Momentum Autocorrelation Function of a Heavy Particle in a Finite Crystal

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Abstract: The momentum autocorrelation function of a heavy particle in a finite one-dimensional crystal, $\rho_0^{(N)}(\tau)$, is compared with the same function in an infinite crystal, $\rho_0^{(\infty)}(\tau)$, by obtaining an explicit upper bound for the magnitude of the difference, $|\rho_0^{(N)}(\tau) - \rho_0^{(\infty)}(\tau)|$. The precise meaning of the statement that $\rho_0^{(\infty)}(\tau)$ is approximately a simple exponential is reviewed, and precise meaning is given to the statement that $\rho_0^{(N)}(\tau)$ decays exponentially.

Over 50 years ago, Professor Debye recognized that density variations or fluctuations play an essential role in the interpretation of the thermal conductivity of crystalline solids.[1] His paper was one of the first on the properties of crystals containing defects. There is now an enormous and still-growing literature on the subject.

The investigations of the time-dependent properties of a heavy particle substituted in a harmonic crystal have been extensive and numerous[2-17] because of the relevance of this system to statistical mechanical theories of Brownian motion. In these investigations, the momentum autocorrelation function of the heavy Brownian particle has been evaluated only in the limit of an infinite crystal. In the present paper we obtain estimates of the same momentum autocorrelation function in the case of a finite one-dimensional crystal. This work was stimulated by a discussion with R. W. Zwanzig, and it is based on a method used recently by Rubin and Ullersma[18] for estimating the momentum autocorrelation function of particles in a special finite harmonic oscillator system, the Bernoulli chain.

The one-dimensional, nearest neighbor crystal model, which we consider, consists of $2N + 1$ particles with periodic boundary conditions. The particles are labeled from $-N$ to N, and all particles except 0 have a mass m while particle 0 has the mass $M > m$. There are two equivalent expressions for the momentum autocorrelation function of particle 0 in a finite crystal. The first, which was obtained by Rubin,[6] is

$$\rho_0^{(N)}(t) = \frac{Q+1}{2\pi i}\int_{\mathrm{L}} \frac{p\zeta[0,p]\exp(p\omega_0 t)}{1 + Qp^2\zeta[0,p]}\,\mathrm{d}p \qquad (1)$$

where

$$\zeta[0,p] = (2N+1)^{-1}\sum_{S=-N}^{N}\left[p^2 + \sin^2\frac{\pi s}{2N+1}\right]^{-1}$$

$Q = (M - m)/m$, $\omega_0 = 2(k/m)^{1/2}$ is the maximum frequency of an infinite and perfect one-dimensional crystal, and k is the nearest neighbor force constant. The path of the line integral in eq 1 is a line parallel to the imaginary p axis and to the right of all singularities of the integrand. The second expression for the momentum autocorrelation function is[3,19-21]

$$\rho_0^{(N)}(t) = \sum_{\nu=1}^{2N+1} X_{0\nu}^2\cos(\omega_\nu t) \qquad (2)$$

where $X_{0\nu}$ is the amplitude of particle 0 in the νth normalized normal mode vector and ω_ν is the frequency of the νth normal mode.

In estimating the value of $\rho_0^{(N)}(t)$ for a finite crystal, we will need the second of the foregoing representations. The explicit form for eq 2 is given in Hemmer's thesis.[3] Because the thesis is not readily available, we will derive the explicit form of eq 2 from eq 1 in the remainder of this section, and then obtain estimates of eq 2 for finite N in section II.

In the case of a finite crystal, the only singularities of the integrand in eq 1 are simple poles located on the imaginary p axis. Among these is a pole at $p = 0$, corresponding to zero frequency, free translation of the system. The remaining poles occur at zeros of the denominator

$$D(iy) = 1 - Qy^2\zeta[0,iy], \qquad p = iy \qquad (3)$$

The function $\zeta[0,iy]$ in eq 3 has been evaluated by Wallis and Maradudin.[22] Its value is

$$\zeta[0,iy] = -y^{-1}(1 - y^2)^{-1/2}\cot[(2N+1)\sin^{-1} y] \qquad (4)$$

Substituting eq 4 in eq 3, we obtain the following transcendental equation for the zeros of the denominator $D(iy)$

