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The solution to the 4-phonon Boltzmann equation for a 1D chain in a thermal gradient

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Abstract

The phonon distribution function in a weakly anharmonic one-dimensional chain in a thermal gradient is determined in the high temperature or, equivalently, classical regime. Thermal relaxation is dominated by 4-phonon scattering processes in this limit and these are treated using Peierls' Boltzmann equation approach. An analytical analysis of the Boltzmann equation for small wave vector k shows that the distribution is singular and that this singularity at $k = 0$ is of the form of an infinite sum of power law branch points with powers that are rational and dense on the real axis above some critical value. The value of the smallest discrete power implies that the thermal conductivity is infinite in the thermodynamic limit. For finite systems, whenever 4-phonon scattering is the dominant mechanism inhibiting energy transport, the thermal conductivity will scale as (system length)$^{2/5}$/(temperature)$^{6/5}$.

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1. Introduction

There is a long history of interest in the thermal transport properties of one-dimensional arrays of particles. Some of it stems from the Fermi, Pasta and Ulam puzzle (cf the review by Ford [1]) of the lack of energy sharing between modes in small systems; there is also the allure of the simplicity of one-dimensional systems compared to those in two and three. The review by Lepri *et al* [2] shows that computer simulations have continued to play a significant role in recent years while the theoretical work has been largely confined to making estimates of scaling behaviour with system size, temperature, frequency, etc. There can be considerable difficulty in relating the theory and simulation because in both cases one needs to know when the results are in the appropriate asymptotic limit. Detailed calculations and explicit results based on microscopic models can clearly provide guidance and the present paper is a first step for the case of a nearly harmonic system that relaxes by 4-phonon scattering. Somewhat surprisingly, one can get quite far in solving the Boltzmann equation for this problem by purely analytic methods.

Peierls' derivation and description [3] of the phonon Boltzmann equation is now standard textbook material (cf Peierls [4] or Lifshitz and Pitaevskii [5] and also Maradudin *et al* [6] as a useful source for technical detail) and I will only record a few relevant formulae here to establish notation. The specific model treated below is that of equal mass particles on a line and interacting via nearest-neighbour forces. A crucial observation by Peierls is that energy and (pseudo) momentum conservation prevents 3-phonon scattering processes from occurring which reduces to zero the leading effect of cubic anharmonicity. Thus for understanding what happens in the weak anharmonic limit one can take, without loss of generality, the model classical Hamiltonian as the harmonic plus quartic

$$H = \sum_i \left(\frac{1}{2} p_i^2 \big/ m + \frac{1}{2} K_2\, \delta x^2_{i+\frac{1}{2}} + \frac{1}{4} K_4 \delta x^4_{i+\frac{1}{2}} \right) \tag{1}$$

where the sum extends over the N particles in the chain with $x_{i+N} = x_i$ while $\delta x_{i+\frac{1}{2}} = x_{i+1} - x_i - a$ is the deviation of a nearest-neighbour pair from the equilibrium spacing a. The equilibrium spacing can have no dynamical effect and the final formulae will be written to be explicitly independent of it. Thus, for example, Fourier transforms are defined by particle number rather than particle position resulting in N independent wave vectors $k_n = 2\pi n/N$ on any interval of length 2π. The quantum-mechanical version of (1) in terms of phonon annihilation and creation operators is

$$H = \sum_k \hbar\omega_k a_k^\dagger a_k + (3/8N)\hbar^2 \left(K_4 \big/ K_2^2\right) \sum_{\{k\}} (\omega_{k1}\omega_{k2}\omega_{k3}\omega_{k4})^{1/2} a_{k1}^\dagger a_{k2}^\dagger a_{k3} a_{k4} \tag{2}$$

where the sum over the four wave vectors in the last term is constrained by $\Sigma k_i = 0 \bmod 2\pi$. The phonon frequency

$$\omega_k = \omega_{ZB} \left|\sin \tfrac{1}{2}k\right|, \qquad \omega_{ZB} = 2(K_2/m)^{1/2} \tag{3}$$

has its maximum ω_{ZB} at the Brillouin zone boundary. It is this very simple form of ω_k that makes the calculations described below possible although the qualitative features of the singularity structure of the results are almost certainly generic and dependent only on the fact that the leading deviation of ω_k from linearity is a term $\propto k^3$.

The Boltzmann equation for a steady-state situation is the equality of a rate of change of a density due to transport with that due to collisions with the approximation that memory effects are absent so that the collisions depend only on local conditions. For the situation of a steady-state temperature gradient, one imagines the local densities to be that of phonon wave packets whose size is large compared to their mean wavelength but small compared to their collision mean free path. This requires that K_4 in the Hamiltonian (1) or (2) be appropriately small—a restriction I take as given in everything that follows. One need not actually construct wave packets; it is legitimate to use the phonon occupation number n_k as a proxy for the local density and take the rate of change due to transport as $u_k \partial n_k/\partial x$ provided one identifies u_k as the phonon group velocity, i.e. $u_k = \mathrm{d}\omega_k/\mathrm{d}k$. To linear order in the temperature gradient one can rewrite the gradient $\partial n_k/\partial x$ as $\frac{\partial n_k}{\partial T} \cdot \frac{\partial T}{\partial x}$ and replace $\partial n_k/\partial T$ by $\partial\, {}^{\mathrm{eq}}n_k/\partial T$ where the equilibrium density ${}^{\mathrm{eq}}n_k$ is the Bose factor $1/(\exp(\hbar\omega_k/k_B T) - 1)$. The resulting transport term is

$$u_k \partial n_k/\partial x = \tfrac{1}{2} \cot \tfrac{1}{2}k\; {}^{\mathrm{eq}}n_k ({}^{\mathrm{eq}}n_k + 1)(\hbar\omega_k/k_B T)^2 k_B \nabla T/\hbar \tag{4}$$

where $\nabla T = (T_{i+j} - T_i)/j$ is the constant temperature gradient on a particle basis thus making it independent of the lattice spacing a. The collision term in the Boltzmann equation is the Fermi golden rule rate based on the second term in (2) and one can show that the only process that is allowed by energy conservation is the scattering $k + k_3 \leftrightarrow k_1 + k_2$. The difference between the scattering rate out of state k and into k depends on the phonon distribution n_k and vanishes if this distribution is the equilibrium ${}^{\mathrm{eq}}n_k$. Standard practice is to write the deviation from equilibrium in terms of a new function g_k defined by

$$\delta n_k = n_k - {}^{\mathrm{eq}}n_k = {}^{\mathrm{eq}}n_k({}^{\mathrm{eq}}n_k + 1)g_k \tag{5}$$

in which case the net collision rate to linear order in g is

$$\begin{aligned} R_k(g) = -(9/16\pi)\hbar^2\big(K_4^2\big/K_2^4\big)\int \mathrm{d}k_1 \int \mathrm{d}k_2\, \omega_k\omega_{k1}\omega_{k2}\omega_{k3} \\ \times {}^{\mathrm{eq}}n_k\, {}^{\mathrm{eq}}n_{k3}({}^{\mathrm{eq}}n_{k1}+1)({}^{\mathrm{eq}}n_{k2}+1)\delta(\omega_k-\omega_{k1}-\omega_{k2}+\omega_{k3}) \\ \times (g_k - g_{k1} - g_{k2} + g_{k3}) \end{aligned} \tag{6}$$

where the k_1, k_2 integrations are understood to be over an interval of 2π and $k_3 = k_1 + k_2 - k \bmod 2\pi$. Now make the high temperature, or equivalently, classical approximation of ${}^{\mathrm{eq}}n_k \approx {}^{\mathrm{eq}}n_k + 1 \approx k_B T/\hbar\omega_k$. The Boltzmann equation, namely the equality of (4) and (6), then simplifies to

$$\begin{aligned} \frac{1}{2}\cot\frac{1}{2}k\, k_B\nabla T/\hbar = -(9/16\pi)\big(K_4^2\big/K_2^4\big)(k_B T)^4/\hbar^2 \\ \times \int \mathrm{d}k_1 \int \mathrm{d}k_2\, \delta(\omega_k-\omega_{k1}-\omega_{k2}+\omega_{k3})(g_k-g_{k1}-g_{k2}+g_{k3}). \end{aligned} \tag{7}$$

By introducing a new deviation function χ that is just a rescaled g defined by

$$g = -(16\pi/9)\big(K_2^4\big/K_4^2\big)\hbar\omega_{ZB}/(k_B T)^4 k_B \nabla T\,\chi, \tag{8}$$

the Boltzmann equation (7) becomes the dimensionless and parameter independent

$$\frac{1}{2}\cot\frac{1}{2}k = I_k(\chi), \tag{9a}$$

$$I_k(\chi) = \int \mathrm{d}k_1 \int \mathrm{d}k_2\, \omega_{ZB}\delta(\omega_k-\omega_{k1}-\omega_{k2}+\omega_{k3})(\chi_k-\chi_{k1}-\chi_{k2}+\chi_{k3}) \tag{9b}$$

where again $k_3 = k_1 + k_2 - k \bmod 2\pi$ is understood. It is the invariant Boltzmann equation (9*a*) and associated dimensionless collision integral (9*b*) that I will analyse in detail in the sections below.

