omega_p \pm \omega_k)^2 - \omega^2_{\boldsymbol{p}\pm\boldsymbol{k}} \sim \pm\{2pkv^2(1-\mu) - 3\gamma pk(p\pm k)^2\} + o(\gamma). \tag{A 3}$$

Substituting this asymptotic relation into equation (A 1) and noting that

$$\text{p.v.}\int_{-1}^1 \frac{A+B\mu}{1-\mu+C}\,\mathrm{d}\mu = -2B + [A + B(1+C)]\ln\left(\frac{2+C}{|C|}\right) \tag{A 4}$$

yields

$$\begin{aligned}\Delta\omega_p \sim \frac{\pi G^2\hbar\omega_p}{2(2\pi)^3\rho v^2 p}\int_0^\infty \Bigg\{&4pk\left[\ln\left(\frac{4v^2}{3|\gamma|p^2}\right)-2\right]\\ &-p^2\left[\left(1+\frac{k}{p}\right)^2\ln\left(1+\frac{k}{p}\right)^2-\left(1-\frac{k}{p}\right)^2\ln\left(1-\frac{k}{p}\right)^2\right]\\ &+\mathcal{O}(\gamma)\Bigg\}\frac{\omega_k}{\mathrm{e}^{\beta\hbar\omega_k}-1}\,k\,\mathrm{d}k,\end{aligned}\tag{A 5}$$

where the approximation error in our expansion of the terms within the braces in the integrand is $\mathcal{O}(\gamma)$. Thus we ignore $\mathcal{O}(\gamma)$ terms in the remainder of the integrand and approximate ω_k by vk.

This expansion for small dispersion is only valid for $\gamma p^2/v^2 \ll 1$ and $\gamma k^2/v^2 \ll 1$. Although the range of integration in equation (A 5) is unbounded, the asymptotic bound on the wavenumber $\boldsymbol{k}$ can be achieved by requiring $\beta\hbar\omega_k \gg 1$ when $\gamma k^2/v^2 = \mathcal{O}(1)$. Thus, we require $\beta\hbar v^2/|\gamma|^{1/2} \gg 1$ which sets a lower bound on the inverse temperature β for equation (A 5).

In the low-temperature limit $\beta\hbar vp \gg 1$, we define $p' = \beta\hbar vp$, make the change of variables $u = k/p$, and substitute $\omega_k = vk$. We then evaluate the integral of the first term in the integrand exactly producing

$$\begin{aligned}\Delta\omega_p \sim{}& \frac{G^2U\omega_p}{2\rho v^2}\left[\ln\left(\frac{4v^2}{3|\gamma|p^2}\right)-2\right]\\ &-\frac{\pi G^2\hbar\omega_p}{2(2\pi)^3\rho v^2}vp^4\int_0^\infty[(1+u)^2\ln(1+u)^2-(1-u)^2\ln(1-u)^2]\frac{u^2}{\mathrm{e}^{p'u}-1}\,\mathrm{d}u\end{aligned}\tag{A 6}$$

plus an $\mathcal{O}(\gamma)$ error. Since $p' \gg 1$, the only values of u which contribute to the integral are $u \ll 1$. Performing a regular perturbation expansion of the term in brackets to $\mathcal{O}(u)$ and integrating produces the low temperature limit (6.22).

In the high temperature limit $p' \ll 1$ so that the integral in equation (A 6) is determined by $u \gg 1$. Expanding the term in brackets in the integral in equation (A 6) and retaining terms to $\mathcal{O}(1)$ in $1/u$ produces

$$\int_0^\infty [\cdot]\frac{u^2}{\mathrm{e}^{p'u}-1}\,\mathrm{d}u \sim \frac{8}{p'^4}\int_0^\infty\frac{w^3\ln w}{\mathrm{e}^w-1}\,\mathrm{d}w-\frac{24\zeta(4)(\ln p'^2-1)}{p'^4}\tag{A 7}$$

after the change of variables $w = p'u$. Since

$$\Gamma(s)\zeta(s)=\int_0^\infty\frac{z^{s-1}}{\mathrm{e}^z-1}\,\mathrm{d}z=\int_0^\infty\frac{\mathrm{e}^{(s-1)\ln z}}{\mathrm{e}^z-1}\,\mathrm{d}z\tag{A 8}$$

we have

$$\frac{\mathrm{d}}{\mathrm{d}s}\Big(\Gamma(s)\zeta(s)\Big)=\int_0^\infty\frac{(\ln z)\mathrm{e}^{(s-1)\ln z}}{\mathrm{e}^z-1}\,\mathrm{d}z=\int_0^\infty\frac{z^{s-1}\ln z}{\mathrm{e}^z-1}\,\mathrm{d}z\tag{A 9}$$

and the high temperature limit (6.23) is obtained.

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