$$1 + Q\tan(\sin^{-1} y)\cot[(2N+1)\sin^{-1} y] = 0 \qquad (5)$$

(1) P. Debye in "Vorträge über die Kinetische Theorie der Materie," Teubner, Leipzig and Berlin, 1914.
(2) R. J. Rubin in "Proceedings of the International Symposium on Transport Processes in Statistical Mechanics, August 1956," I. Prigogine, Ed., Interscience Publishers, Inc., New York, N. Y., 1958, p 155.
(3) P. C. Hemmer, Thesis, Norges Tekniske Hogskole, Trondheim, Norway, 1959.
(4) R. J. Rubin, *J. Math. Phys.*, **1**, 309 (1960).
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(11) P. Mazur and E. Braun, *Physica*, **30**, 1973 (1964).
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(13) P. Ullersma, *Physica*, **32**, 74 (1966).
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(18) R. J. Rubin and P. Ullersma, *J. Math. Phys.*, **7**, 1877 (1966).
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(20) R. E. Turner, *Physica*, **26**, 274 (1960).
(21) R. J. Rubin, *Phys. Rev.*, **131**, 964 (1963).
(22) R. F. Wallis and A. A. Maradudin, *Progr. Theoret. Phys.* (Kyoto), **24**, 1055 (1960).

In our model, when $Q > 0$, there is one zero of $D(iy)$ located in each of the intervals

$$\sin\left(\frac{\pi(\nu - 1)}{2N + 1}\right) < y_\nu < \sin\left(\frac{\pi\nu}{2N + 1}\right)$$
$$\nu = 1, \ldots, N$$

In addition, it is clear from the form of eq 5 that there is also a zero at $-y_\nu$. The value of the integral in eq 1 is simply the sum of the residues of the integrand at each of the poles

$$\rho_0^{(N)}(t) = \frac{Q + 1}{2N + 1 + Q} + (Q + 1) \times \sum_{\nu=1}^{N}\left[\frac{iy_\nu\zeta[0,iy_\nu]\exp(iy_\nu\omega_0 t)}{(\mathrm{d}D(p)/\mathrm{d}p)_{p=iy_\nu}} + \frac{-iy_\nu\zeta[0,-iy_\nu]\exp(-iy_\nu\omega_0 t)}{(\mathrm{d}D(p)/\mathrm{d}p)_{p=-iy_\nu}}\right] \quad (6)$$

For the denominator in eq 6, we obtain

$$(\mathrm{d}D(p)/\mathrm{d}p)|_{p=iy_\nu} = 2Qiy_\nu\zeta[0,iy_\nu] + 2iQy_\nu^3(2N + 1)^{-1}\sum_{s=-N}^{N}\left[\sin^2\left(\frac{\pi s}{2N + 1}\right) - y_\nu^2\right]^{-2} = 2Qiy_\nu\zeta[0,iy_\nu] + iQy_\nu^2(\mathrm{d}\zeta[0,iy_\nu]/\mathrm{d}y_\nu) = iy_\nu\{2Q\zeta[0,iy_\nu] + Q(1 - y_\nu^2)^{-1/2}(2N + 1) \times \csc^2[(2N + 1)\sin^{-1} y] - Qy_\nu[(1 - y_\nu^2)^{-3/2} - y_\nu^{-2}(1 - y_\nu^2)^{-1/2}] \times \cot[(2N + 1)\sin^{-1} y]\} \quad (7)$$

Equation 6, after insertion of eq 7, can be considerably simplified with the aid of the following identities.

$$\zeta[0,iy_\nu] = (Qy_\nu^2)^{-1}$$
$$\cot[(2N + 1)\sin^{-1} y_\nu] = -(1 - y_\nu^2)^{1/2}/Qy_\nu$$
$$\csc^2[(2N + 1)\sin^{-1} y_\nu] = [(Q^2 - 1)y_\nu^2 + 1]/Q^2y_\nu^2$$

The final form of the expression for the momentum autocorrelation function is

$$\rho_0^{(N)}(\tau) = \frac{Q + 1}{2N + 1}\left\{\frac{1}{1 + Q(2N + 1)^{-1}} + 2\sum_{\nu=1}^{N}\frac{(1 - y_\nu^2)\cos(y_\nu\tau)}{(Q^2 - 1)y_\nu^2 + 1 + Q(2N + 1)^{-1}}\right\} \quad (8)$$

where y_ν is the νth zero of

$$Q^{-1}D(iy_\nu) = Q^{-1} + y_\nu(1 - y_\nu^2)^{-1/2}\cot[(2N + 1)\sin^{-1} y_\nu] \quad (8a)$$

and where $\tau = \omega_0 t$. Equation 8 has the form of eq 2, a sum over the normal modes, and was obtained by Hemmer.[3] Note that of the $2N + 1$ distinct normal mode frequencies of the system, only $N + 1$ appear in eq 8. Montroll and Potts,[23] in investigating the normal modes of vibration of such a single defect system, have noted that aside from the zero frequency mode, N of the normal mode eigenvectors are even with respect to the position of the defect particle and N are odd. Consequently, only the former appear explicitly in eq 8.

(23) E. W. Montroll and R. B. Potts, *Phys. Rev.*, 100, 525 (1955).