In section 2 the solution to the kinematical problem of 4-phonon scattering will be given together with the evaluation of the kinematical integral $\int \mathrm{d}k_1 \int \mathrm{d}k_2\, \omega_{ZB}\delta(\omega_k-\omega_{k1}-\omega_{k2}+\omega_{k3})$. In section 3 these results are extended by a local analysis of equation (9*a*) near $k = 0$. I find that χ is singular at $k = 0$, the singularity being of the form of a sum of branch points of the form k^p with $p = 2\,(3m-1)/3^n$ and $2(3m+1)/3^n$, $m, n = 0, 1, 2, \ldots, \infty$. The amplitudes of the leading terms are determined explicitly; for example

$$\chi = A(2/k)^{2/3} + O(1/k^{2/9}), \qquad A = (3/64)2^{2/3}/B(1/3, 1/3) \tag{10}$$

where $B(x, y) = \Gamma(x)\Gamma(y)/\Gamma(x+y)$ is the beta function. This local analysis is supplemented with numerical work in section 4 to determine χ for all k. Incorporation of the dominant known singular terms into the numerical approximation is crucial for obtaining rapid numerical convergence. With about 60 singular terms plus a 20-term Chebyshev polynomial expansion one can achieve equality of the two sides of equation (9*a*) to a few parts in 10^{12}. A phenomenological fit to the essentially exact numerical solution is

$$\chi \approx A\cos\frac{1}{2}k\left[1\Big/\left(\sin\frac{1}{2}k\right)^{2/3}+2.9013\Big/\left(\sin\frac{1}{2}k\right)^{2/9}-5.7269\Big/\left(\sin\frac{1}{2}k\right)^{2/27}\right.$$
$$\left.+3.7800+0.5897\left(\sin\frac{1}{2}k\right)^{2/3}-0.6820\left(\sin\frac{1}{2}k\right)^{4/3}\right],\qquad 0<k<2\pi \tag{11}$$

with A given in (10). The relative accuracy of (11) is better than 0.1% and gives the leading divergence at small k exactly.

The divergence of χ at small k has implications for the thermal conductivity of the 4-phonon scattering model. For a chain of N particles, the energy density in mode k is $n_k\hbar\omega_k/(Na)$ and the net energy current carried by this mode is $J_k = u_k\delta n_k\hbar\omega_k/(Na)$. In the classical regime δn_k given in (5) reduces to $(k_BT/\hbar\omega_k)^2 g_k$ so we get $J_k = \frac{1}{2}\cot\frac{1}{2}k(k_BT)^2 g_k/(N\hbar)$ and on using (8),

$$J_k = -(16\pi/9N)\left(K_2^4\big/K_4^2\right)\frac{\omega_{ZB}}{k_BT^2}\nabla T\frac{1}{2}\cot\frac{1}{2}k\chi_k. \tag{12}$$

The total energy current is $J_\varepsilon = (N/2\pi)\int \mathrm{d}k\, J_k$ while the thermal conductivity κ, here defined on a particle number basis as is ∇T, is the coefficient in $J_\varepsilon = -\kappa\nabla T$. Thus our formal expression for the thermal conductivity in the thermodynamic limit is

$$\kappa = \omega_{ZB}k_B\frac{8}{9}\frac{K_2^4}{(K_4k_BT)^2}\int \mathrm{d}k\frac{1}{2}\cot\frac{1}{2}k\chi_k \tag{13}$$

where the integration interval is $0<k<2\pi$. Since the integral diverges at both endpoints we confirm, the by now well-accepted expectation, that κ as a thermodynamically intensive quantity in one-dimensional systems does not exist. However, (13) can still be used to estimate the thermal conductivity of samples of finite length. Clearly our expression (12) of the mode current J_k must be replaced for those k for which the mean free path exceeds the sample length. Approximations appropriate in this case are discussed in section 5 and I conclude that the conductivity of a large but finite sample of N particles is approximately given by

$$\kappa(N) \approx 5\omega_{ZB}k_B(N/4\pi)^{2/5}\left[(8A/9)K_2^4\big/(K_4k_BT)^2\right]^{3/5} \tag{14}$$

with $A \approx 0.014\,04$ as given in (10).

2. Kinematics

Peierls showed that on a linear chain with the simple dispersion law $\omega_k = \omega_{ZB}|\sin\frac{1}{2}k|$ energy and momentum conservation laws prevent a single phonon from breaking up into two or conversely two combining into one. That is, 3-phonon processes cannot change the occupation number distribution. Consequently, cubic terms in the Hamiltonian can only lead to effects of higher order than calculated in the present paper and this is the reason they were not included in (1) and (2). For four phonons it is also the case that one phonon cannot break up into three so that the only relevant 4-phonon process is the scattering $k+k_3 \leftrightarrow k_1+k_2$. As a first step in determining the effect of such scattering one needs to find the combinations allowed by energy and (pseudo) momentum conservation, namely

$$\left|\sin\tfrac{1}{2}k\right|+\left|\sin\tfrac{1}{2}k_3\right| = \left|\sin\tfrac{1}{2}k_1\right|+\left|\sin\tfrac{1}{2}k_2\right|,\qquad k+k_3 = k_1+k_2 \bmod 2\pi. \tag{15}$$

Two of the four momenta are to be specified but with k and k_3 fixed the solutions to (15) for, say, k_1 are not single valued. This can be seen simply by noting that if k_1 is a solution

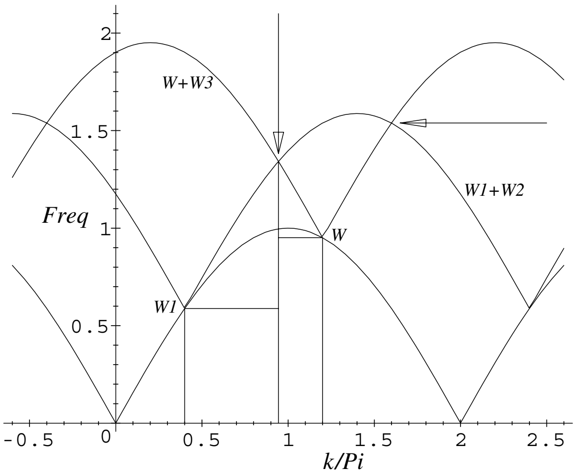

Figure 1. The summed phonon frequencies, ω_3 additive to a fixed ω and ω_2 additive to a fixed ω_1, as functions of wave vector k/π and scaled by the zone boundary ω_{ZB}. The intersection point marked by the vertical arrow is the non-trivial energy conserving solution to the scattering process $k + k_3 \leftrightarrow k_1 + k_2$. This is an example with $0 < k_1 < k < 2\pi$ in which case it is always true that $|\sin\frac{1}{2}k_2| = \sin\frac{1}{2}k_2$ and $|\sin\frac{1}{2}k_3| = -\sin\frac{1}{2}k_3$. For the solution marked by the horizontal arrow, k_1 and k_2 are just a relabelled k and k_3 combination.

then so is k_2 and of course these will not in general be equal. The situation is simpler if k and k_1 are chosen as the independent momenta. One can also, without loss of generality, restrict $0 < k < 2\pi$ and $0 < k_1 < 2\pi$ so that both $\sin\frac{1}{2}k$ and $\sin\frac{1}{2}k_1$ are always positive. An example of a graphical solution to (15) is shown in figure 1. One can infer from this figure that there are always exactly two intersection points satisfying (15) on any interval of length 2π. However, for one of these k_2 and k_3 are just a relabelling of k and k_1 and cannot change phonon occupation numbers. That leaves only one solution as non-trivial and again from the graphical solution in figure 1 it is clear that the total momentum $k + k_3 = k_1 + k_2$ will always lie between k and k_1. If $k_1 > k$, then $\left|\sin\frac{1}{2}k_3\right| = \sin\frac{1}{2}k_3$ and $\left|\sin\frac{1}{2}k_2\right| = -\sin\frac{1}{2}k_2$ always. If $k_1 < k$ the signs are reversed.

It is useful in solving for k_2 and k_3 to treat them symmetrically and write

$$k_2 = 2\psi - (k_1 - k)/2, \qquad k_3 = 2\psi + (k_1 - k)/2, \tag{16}$$

thus recasting the problem into finding ψ. I return to this below but first note a useful bound on ψ. The argument is that (16) can be written as $k + k_3 = k_1 + k_2 = 2\psi + (k + k_1)/2$ which is to say that 2ψ is the total momentum minus the mean of k and k_1. But k and k_1 lie on the interval $(0, 2\pi)$ so that the mean differs from k or k_1 by less than $\pm\pi$. Furthermore, we concluded that the total always lies between k and k_1. It follows that $|2\psi| < \pi$.

For the next step in the analysis take for definiteness $k_1 > k$. Then one must find the solution to $\sin\frac{1}{2}k + \sin\frac{1}{2}k_3 - \sin\frac{1}{2}k_1 + \sin\frac{1}{2}k_2 = 0$ which can be written as

$$\sin\left(\tfrac{1}{4}(k_1 + k) - \tfrac{1}{4}(k_1 - k)\right) + \sin\left(\psi + \tfrac{1}{4}(k_1 - k)\right) - \sin\left(\tfrac{1}{4}(k_1 + k) + \tfrac{1}{4}(k_1 - k)\right) + \sin\left(\psi - \tfrac{1}{4}(k_1 - k)\right) = 0. \tag{17}$$

If (17) is expanded keeping the combinations $\frac{1}{4}(k_1 + k)$ and $\frac{1}{4}(k_1 - k)$ intact one finds directly

$$\sin\psi = \tan\tfrac{1}{4}(k_1 - k)\cos\tfrac{1}{4}(k_1 + k) \tag{18}$$

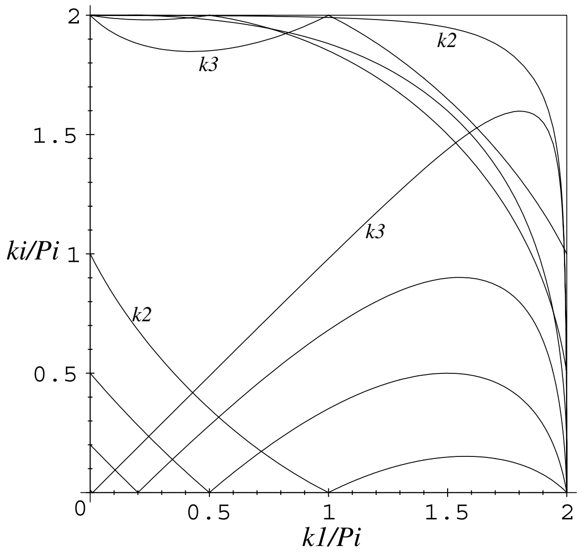

Figure 2. The solutions to equations (19*a*)–(19*c*): $k_i/\pi, i = 2, 3$, versus k_1/π for fixed $k/\pi =$ 0.01, 0.2, 0.5 and 1.0. The solutions are periodic and continuous and only the intervals $(0, 2\pi)$ are shown. The wave vector k_3 vanishes both at $k_1 = 0$ and $k_1 = k$. The k_2 vanishes only at $k_1 = k$ while at $k_1 = 0$ it takes on the value $k_2 = k$. In the limit $k \to 0$ the local maximum in k_3 is $2\pi - 4k^{1/3}$ at $k_1 = 2\pi - 2k^{1/3}$ while the local minimum is $2\pi - (k/4)^3$ at $k_1 = k/2$.

and from (18) the unique ψ since $-\pi/2 < \psi < \pi/2$. One can repeat the argument for $k_1 < k$ and show that under all circumstances the solution for k_2 and k_3 is

$$k_2 = 2\psi - (k_1 - k)/2 \bmod 2\pi, \qquad k_3 = 2\psi + (k_1 - k)/2 \bmod 2\pi, \tag{19a}$$

$$\psi = \arctan\left[\sin\tfrac{1}{4}|k_1 - k| \cos\tfrac{1}{4}(k_1 + k)/\Delta\right], \tag{19b}$$

$$\Delta = \left[\sin\tfrac{1}{2}k \sin\tfrac{1}{2}k_1 + \left(\cos\tfrac{1}{4}(k_1 - k)\cos\tfrac{1}{4}(k_1 + k)\right)^2\right]^{1/2} \tag{19c}$$

with the arctan function in (19*b*) understood to be on the principle branch to yield $-\pi/2 < \psi < \pi/2$. While the change from (16) to (19*a*) is only a matter of aesthetics to map k_2 and k_3 onto the common interval $(0, 2\pi)$, the constraints $0 < k < 2\pi$ and $0 < k_1 < 2\pi$ are absolute and are maintained throughout this paper. Examples of the solution (19*a*)–(19*c*) are shown in figure 2.

The Boltzmann equation integrals can now be simplified. For fixed k and k_1,

$$\int \mathrm{d}k_2\, \omega_{ZB}\delta(\omega_k - \omega_{k1} - \omega_{k2} + \omega_{k3}) = 2 \Big/ \left|\cos\frac{1}{2}k_2 + \cos\frac{1}{2}k_3\right|$$
$$= 1 \Big/ \left(\cos\psi \cos\frac{1}{4}(k_1 - k)\right) = 1/\Delta \tag{20}$$

where the first evaluated term is just the reciprocal of the derivative of the argument of the δ-function. The relative sign between the two cosine functions follows from the discussion preceding (16) that the combination $\omega_{k2} - \omega_{k3}$ will always appear as the form $\pm\left(\sin\frac{1}{2}k_2 + \sin\frac{1}{2}k_3\right)$. The second equality in (20) follows from the definitions (16) while the last depends on the solution (19*b*).

The remaining integrations $\int \mathrm{d}k_1/\Delta \ldots$ can be simplified by change(s) of variable. Note that Δ can become very small if k approaches 0 and k_1 approaches 2π. Hence for most evaluations it is preferable to use $\ell_1 = 2\pi - k_1$ in which case (19*c*) becomes

$$\Delta = \left[\sin \tfrac{1}{2}k \sin \tfrac{1}{2}\ell_1 + \left(\sin \tfrac{1}{4}(\ell_1 + k) \sin \tfrac{1}{4}(\ell_1 - k)\right)^2\right]^{1/2}. \tag{21}$$

By far the most useful transformation is $s = \tan \frac{1}{4}\ell_1$ and with the definition $t = \tan \frac{1}{4}k$ one finds

$$\Delta = \left(\cos \tfrac{1}{4}k \cos \tfrac{1}{4}\ell_1\right)^2 \sqrt{D}, \qquad D = 4st(1 + s^2)(1 + t^2) + (s^2 - t^2)^2, \tag{22}$$

and the collision integral (9*b*)

$$\begin{aligned} I_k(\chi) &= \int \mathrm{d}k_1/\Delta(\chi_k - \chi_{k1} - \chi_{k2} + \chi_{k3}) \\ &= 4(1 + t^2) \int_0^\infty \mathrm{d}s/\sqrt{D}(\chi_k - \chi_{k1} - \chi_{k2} + \chi_{k3}). \end{aligned} \tag{23}$$

Since D is a quartic polynomial in s, the kinematical part of the collision integral, namely

$$K_k = \int \mathrm{d}k_1/\Delta = 4(1 + t^2) \int_0^\infty \mathrm{d}s/\sqrt{D} \tag{24}$$

can be expressed exactly in terms of elliptic integrals and the result is given in the appendix. However, for purposes of understanding the small momentum behaviour of the Boltzmann equation a simpler approach is preferable. First note that $D(s)$, for any t, has two negative real roots and a complex pair. Specifically,

$$D = (s + s_1)(s + s_2)(s - a - \mathrm{i}b)(s - a + \mathrm{i}b) \tag{25}$$

and for small t,

$$\begin{aligned} &s_1 = t^3/4 + \mathrm{O}(t^5) = k^3/256 + \mathrm{O}(k^5), \qquad s_2 = (4t)^{1/3} + \mathrm{O}(t) = k^{1/3} + \mathrm{O}(k), \\ &a \pm \mathrm{i}b = s_2 \exp(\pm \mathrm{i}\pi/3) + \mathrm{O}(t) = k^{1/3} \exp(\pm \mathrm{i}\pi/3) + \mathrm{O}(k). \end{aligned} \tag{26}$$

The numerical coefficients in (26) are of course specific to the dispersion law $\omega_k = \omega_{ZB}\left|\sin \frac{1}{2}k\right|$ for the nearest-neighbour model but the fact that D has structure at $\sim k^3$ and $\sim k^{1/3}$ arises simply because the phonon dispersion curve deviates from linearity by a term of order k^3. Hence one can expect the qualitative features found here to be generic. In particular, any structure in the deviation function χ at some small momentum scale k will be reflected in structure in the evaluated collision integral at scales k^3 and $k^{1/3}$. That is, phonon collisions in the 4-phonon model will redistribute phonons to these very specific higher and lower scales.

I conclude this section with an evaluation of the kinematic integral K_k in (24) for small k. The leading term in K_k in the limit $k \to 0$ can be obtained by setting $D = 4st + s^4 = sk + s^4$ and substituting $s = (k\sigma)^{1/3}$. The result is

$$\begin{aligned} K_k &\approx 4 \int_0^\infty \mathrm{d}s/\sqrt{(sk + s^4)} = 4/(3k^{1/3}) \int_0^\infty \mathrm{d}\sigma\, \sigma^{-5/6}(1 + \sigma)^{-1/2} \\ &= 4/(3k^{1/3})B(1/6, 1/3) = (4/3)(4/k)^{1/3}B(1/3, 1/3) \end{aligned} \tag{27}$$

where $B(x, y) = \Gamma(x)\Gamma(y)/\Gamma(x + y)$ is the beta function. On Taylor expanding $1/\sqrt{D}$ about this lowest order term as described in the appendix one can generate corrections whose evaluation is very similar to that in (27). The result, based on analytical integration, is

$$\begin{aligned} K_k = {} & (4/3)(4/k)^{1/3}B(1/3, 1/3) - (4/9)(2k)^{1/3}B(2/3, 2/3) \\ & + 0k + (88/243)(k/4)^{5/3}B(1/3, 1/3) + \mathrm{O}(k^2) \end{aligned} \tag{28}$$

which shows the gap between successive terms in K_k is a factor of $k^{2/3}$ barring, possibly accidental, zero coefficients. An exact summation of the series (28) valid for all $0 < k < 2\pi$ is equation (A.10) in the appendix. While I do not use the exact representation in this paper it is the integral result one needs for obtaining solutions to the Boltzmann equation in the relaxation time approximation.

3. Small *k* asymptotics

Probably the most striking feature of the Boltzmann equation (9*a*) is the divergence of the left, transport, side of the equation at small k as $1/k$. This is a very strong constraint on the form of the deviation function χ on the right, collision, side. Now we have already seen in (28) in the previous section that the kinematical part of the collision integral, namely K_k, only diverges as $1/k^{1/3}$ so that χ itself must diverge. We can guess, since $\chi_k K_k$ is one contribution to $I_k(\chi)$, that $\chi \propto 1/k^{2/3}$. There are also constraints of symmetry; since we are dealing with a linearized Boltzmann equation in a thermal gradient, χ must be an anti-symmetric function of k and because of periodicity, anti-symmetric about $k = \pi$ as well.