It should also be noted that in the limit $Q \rightarrow 0$, *i.e.*, $M \rightarrow m$, the expression for $\rho_0^{(N)}(\tau)$ assumes the form obtained by Mazur and Montroll[24]

$$\rho_0^{(N)}(\tau) = (2N + 1)^{-1}\left\{1 + 2\sum_{\nu=1}^{N}\cos(y_\nu^{(0)}\tau)\right\} \quad (9)$$

where $y_\nu^{(0)} = \pi\nu/(2N + 1)$ and $\nu = 1, \ldots, N$ are the roots obtained from eq 8a. It was noted[4] in the $N = \infty$ limit that there is some simplification in the form of $\rho_0^{(\infty)}(\tau)$ when $Q = 1$, *i.e.*, $M = 2m$. When $Q = 1$ and N is finite, eq 8 becomes

$$\rho_0^{(N)}(\tau) = (N + 1)^{-1}\left\{1 + 2\sum_{\nu=1}^{N}(1 - y_\nu^2)\cos(y_\nu\tau)\right\} \quad (10)$$

Estimate of Time Dependence of $\rho_0^{(N)}(\tau)$. The method of estimating the time dependence of $\rho_0^{(N)}(\tau)$ in eq 8 is straightforward and is identical with that used by Rubin and Ullersma[18] in a related problem. In the limit in which $N \rightarrow \infty$, the sum in eq 8 can be replaced by an integral

$$\rho_0^{(\infty)}(\tau) = (Q + 1)\int_0^1\frac{[1 - y^2(\mu)]\cos[y(\mu)\tau]}{(Q^2 - 1)y^2(\mu) + 1}\,\mathrm{d}\mu \quad (11)$$

where $y(\mu) = \sin(\pi\mu/2)$, and so

$$\rho_0^{(\infty)}(\tau) = (Q + 1)2\pi^{-1}\int_0^1\frac{(1 - y^2)^{1/2}\cos(y\tau)}{(Q^2 - 1)y^2 + 1}\,\mathrm{d}y \quad (12)$$

Equation 12 was obtained by Hemmer[3] and is equivalent to the contour integral obtained by Rubin.[2,4] Our problem now is to obtain an explicit estimate of the difference between $\rho_0^{(N)}(\tau)$ and $\rho_0^{(\infty)}(\tau)$. First note that the magnitude of the difference between $\rho_0^{(N)}(\tau)$ and the related sum in eq 13 satisfies the following inequality

$$\left|\rho_0^{(N)}(\tau) - \left(\frac{Q + 1}{N}\right)\sum_{\nu=1}^{N}\frac{(1 - y_\nu^2)\cos(y_\nu\tau)}{(Q^2 - 1)y_\nu^2 + 1}\right| \leqslant \frac{Q + 1}{2N + 1} \quad (13)$$

where y_ν is the root of eq 8a which lies between $\sin[\pi(\nu - 1)/(2N + 1)]$ and $\sin[\pi\nu/(2N + 1)]$. Next consider the magnitude of the difference between the integral $\rho_0^{(\infty)}(\tau)$ in eq 11 and its approximating sum $\hat{\rho}_0(\tau)$ based on the points

$$y(\nu/n) = \sin(\pi\nu/2N), \qquad \nu = 1, \ldots, N$$

The magnitude of the difference satisfies the inequality[25]

$$|\rho_0^{(\infty)}(\tau) - \hat{\rho}_0(\tau)| \leqslant N^{-1}\mathcal{V} \quad (14)$$

where $\mathcal{V}$, the variation of the integrand in (11), is

$$\mathcal{V} = (Q + 1)\int_0^1\left|\frac{\mathrm{d}}{\mathrm{d}\mu}\left(\frac{[1 - y^2(\mu)]\cos[y(\mu)\tau]}{(Q^2 - 1)y^2(\mu) + 1}\right)\right|\mathrm{d}\mu \quad (15)$$

By an identical argument, the magnitude of the difference between $\hat{\rho}_0(\tau)$ and the sum in eq 13 satisfies the inequality

$$\left|\hat{\rho}_0(\tau) - \frac{Q + 1}{N}\sum_{\nu=1}^{N}\frac{(1 - y_\nu^2)\cos(y_\nu\tau)}{(Q^2 - 1)y_\nu^2 + 1}\right| \leqslant N^{-1}\mathcal{V} \quad (16)$$

(24) P. Mazur and E. W. Montroll, *J. Math. Phys.*, 1, 70 (1960).
(25) G. Polya and G. Szegö, "Aufgaben und Lehrsätze aus der Analysis," Vol. 1, 3rd ed, Springer-Verlag, Berlin, p 37.