In view of the above, I will suppose that the singular, non-analytic, part of χ can be constructed from a superposition of functions of the form

$$ {}^S\chi_k(p) = \cos \tfrac{1}{2}k\left(\sin \tfrac{1}{2}k\right)^p \tag{29} $$

with, of course, $p = -2/3$ being one likely candidate. The simplest analytic function with the correct symmetry is $\cos\frac{1}{2}k \sin\frac{1}{2}k$ and it is reasonable to take the regular part of χ as

$$ {}^R\chi_k = \cos \tfrac{1}{2}k \sin \tfrac{1}{2}k \times (\text{orthogonal polynomial expansion}). \tag{30} $$

The numerical procedure involved in evaluating the contribution (30) to the collision integral is discussed in the next section. But as already noted, this contribution cannot lead to anything more singular than $1/k^{1/3}$ and therefore a local analysis in the vicinity of $k = 0$ based on (29) suffices to obtain a significant part of the solution to the Boltzmann equation. I now describe this local analysis.

The collision integral with (29) as integrand needs to be evaluated, at least in the limit of small k. With the representation (23) for $I_k(\chi)$ these calculations are reasonably straightforward and are outlined in the appendix. The results, adequate for our purpose here, are

$$ I_k({}^S\chi(p)) = \Sigma\beta(p,q)k^q + \mathrm{O}(k^r), \tag{31} $$

$$ \beta(p, p-1/3) = \frac{4}{3}\frac{2^{2/3}}{2^p}B(1/3, 1/3), \tag{31a} $$

$$ \beta(p, 3p+1) = 1/2^{5p}\{2B(p+1, -2p-1) - B(p+1, p+1)\}, \tag{31b} $$

$$ \begin{aligned} \beta(p, (p-1)/3) = (4/3)2^{(2+p)/3}\{&2B((2p+1)/3, (1-p)/3) \\ &- B((1-p)/3, (1-p)/3)\}, \end{aligned} \tag{31c} $$

$$ \beta(p, p+1/3) = (-4/9)\frac{2^{1/3}}{2^p}B(2/3, 2/3), \tag{31d} $$

$$ \begin{aligned} \beta(p, (p+1)/3) = (4/9)(5+2p)2^{(1+p)/3}\Bigg\{&2B((2p+2)/3, (2-p)/3) \\ &- \frac{(1-2p)}{(1+p)}B((2-p)/3, (2-p)/3)\Bigg\}, \end{aligned} \tag{31e} $$

$$\beta(p, p+1) = 0, \tag{31f}$$

and, given the six terms above, the remainder power in (31) is

$$r = \min(1, p/3 + 1), \qquad p \geqslant -2/3. \tag{32}$$

Equations (31*b*), (31*c*) are an explicit realization of the comments following (26). Namely, structure on scale k is transferred to scales k^3 and $k^{1/3}$ which we see here as a power p in the integrand becoming a power $3p$ (+1) and $p/3$ (−1/3) in the evaluated integral. We also see in (31*d*), (31*e*), just as in the evaluation of K_k, correction terms that differ from the dominant expressions by factor $k^{2/3}$.

We can now conclude unambiguously that for the collision integral to reproduce the divergence on the transport side of (9*a*),

$$\chi = A\,{}^S\chi(p = -2/3) + \text{less singular terms}, \tag{33}$$

$$A = (3/64)2^{2/3}/B(1/3, 1/3), \tag{34}$$

which is the result copied to (10). The amplitude A of the leading term in (33) is determined from a combination of the amplitudes in (31*a*), (31*b*) but note that the presence of this term also generates a singularity $\propto 1/k^{5/9}$. There is no corresponding term on the transport side of the Boltzmann equation so this new divergence must be cancelled by another contribution to χ. With this contribution included,

$$\chi = A\{{}^S\chi(p = -2/3) - \beta(-2/3, -5/9)/\beta(-2/9, -5/9)\,{}^S\chi(p = -2/9) + \text{less singular terms}\}, \tag{35}$$

but then there is another divergence to be cancelled. The result is a cascade of divergences $\propto k^q$ and because $q < -1/3$ the local analysis uniquely determines the amplitudes in the singular χ expansion. The formal infinite sum of all these contributions is our zeroth-order approximation

$$\chi \approx {}^{(0)}\chi = A\,{}^S X(p = -2/3), \tag{36}$$

$${}^S X(p) = \sum_{n=0}^{\infty} \alpha_n(p)\,{}^S\chi(p/3^n) \tag{37}$$

with the $\alpha_n(p)$ satisfying the recursion

$$\alpha_{n+1}(p) = -\beta(p/3^n, p/3^{n+1} - 1/3)/\beta(p/3^{n+1}, p/3^{n+1} - 1/3)\alpha_n(p), \qquad a_0(p) = 1. \tag{38}$$

The powers in the successive ${}^S\chi$ terms in (37) approach zero and this suggests a rather intuitive physical picture—the thermal gradient generates a very large disturbance (i.e. power law divergence) in the phonon distribution at small k but successive scattering events smooth out this distribution and ultimately flatten it entirely.

The convergence of the series (37) needs to be explored with particular emphasis on how to replace the infinite sum by a rapidly convergent sequence of approximants based on finite sums. We begin with the recursion (38) and Taylor expand the gamma functions in the defining equations for the $\beta(p, q)$. This shows that the successive α_{n+1}/α_n ratios converge to -1 exponentially in n; specifically,

$$-\alpha_{n+1}(p)/\alpha_n(p) = 1 + 2Bp/3^{n+1} + \mathrm{O}(1/9^n), \qquad B = 2\psi(1/3) - 2\psi(2/3) + \ln(2) \tag{39}$$

where $\psi(x)$ is the digamma function. This exponential convergence implies convergence of $(-1)^n\alpha_n(p)$ and from (39) we deduce that

$$\alpha_n(p) = C(-1)^n[1 - Bp/3^n + \mathrm{O}(1/9^n)] \tag{40}$$

where C is a constant. Furthermore, for finite k, ${}^S\chi(p/3^n) = \cos\frac{1}{2}k\big[1 + \ln\big(\sin\frac{1}{2}k\big)p/3^n + \mathrm{O}(1/9^n)\big]$ so that the individual terms in the sum (37) vary as

$$\alpha_n(p)\,{}^S\chi(p/3^n) = C(-1)^n\cos\tfrac{1}{2}k\big[1 - \big(B - \ln\big(\sin\tfrac{1}{2}k\big)\big)p/3^n + \mathrm{O}(1/9^n)\big] \qquad (41)$$

which shows that replacing (37) by partial sums truncated at $n = N$ is not going to form a practical sequence of approximants. However we can use (41) to make a reasonable guess for the truncation error in (37) and include this together with the partial sum to $n = N$. If we consider only the terms explicitly shown in (41) then there are two series to consider. The remainder series $(-1)^{N+1}(1 - 1 + 1 - \cdots)$ modified by any reasonable convergence device will sum to $\frac{1}{2}(-1)^{N+1}$ while the other $(-1)^{N+1}/3^{N+1}(1 - 1/3 + 1/9 - \cdots) = \frac{1}{4}(-1)^{N+1}/3^N$. Including both sums gives the remainder

$$\begin{aligned}{}^SX(p) - \sum_{n=0}^{N}\alpha_n(p)\,{}^S\chi(p/3^n) &\approx C(-1)^{N+1}\cos\frac{1}{2}k\left[\frac{1}{2} - \frac{1}{4}\left(B - \ln\left(\sin\frac{1}{2}k\right)\right)p/3^N\right]\\ &\approx C(-1)^{N+1}\,{}^S\chi\left(\frac{\frac{1}{2}p}{3^N}\right)\left[\frac{1}{2} - \frac{\frac{1}{4}Bp}{3^N}\right]\\ &\approx -\alpha_N(p)\,{}^S\chi\left(\frac{\frac{1}{2}p}{3^N}\right)\left[\frac{1}{2} + \frac{\frac{1}{4}Bp}{3^N}\right] \end{aligned} \qquad (42)$$

and all forms have error $\mathrm{O}(1/9^N)$. The $\mathrm{O}(1/3^N)$ correction can also be eliminated by utilizing $\alpha_{N+1}(p)$ in addition to $\alpha_N(p)$ in the last expression in (42). The result is the Nth approximant, correct to $\mathrm{O}(1/9^N)$,

$${}^SX(p) = \left(\sum_{n=0}^{N}\alpha_n(p)\,{}^S\chi(p/3^n)\right) + (3\alpha_{N+1}(p) - a_N(p))/8\,{}^S\chi\left(\frac{\frac{1}{2}p}{3^N}\right). \qquad (43)$$

Further refinement is possible but the convergence $\propto 1/9^N$ is already sufficiently rapid that (43) is numerically practical and is the approximant that has been used for all the numerical work discussed in the following section.

To see what has been achieved and more importantly what remains to be done, I show in figure 3 the relationships between the power p in the collision integral integrand and the power q in the evaluated integral as given by (31a)–(31f). The cascade defining ${}^SX(p = -2/3)$ is readily apparent as are singularities in the evaluated collision integral we have not yet cancelled. The most significant singularity is that at $q = -1/3$ which requires we add to χ a single term with $p = 0$. The resulting change to (36) is

$$\chi \approx {}^{(1)}\chi = A\left\{{}^SX(p = -2/3) + 2^{-2/3}\frac{\Gamma^3(2/3)}{\Gamma^3(1/3)}\,{}^S\chi(p = 0)\right\}. \qquad (44)$$

The leading singularity of the approximation (44) is now at $q = 1/9$ and to cancel this singularity we can add terms with $p = 4/9$ or $p = 4/3$. There is no reason to exclude one or the other and it will require a global analysis to determine the relative weights of the two terms. Note however that if we add ${}^S\chi(p = 4/9)$ we will be generating a singularity at $q = -5/27$ that needs to be cancelled. This is the start of another cascade and the formulae (37) and (38) apply here as well; the result is that we should add, with some amplitude, ${}^SX(p = 4/9)$ to (44). The ambiguity in amplitude is resolved if we choose to also add ${}^SX(p = 4/3)$ rather than ${}^S\chi(p = 4/3)$. The former has no $q = 1/9$ singularity by construction and thus local analysis imposes no constraint on its amplitude. On the other hand, local analysis now uniquely

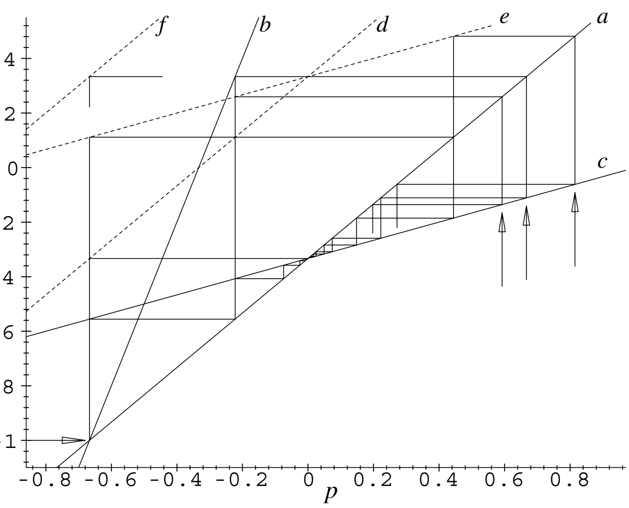

Figure 3. The six sloping lines labelled $a, b, \ldots, f$ are the relationships (31a)–(31f) between the exponent q characterizing the evaluated integral $I_k({}^S\chi)$ and the exponent p of the integrand ${}^S\chi(p)$. The exponent $q = -1$ indicated by the arrow at the lower left is demanded by the transport side of the Boltzmann equation. The vertical arrows indicate the powers of the three terms with $p < 1$ that are included with adjustable amplitudes in the variational numerical solution discussed in section 4.

fixes the ${}^S X(p = 4/9)$ amplitude. In summary,

$$\chi \approx {}^{(2)}\chi = A\left\{ {}^S X(p=-2/3) + 2^{-2/3}\frac{\Gamma^3(2/3)}{\Gamma^3(1/3)}\,{}^S\chi(p=0) - \frac{[\beta(-2/3,1/9)+\alpha_1(-2/3)\beta(-2/9,1/9)]}{\beta(4/9,1/9)}\,{}^S X(p=4/9) + a_{4/3}\,{}^S X(p=4/3)\right\} \tag{45}$$

where $a_{4/3}$ is not determined by local analysis. The ${}^S X$ are defined in terms of the ${}^S\chi$ by (37) and (38); a rapidly convergent sequence for approximating (37) is (43).

The local analysis described above illustrates the complicated nature of the singularity at $k = 0$. Every correction term is going to be part of a cascade of singularities that require yet more correction terms. Barring accidental cancellation, one can expect every power $2(3m - 1)/3^n$ and $2(3m + 1)/3^n$ with $m, n = 0, 1, 2, \ldots, \infty$. The negative powers $-2/3^n$ are isolated but converge to an accumulation point $p = 0$. The positive powers are dense on the real line $p \geqslant 0$. Presumably the singularities are not equally important and (45) is an exact representation of the negative powers and a first attempt at representing the most important positive powers. As such it is reasonably successful. Numerical integration of the collision integral using (45) with $a_{4/3} = 0$ shows that the ratio of the two sides of the Boltzmann equation (9a) has a maximum deviation from unity at $k = \pi$ and there by less than 6%. It is worth remarking that numerical integration can be replaced by the analytic formula (31) together with the explicit $\beta(p, q)$ in (31a)–(31f) if k is small enough.

To help visualize the effect of the truncation process that replaces (37) by (43) I show in figure 4 the difference $\frac{1}{2}\cot\frac{1}{2}k - I({}^{(2)}\chi)$ on a logarithmic scale in k. Since the truncation error in (43) is $O(1/9^N)$ and multiplies a k dependence that is approximately $1/k^{1/3}$ we can conclude that for every increase $N \to N + 1$ the minimum k above which the error is below

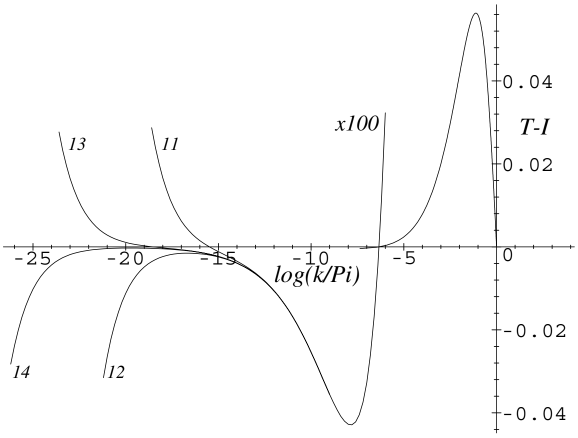

Figure 4. The Boltzmann equation transport minus collision integral difference $T - I = \frac{1}{2}\cot\frac{1}{2}k - I_k(\chi)$ versus $\log_{10}(k/\pi)$ based on the approximate $\chi = {}^{(2)}\chi$ given in (45) with $a_{4/3} = 0$. The curves at the left end have been scaled up by factor 100 for clarity. The four separate diverging curves are the differences based on the cutoffs $N = 11, \ldots, 14$ in (43).

some fixed value decreases by factor 9^3 or nearly 3 decades. This rapid convergence is seen in figure 4 and confirms that very reasonable values for the cutoff N are adequate. A perhaps surprising feature in figure 4 is the very small k at which there is a sign reversal followed by a local maximum indicating that the asymptotic region in which the difference is reasonably described by a *single* power law in k is limited to extremely small k. It is the *confluence* of many closely spaced power laws that is responsible for the structure and to accurately model this makes the numerical work somewhat more involved than one might have initially guessed.

4. Numerical solution

The method described here for the numerical solution to the Boltzmann equation (9*a*) is variational—I start with (45) as an approximation for χ and add functions with undetermined amplitudes. The amplitudes are then adjusted to minimize the relative error between the two sides of (9*a*). The convergence depends crucially on the function choice. One complication is that at least some of the included functions must adequately describe the undetermined confluent singularities at $k = 0$. Another is that structure in χ is most likely to appear at small k and not uniformly in k.

With regard to the first complication note that the approximation (45) for χ was designed to eliminate the $q = 1/9$ singularity in the evaluated collision integral. A quick look at figure 3 shows the next singularity is at $q = 7/27$ and that $q = 1/3$ is an accumulation point of singularities. As a practical matter one hopes that the infinity of power law singularities can be adequately represented by a few effective power law singularities but I do not know of a systematic way of optimizing the choice of exponents. For the numerical work described below I have supplemented the term $a_{4/3}{}^{S}X(p = 4/3)$ in (45) by

$$a_{16/27}\,{}^{S}X(p = 16/27) + a_{2/3}\,{}^{S}X(p = 2/3) + a_{22/27}\,{}^{S}X(p = 22/27) \qquad (46)$$

and this appears to be both a minimal and adequate set. The term $p = 16/27$ has been chosen because it generates the $q = 7/27$ singularity; the term $p = 2/3$ because it generates $q = 1/3$ which is the accumulation point. The term $p = 22/27$ is there to fill the gap between $p = 2/3$

and the regular $p = 1$ described below. It is also chosen because it generates the same $q = 13/27$ as generated by the $p = 4/9$ that appears in (45). I have not systematically explored variations of (46).

The term $p = 4/3$ in (45) already lies beyond $p = 1$ and exponents $p > 4/3$ are ignored on the assumption that they will be reasonably approximated by the variational regular contribution (30). But note the regular ${}^R\chi$ is just, in part, the special singular case ${}^S\chi(p = 1)$ and will itself generate singularities at various q. From the explicit expression (31c) one finds limit $p \to 1$ $\beta(p, (p-1)/3) = 0$ so that no 'singular' $q = 0$ term is generated and instead the first singularity is at $q = 2/3$. Thus the combination of (30) and (46) is self-consistent in the sense that no singularities at $q < 7/27$ are generated.

The complication of structure at small k is handled in two ways. First the Boltzmann equation (9a) is sampled on a non-uniform grid of 359 points given by

$$k = k_n = [2(n/360)^3 - (n/360)^4]\pi, \qquad n = 1, 2, \ldots, 359. \tag{47}$$

This makes the smallest $k \approx 1.3 \times 10^{-7}$ and it is unlikely that we are missing any structure below this value. Second, I use Chebyshev polynomials $U_{2m}(x)$ in (30) but I do not use the uniform mapping $x = \frac{k}{\pi} - 1$. Instead I set $x = (2/\pi)\arcsin\left(\frac{k}{\pi} - 1\right)$ so as to effectively stretch small k (and small $2\pi - k$) relative to $k \approx \pi$. Note that this implies the polynomial expansion at small k is an expansion in $\sqrt{k}$ so that the solution ${}^R\chi$ contains powers $p = 1, 3/2, 2, 5/2$ etc and is not 'regular' at all. The term $p = 3/2$ will generate a singularity with $q = 1/6$ that violates the constraint $q \geqslant 7/27$ we hoped to satisfy. It is possible that the variational calculation will result in a zero amplitude for this term and I return to this point below.