The following upper bound can be obtained for the variation of the integrand in (11)

$$\mathcal{V} \leqslant (Q + 1)(\tfrac{1}{2}\pi\tau Q^{-1} + 1)$$

Consequently we obtain an explicit upper bound on the difference $|\rho_0^{(\infty)}(\tau) - \rho_0^{(N)}(\tau)|$. It is

$$|\rho_0^{(\infty)}(\tau) - \rho_0^{(N)}(\tau)| \leq 2N^{-1}\mathcal{V} + (Q + 1)(2N + 1)^{-1} \leqslant (1 + Q^{-1})\pi\tau N^{-1} + (Q + 1)[2N^{-1} + (2N + 1)^{-1}] \quad (17)$$

It is known from earlier work[4,6] that when $Q \gg 1$ and $N = \infty$

$$\left|\rho_0^{(\infty)}(\tau) - \left(\frac{Q + 1}{Q + Q^{-1}}\right)\exp[-\tau(Q^2 - 1)^{-1/2}]\right| \leqslant \begin{cases} 2^{1/2}Q^{-1} & 0 \leqslant \tau \leqslant \pi^{-1/3} \\ (2/\pi)^{1/2}Q^{-1}\tau^{-3/2} & \tau \geqslant \pi^{-1/3} \end{cases} \quad (18)$$

Combining (17) and (18), we obtain finally

$$|\rho_0^{(N)}(T) - \exp(-T)| \leq 2^{1/2}Q^{-1} \times \min\{1,\pi^{-1/2}(QT)^{-3/2}\} + (\pi T + \tfrac{1}{2})QN^{-1} \quad (19)$$

where we have introduced the new time variable $T = \tau/Q$ measured in units of the relaxation time of the exponential. In addition, terms of order N^{-1} and Q^{-1} have been neglected in comparison with unity. The estimate for the momentum autocorrelation function $\rho_0^{(N)}(T)$ is useful provided that the error bound on the right-hand side of eq 19 is small compared to the exponential on the left-hand side. We will now examine the nature of the error estimate in (19) in more detail. First we consider the special case $N = \infty$ and then the general case of finite N.

N = ∞ and Q ≫ 1. In the limit $N = \infty$, it is readily verified that when $T = \alpha \ln Q$, the ratio of the error bound to the exponential in eq 19 is

$$\mathcal{R} = (2/\pi)^{1/2}Q^{\alpha-(5/2)}(\alpha \ln Q)^{-3/2} \quad (20)$$

The ratio approaches zero for $\alpha < 5/2$. For example, when $\alpha = 2$ and $Q = 10^4$, the ratio $\mathcal{R} \cong 1.01 \times 10^{-4}$ and $T \cong 18.42$. Thus in this example, after 18 relaxation times, the correction to the exponential is less than 10^{-4} of the value of the exponential. It is clear that as Q increases, the T interval in which the exponential is a good approximation to $\rho_0^{(\infty)}(T)$ increases $\sim \alpha \ln Q$ and the error in the approximation approaches zero $\sim Q^{\alpha-(5/2)} (\ln Q)^{-3/2}$ where $\alpha < 5/2$.

Finite N, $N \gg Q \gg 1$. We now consider the inequality (19) when $N \gg Q \gg 1$. For $T = \alpha \ln Q$, the ratio of the error bound to the exponential in eq 19 is

$$\mathcal{R} = (2/\pi)^{1/2}Q^{\alpha-(5/2)}(\alpha \ln Q)^{-3/2} + N^{-1}Q^{1+\alpha}(\pi\alpha \ln Q + \tfrac{1}{2}) \quad (21)$$

In the preceding case the term proportional to N^{-1} was absent. In the present case, if $Q \gg 1$ and $N = Q^{1+\alpha+\beta}$, where $0 < \beta < (5/2) - \alpha$, then the second term on the right-hand side dominates the first

$$\mathcal{R} \cong Q^{-\beta}(\pi\alpha \ln Q + \tfrac{1}{2}) \quad (22)$$

and the ratio $\mathcal{R}$ approaches zero in the limit $Q \to \infty$, $N = Q^{1+\alpha+\beta}$. For example, when $\alpha = 1$, $Q = 10^4$, and $\beta = 1$, the ratio $\mathcal{R} \cong 2.94 \times 10^{-3}$ and $T \cong 9.21$. In this example the correction to the exponential is less than 3×10^{-3} of the value of the exponential after nine relaxation times. It is clear that, as Q increases and with $N = Q^{1+\alpha+\beta}$, the T interval in which the exponential is a good approximation to $\rho_0^{(N)}(T)$ increases $\sim\alpha \ln Q$ and the error in the approximation approaches zero at least as fast at $Q^{-(\alpha+\beta)} \ln Q$, where $\alpha > 0$ and $\beta + \alpha < 5/2$.

It is in the above sense that the momentum autocorrelation function of a heavy particle in a finite crystal is a simple exponential.