The complete variational χ treated numerically is

$$\begin{aligned}\chi \approx {}^{(3)}\chi = A\Bigg\{ & {}^S X\left(p = -\frac{2}{3}\right) + 2^{-2/3}\Gamma^3\left(\frac{2}{3}\right)\Big/\Gamma^3\left(\frac{1}{3}\right)\, {}^S\chi(p = 0) \\ & - \left[\beta\left(-\frac{2}{3}, \frac{1}{9}\right) + \alpha_1\left(-\frac{2}{3}\right)\beta\left(-\frac{2}{9}, \frac{1}{9}\right)\right]\Big/\beta\left(\frac{4}{9}, \frac{1}{9}\right) {}^S X\left(p = \frac{4}{9}\right) \\ & + a_{16/27}\, {}^S X\left(p = \frac{16}{27}\right) + a_{2/3}\, {}^S X\left(p = \frac{2}{3}\right) + a_{22/27}\, {}^S X\left(p = \frac{22}{7}\right) \\ & + \cos\frac{1}{2}k \sin\frac{1}{2}k \sum_{m=0}^{M} b_m U_{2m}\left(\left(\frac{2}{\pi}\right)\arcsin\left(\frac{k}{\pi} - 1\right)\right) \\ & + a_{4/3}\, {}^S X\left(p = \frac{4}{3}\right)\Bigg\}\end{aligned} \tag{48}$$

and the weighted square error $(1 - 2\tan\frac{1}{2}k\, I_k({}^{(3)}\chi))^2/\sin\frac{1}{2}k$ summed over the $k = k_n$ in (47) is minimized with respect to the parameters a_p and b_m. The weighting factor $\sin\frac{1}{2}k$ is chosen to strike a balance between minimizing the absolute versus relative error between the two sides of (9a). Changing this weighting has only a small effect on the rate of convergence with respect to the cutoff M and is otherwise of little significance.

An example of the accuracy that is achieved by (48) is shown in figure 5(a) which gives the relative error, scaled by 10^{12}, between the two sides of the Boltzmann equation (9a) versus the sampling index n in (47). The cutoffs for this case are $M = 22$ in (48) and $N = 11$ in the ${}^S X$ definitions (43). An important observation is that the oscillations in the deviation are relatively uniform suggesting that the 'stretching' choice both in sampling and in the orthogonal polynomials has been very reasonable. Figure 5(b) displays the relative error versus $\log_{10}(k/\pi)$ for small k and shows that the assumption of lack of structure below the smallest $k \approx 1.3 \times 10^{-7}$ in (47) is justified. Note that the data for figure 5(b) were generated

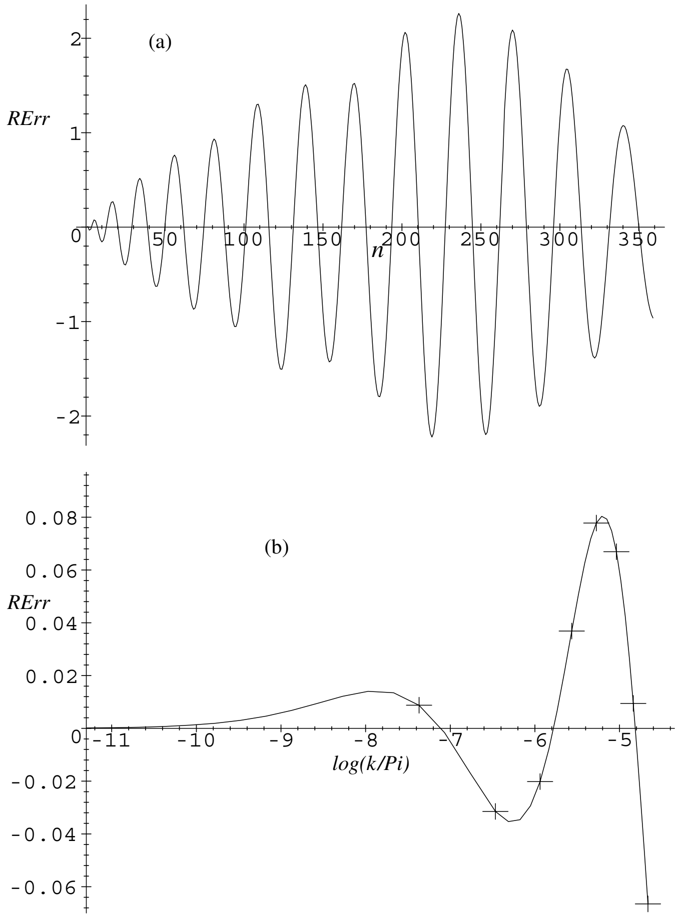

Figure 5. (*a*) The scaled relative error $\mathrm{RErr} = 10^{12} \times (1 - 2\tan\frac{1}{2}k_n I_{kn}(\chi))$ for the solution $\chi = {}^{(3)}\chi$ with parameters (49). The horizontal axis is the wave vector index n in (47). (*b*) The same relative error as in (*a*) but versus $\log_{10}(k/\pi)$ for small k. The crosses mark the index $n = 1, 2, \ldots, 8$ in (47) and correspond to those k_n that were used in the least-squares minimization.

by numerical integration of (48) but none of these data points was used in the variational calculation other than those corresponding to the k_n in (47). The coefficients for the fit in figure 5 are

$$
\begin{aligned}
&a_{16/27} = 3.187\,327\,505\,368\,166, \qquad a_{2/3} = -2.472\,562\,835\,834\,634,\\
&a_{22/27} = 5.950\,179\,702\,003\,351, \qquad a_{4/3} = -2.367\,232\,977\,843\,359,\\
&b_m = -3.303\,888\,356\,255\,044, -0.456\,791\,719\,832\,596, 0.083\,486\,787\,842\,960,\\
&\quad -0.007\,035\,230\,913\,126, 0.000\,275\,510\,608\,921, 0.000\,669\,791\,938\,783,\\
&\quad 0.000\,151\,287\,256\,424, 0.000\,074\,032\,718\,416, 0.000\,035\,487\,814\,215,\\
&\quad 0.000\,020\,018\,231\,683, 0.000\,010\,682\,539\,894, 0.000\,006\,160\,762\,154,\\
&\quad 0.000\,003\,538\,876\,077, 0.000\,002\,058\,496\,637, 0.000\,001\,182\,722\,509,\\
&\quad 0.000\,000\,667\,628\,081, 0.000\,000\,364\,455\,390, 0.000\,000\,189\,753\,146,\\
&\quad 0.000\,000\,092\,282\,338, 0.000\,000\,040\,687\,457, 0.000\,000\,015\,480\,270,\\
&\quad 0.000\,000\,004\,613\,096, 0.000\,000\,000\,844\,587, \qquad m = 0, 1, \ldots, 22.
\end{aligned} \tag{49}
$$

The values of the a_p are relatively stable with order but at best they represent the average amplitudes over a range of exponent values. A particular a_p can certainly not be construed as a true indicator of the amplitude of ${}^S\chi(p)$. I have not investigated what happens when more a_p are included in (48) but dropping just the single $a_{22/27}$ increases the root mean square error by about three orders of magnitude. In addition the parameter stability with order is lost. Thus the number of a_p that has been kept does appear to be a minimal number.

The small k expansion of a Chebyshev $U_{2m}\left(\left(\frac{2}{\pi}\right)\arcsin\left(\frac{k}{\pi}-1\right)\right)$ is

$$U_{2m} = 2m + 1 - \frac{2}{3}(2m)_3 x_k + \frac{2}{15}(2m-1)_5 x_k^2 - \left[\frac{4}{315}(2m-2)_7 + \frac{\pi^2}{36}(2m)_3\right] x_k^3 + \cdots, \qquad x_k = \sqrt{\left(\frac{2k}{\pi^3}\right)} \tag{50}$$

where $()_n$ is the Pochhammer symbol. Given the explicit values for b_m in (49) the 'regular' contribution ${}^R\chi$ to (48) is approximately

$${}^R\chi = A\cos\tfrac{1}{2}k\sin\tfrac{1}{2}k[-4.291\,58 + 0.1674\,k^{1/2} + 5.175k - 47.7\,k^{3/2} + \cdots]. \tag{51}$$

The coefficients in this expansion drift with cutoff order M and the terms in [ ] become, for example,

$$\begin{aligned} &[-4.279\,39 + 0.0649k^{1/2} + 10.015k - 196.6k^{3/2} + \cdots], && M = 31, \\ &[-4.276\,99 - 0.0404k^{1/2} + 240.27k - 280\,92k^{3/2} + \cdots], && M = 40. \end{aligned} \tag{52}$$

The strong variation in constants between (51) and (52) does not imply an inaccurate numerical χ. The difference in $({}^{(3)}\chi/A)\left(\sin\frac{1}{2}k\right)^{1/3}$ with $M = 22$ and $M = 31$ never exceeds 3×10^{-11}; the difference with $M = 31$ and $M = 40$ never exceeds 5×10^{-12}. The variation is instead just a characteristic feature of multiple exponential fitting—namely that such fitting is prone to instability with many combinations of constants giving equally good approximations. There is a consistency to (51) and (52) in that the coefficient of $k^{1/2}$ which should rigorously be zero has turned out to be small. This would almost certainly not have been the case had the more singular terms as determined by the analytical analysis not been incorporated correctly.

Higher accuracy could no doubt be obtained but the present results already confirm the analytically obtained picture in section 3 and illustrate the special features that one must watch for in a numerical treatment. For those applications where high accuracy is not needed, I have fit this solution to a much simpler functional form and obtained the result quoted in (11).

5. Physical consequences

As discussed in the introduction, the formal expression for the thermal conductivity (13) diverges because phonon wave packets are allowed to travel arbitrarily large distances. This of course is not possible in a finite system but including boundaries in the problem introduces spatial dependence which will make the solution of the Boltzmann equation much more difficult. On the other hand, one can give a simple but realistic estimate of the effect of the boundaries by comparing phonon wave packets at the centre of a chain of N particles with those in the infinite system.

The crucial observation is that any wave packet one detects is not representative of the point of detection but rather of the point of origin. In the infinite system this is always, on average, one mean free path distant. The number of packets of mean wave vector k one detects is therefore characteristic of a temperature that differs from the local temperature by $-\lambda_k\,\nabla T$ where λ_k is the mean free path, here measured in numbers of particles for consistency with the number representation used for ∇T. We can then deduce that the deviation δn_k from equilibrium is $-\frac{\partial^{\text{eq}} n_k}{\partial T}\lambda_k \nabla T$ which is $-\lambda_k k_B \nabla T/\hbar\omega_k$ in the high temperature limit. But δn_k is known from the solution to the Boltzmann equation; combining δn_k in terms of mean free path with $\delta n_k = (k_B T/\hbar\omega_k)^2 g_k$, the high temperature limit of (5), and the definition of χ from (8) gives

$$\lambda_k = \left(\frac{16\pi}{9}\right) K_2^4 \Big/ (K_4 k_B T)^2 \chi_k \Big/ \sin\frac{1}{2}k\,, \qquad 0 < k < \pi. \tag{53}$$

For those wave vectors representing phonon wave packets whose mean free path λ_k is less than the distance $N/2$ from centre to boundary, the current J_k in (12) given by our solution of the homogeneous Boltzmann equation is quite reasonable. On the other hand, our estimate of the deviation δn_k for those packets whose mean free path λ_k is greater than $N/2$ is too large by roughly the factor $2\lambda_k/N$ which is just the ratio of the temperature difference over a distance λ_k rather than $N/2$. We can incorporate this by replacing the purely formal total energy current expression,

$$J_\varepsilon = \frac{N}{2\pi}\int \mathrm{d}k\, J_k, \tag{54}$$

by the finite

$$J_\varepsilon(N) = \frac{N}{\pi}\left[\int_0^{k*} \mathrm{d}k \left(\frac{N}{2\lambda_K}\right) J_k + \int_{k*}^{\pi} \mathrm{d}k\, J_k\right] \tag{55}$$

where J_k is given in (12) and k^* is that value in (53) for which $\lambda_k = N/2$. That is, we keep the current J_k as given by the homogeneous Boltzmann equation but apply a correction factor for the long wavelength modes that just cancels the overestimate in δn_k.

Although in the general case of arbitrary N the integrals in (55) must be done numerically, for large N the cutoff k^* will be small and we can truncate χ to the leading term (10) and replace the upper limit $k = \pi$ in the second integral in (55) by $k = \infty$. Both integrals can then be evaluated analytically; they have the same functional form and are in the ratio 2:3. The result for the total is

$$J_\varepsilon(N) \approx -5\omega_{ZB}\left(\frac{N}{4\pi}\right)^{2/5}\left[\frac{\left(\frac{8A}{9}\right)K_2^4}{(K_4 k_B T)^2}\right]^{3/5} k_B \nabla T \tag{56}$$

and the corresponding thermal conductivity $\kappa(N) = -J_\varepsilon(N)/\nabla T$ is given in (14).

A recent simulation by Lee-Dadswell *et al* [7] of equilibrium fluctuations in a system with periodic boundary conditions suggests that one is in the perturbative regime only for $K_2^2\big/(K_4 k_B T)$ greater than about 100 to 200. We also know that boundary impedance severely restricts the magnitude of the energy current; Rieder *et al* [8] have determined for a long harmonic chain coupled stochastically to reservoirs at the two ends that

$$J_\varepsilon \leqslant \omega_{ZB} k_B (T_+ - T_-)/(6\sqrt{3}) \tag{57}$$

where $T_\pm$ are the reservoir temperatures. This should be approximately correct also for weakly anharmonic chains so that the combination of (56) and (57) imposes a very severe constraint on the possible temperature gradient ∇T. This in turn suggests how hard it will be to verify the Boltzmann equation approach described here in a steady-state non-equilibrium molecular dynamics simulation. Furthermore, the rather simplistic reduction of the distribution χ as given in (48) or (11) for the infinite system to the energy current (56) or thermal conductivity (14) for a finite system entails uncontrolled approximation so any numerical simulation could at best be a partial confirmation of the Boltzmann equation approach.

Definitive tests of the Boltzmann equation are more likely to be obtained by direct comparison with equilibrium simulations [7]. This requires an extension of the present calculation to the determination of the eigenvalue spectrum of the Boltzmann collision operator and while probably feasible is beyond the scope of the present paper.

Appendix

For an exact evaluation of the kinematical integral (24), we need to extract from the factorization

$$D = 4st(1+s^2)(1+t^2) + (s^2-t^2)^2 = (s+s_1)(s+s_2)(s^2-2sa+a^2+b^2) \tag{A.1}$$

not only s_1, s_2 with $s_1 < s_2$ but also

$$p_1 = \surd\left(s_1^2+2s_1a+a^2+b^2\right), \qquad p_2 = \surd\left(s_2^2+2s_2a+a^2+b^2\right). \tag{A.2}$$

The substitution $s = (p_1s_2\tau^2 - p_2s_1)/(p_2 - p_1\tau^2)$ puts (24) into the form

$$K_k = \frac{8(1+t^2)}{\surd(p_1p_2)} \int_{\tau_0}^{\tau_\infty} \frac{\mathrm{d}\tau}{\surd[(1+\tau^2)^2 - 4m\tau^2]},$$
$$\tau_0 = \sqrt{\left(\frac{p_2s_1}{(p_1s_2)}\right)}, \qquad \tau_\infty = \sqrt{\left(\frac{p_2}{p_1}\right)}, \qquad m = \frac{[(p_1+p_2)^2 - (s_1-s_2)^2]}{(4p_1p_2)} \tag{A.3}$$

and then with $\tau = \tan\frac{1}{2}\varphi$ into standard elliptic integral form giving

$$K_k = \frac{4(1+t^2)}{\surd(p_1p_2)}[2K(m) - F(2\arctan(\tau_0)|m) - F(2\arctan(1/\tau_\infty)|m)]. \tag{A.4}$$

The remaining $I(\chi)$ integrals appear to be too complicated to do exactly and for purposes of a small k expansion the $s = \tan\frac{1}{4}\ell_1$ and $t = \tan 1/4k$ variable representation seems to be the most useful. To gain experience with the necessary manipulations it is worth re-evaluating K_k as a small k expansion and the result (A.4) is useful for providing a check on these calculations.

One important region of integration in $\int \mathrm{d}s/\surd D$ is the region $s \sim t^{1/3}$. With the proviso that s scales as $t^{1/3}$ the terms in the integrand can be rearranged or Taylor expanded with each successive term smaller by factor $t^{2/3}$. For example, we can rearrange D as given in (A.1) into

$$[4st+s^4] + [4s^3t] + [-2s^2t^2] + [4st^3] + [4s^3t^3+t^4] \tag{A.5}$$

where successive [ ] scale as $t^{2n/3}$, $n = 2, 3, \ldots, 6$. For the integrand in K_k we generate the expansion

$$1/\surd D \approx \frac{1}{(4st+s^4)^{1/2}} - \frac{2s^3t}{(4st+s^4)^{3/2}} + \cdots \tag{A.6}$$

which is convergent provided we restrict s to, say, $s > Ct$. Most integrals in this series can be extended to $0 < s < \infty$ with an error that is $O(t^2)$. Two important exceptions are

$$\int_{Ct}^{\infty} \frac{\mathrm{d}s}{(4st+s^4)^{1/2}} = \int_0^{\infty} \frac{\mathrm{d}s}{(4st+s^4)^{1/2}} - \surd C + O(t^2),$$
$$-\frac{t^4}{2}\int_{Ct}^{\infty} \frac{\mathrm{d}s}{(4st+s^4)^{3/2}} = O(t^2). \tag{A.7}$$

The integral that extends over $0 < s < \infty$ in (A.7) is that in (27); other integrals in the expansion in which $0 < s < \infty$ are similar and easily evaluated. For the remaining region $0 < s < Ct$ where $s \sim t^3$ might give the dominant contribution we rearrange D as

$$[4st+t^4] + [4st^3] + [-2s^2t^2] + [4s^3t] + [4s^3t^3+s^4] \tag{A.8}$$

and perform an expansion analogous to (A.6). In this case only the first term gives a contribution that is not $O(t^2)$. It is

$$\int_0^{Ct} \frac{\mathrm{d}s}{(4st+t^4)^{1/2}} = -\frac{t}{2} + \sqrt{C} + O(t^2) \tag{A.9}$$

and the sum of all terms is that reported in (28). The need to separate the integrals into $s > Ct$ and $s < Ct$ makes the procedure messy and impractical above some order and makes the nature of the series (28) difficult to ascertain. However we know from the behaviour of every term in the exact K_k solution (A.4) that a series expansion with finite radius of convergence exists. The result (28) suggests the series will have a very simple form and in principle analytic differentiation of (A.4) could be used to generate higher order terms. In fact a numerical approach is much more efficient if the structure of (28) is assumed and all one needs to do is to find the rational coefficients in successive terms. Deducing rational coefficients from precise floating-point numbers by their continued fraction representation is straightforward and the extended series that is found this way leads to the conjecture that the exact answer is

$$K_k = 2\left(\frac{2}{3}\right)^{3/2}\left\{z^{-1/6}B\left(\frac{1}{3},\frac{1}{3}\right)F\left(\frac{1}{3},\frac{1}{3};\frac{2}{3};z\right) - z^{1/6}B\left(\frac{2}{3},\frac{2}{3}\right)F\left(\frac{2}{3},\frac{2}{3};\frac{4}{3};z\right)\right\},$$
$$z = \frac{2\left(\sin\frac{1}{2}k\right)^2}{27} \tag{A.10}$$

where F is the hypergeometric function. To go from numerical conjecture to proof it suffices to show that (A.10) satisfies the same differential equation as (24) and this can be done as follows. First note that (A.10) implies $K_k = K(z)$ is a solution to the differential equation $[z^2(1-z)\partial^2/\partial z^2 + z(1-2z)\partial/\partial z - (1+9z)/36]K = 0$. Applying this same differential operator to the integral representation (24) yields an integral of the form $\int \mathrm{d}s\, N/D^{5/2}$ and it remains to show that this vanishes. Now the numerator N in the integrand is a polynomial in s of degree 8 and by explicit calculation one finds that it can be written as the sum of terms $2ns^{n-1}D - 3(s^n + \delta_{n6}t^6)\partial D/\partial s$, $1 \leqslant n \leqslant 6$, with coefficients that are functions of t. Since the contribution of each of the six terms to the integral can be trivially shown to vanish by an integration by parts, the identity of the hypergeometric (A.10) and elliptic integral (24) representations is established. Unfortunately, neither the numerical nor analytical manipulations above give any hint as to whether a transformation exists that gives (A.10) directly from (24) or that might simplify the remaining integrals to which I now return.

The evaluation of $I_k(\chi)$ can be reduced by the $k_1 \leftrightarrow k_2$ symmetry to

$$I_k(\chi) = \chi_k K_k - 8(1+t^2)\int_0^\infty \frac{\mathrm{d}s\,\chi_{k1}}{\sqrt{D}} + 4(1+t^2)\int_0^\infty \frac{\mathrm{d}s\,\chi_{k3}}{\sqrt{D}} \tag{A.11}$$

and we wish to determine the small k behaviour of this when $\chi = {}^S\chi(p)$ given in (29). The first term with the evaluation in (28) gives the contributions (31*a*), (31*d*), (31*f*). To evaluate the other two terms in (A.11) first note that both ${}^S\chi_{k1}$ and ${}^S\chi_{k3}$ can be easily expressed in terms of s and t. For ${}^S\chi_{k1}$ we have

$${}^S\chi_{k1} = -\cos\frac{1}{2}\ell_1\left(\sin\frac{1}{2}\ell_1\right)^p = \frac{-(2s)^p(1-s^2)}{(1+s^2)^{p+1}} \tag{A.12}$$

valid for all $0 < \ell_1 < 2\pi$ while for ${}^S\chi_{k3}$ we need to distinguish the cases $k_1 < k$ and $k_1 > k$. Consider the latter first in which case the definition (16) yields a k_3 on the interval $(0, 2\pi)$ and hence a positive $\sin\frac{1}{2}k_3 = \sin\psi\cos\frac{1}{4}(k_1-k) + \cos\psi\sin\frac{1}{4}(k_1-k)$. On using the solution (19*b*), (19*c*) we get

$$\sin\frac{1}{2}k_3 = \tan\frac{1}{4}(k_1-k)\left[\Delta+\cos\frac{1}{4}(k_1-k)\cos\frac{1}{4}(k_1+k)\right]$$
$$= \cot\frac{1}{4}(\ell_1+k)\left[\Delta+\sin\frac{1}{4}(\ell_1+k)\sin\frac{1}{4}(\ell_1-k)\right]$$
$$= \frac{\left(\cos\frac{1}{4}k\right)^2}{(1+s^2)}\left[\frac{(\surd D+s^2-t^2)(1-st)}{(s+t)}\right]. \tag{A.13}$$

A similar analysis for $\cos\frac{1}{2}k_3$ combined with (A.13) finally yields

$$^S\chi_{k3} = \frac{-\left(\cos\frac{1}{4}k\right)^{2p+2}}{(1+s^2)^{p+1}}\left[\frac{(1-st)^2(s-t)}{(s+t)}-\surd D\right]\left[\frac{(\surd D+s^2-t^2)(1-st)}{(s+t)}\right]^p. \tag{A.14}$$

It is not obvious whether a convergent series analogous to (A.10) exists for $I_k(^S\chi(p))$ but even if the expansion leads to an asymptotic series, the low order terms are still meaningful. To get those contributions that arise out of $s \sim \tilde{t}^{1/3}$ we supplement (A.6) with

$$^S\chi_{k1} = -(2s)^p\{1-(p+2)s^2+\cdots\}, \tag{A.15}$$

$$^S\chi_{k3} = -\left[\frac{(s^2+\surd(4st+s^4))}{s}\right]^p\left\{1-(p+1)s^2-(p+2)t/s-\surd(4st+s^4)\right.$$
$$\left.+\frac{p\left(\frac{2s^3t}{\surd(4st+s^4)}\right)}{(s^2+\surd(4st+s^4))}+\cdots\right\} \tag{A.16}$$

in which only the first correction of relative magnitude $t^{2/3}$ has been kept. The leading contribution of the middle term in (A.11) is now, with $4t$ set to k and the substitution $s=(k\sigma)^{1/3}$,

$$8\int_0^\infty \mathrm{d}s(2s)^p/\surd(sk+s^4) = \left(\frac{8}{3}\right)k^{(p-1)/3}\,2^p\int_0^\infty \mathrm{d}\sigma\;\sigma^{(2p-5)/6}(1+\sigma)^{-1/2}$$
$$= \left(\frac{8}{3}\right)k^{(p-1)/3}2^pB((2p+1)/6,(1-p)/3)$$
$$= \left(\frac{4}{3}\right)k^{(p-1)/3}2^{(2+p)/3}2B((2p+1)/3,(1-p)/3) \tag{A.17}$$

which is one of the contributions in (31*c*). Note that the original integral in (A.11) is defined for $-1 < p < \infty$ but the assumed ordering of terms to get to (A.17) has now limited the range of validity to $-1/2 < p < 1$. The final result in (A.17) defines a function that can be analytically continued outside this range and is correct in the sense that when it is added to all other contributions in (31*a*)–(31*f*) the correct total is obtained. It is just that when p lies outside $(-1/2, 1)$ what we have calculated in (A.17) is still a contribution but not necessarily the dominant contribution. Similar comments apply to all other calculations in this appendix.

The leading contribution of the last term in (A.11), using (A.6) and (A.16) is

$$-4\int_0^\infty \mathrm{d}s\frac{[(s^2+\surd(sk+s^4))/s]^p}{\surd(sk+s^4)} \tag{A.18}$$

and the useful substitution now is $s = k^{1/3}(\sinh\theta)^{2/3}$ followed by $\exp(2\theta) = 1+\sigma$. Contribution (A.18) then becomes

$$-(8/3)k^{(p-1)/3}\int_0^\infty \mathrm{d}\theta\,\frac{\exp(p\theta)}{(\sinh\theta)^{(p+2)/3}}$$
$$= -(4/3)k^{(p-1)/3}2^{(2+p)/3}\int_0^\infty \mathrm{d}\sigma\,\sigma^{-(p+2)/3}(1+\sigma)^{-2(1-p)/3}$$
$$= -(4/3)k^{(p-1)/3}2^{(2+p)/3}B((1-p)/3,(1-p)/3) \qquad \text{(A.19)}$$

which is the remaining contribution to (31*c*). The first correction terms in (A.6) and (A.15), (A.16) yield (31*e*) and although the calculation is quite involved there is nothing fundamentally different.

There remains the term (31*b*) which arises from the integrand region $s \sim t^3$ in the integral over ${}^S\chi_{k1}$ and from the region $k_1 < k$ in the integral over ${}^S\chi_{k3}$. For the former we have an integral that is like (A.17) except that we must approximate $\sqrt{D}$ by $\sqrt{(4st + t^4)}$. The appropriate substitution is now $s = t^3\sigma/4$ and we get the contribution

$$8\int_0^\infty \mathrm{d}s(2s)^p/\sqrt{(4st+t^4)} = t^{3p+1}2^{1-p}\int_0^\infty \mathrm{d}\sigma\,\sigma^p(1+\sigma)^{-1/2}$$
$$= \frac{k^{3p+1}}{2^{7p+1}}B\left(p+1,-p-\frac{1}{2}\right) = \frac{k^{3p+1}}{2^{5p}}2B(p+1,-2p-1). \qquad \text{(A.20)}$$

For the $k_1 < k$ region, it is simpler to leave the integrand in the k and k_1 variables and perform the integration over k_1 directly. The result for $\sin\frac{1}{2}k_3$ is like the first equality in (A.13); when due attention is paid to signs we get

$$\sin\frac{1}{2}k_3 = -\tan\frac{1}{4}(k-k_1)\left[\Delta - \cos\frac{1}{4}(k-k_1)\cos\frac{1}{4}(k_1+k)\right]$$
$$= \frac{-\tan\frac{1}{4}(k-k_1)\sin\frac{1}{2}k\sin\frac{1}{2}k_1}{\left[\Delta+\cos\frac{1}{4}(k-k_1)\cos\frac{1}{4}(k_1+k)\right]}$$
$$\approx \frac{-(k-k_1)kk_1}{32} \qquad \text{(A.21)}$$

and the (small) negative value simply implies that on mapping to the interval $(0, 2\pi)$ we get $k_3 = 2\pi - \ell_3$ with (small) positive ℓ_3. Then $\cos\frac{1}{2}k_3 \approx -1$ and since $\Delta \approx 1$, the integral over ${}^S\chi_{k3}$ is just

$$-\int_0^k \mathrm{d}k_1\left[\frac{(k-k_1)kk_1}{32}\right]^p = \frac{-k^{3p+1}}{2^{5p}}\int_0^1 \mathrm{d}\sigma[\sigma(1-\sigma)]^p$$
$$= \frac{-k^{3p+1}}{2^{5p}}B(p+1,p+1) \qquad \text{(A.22)}$$

giving the final contribution to (31*b*). This completes the description of the evaluation of (31*a*)–(31*f*).

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