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Mean-square displacements of atoms in thin crystal films

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On the basis of a simple model of a simple cubic crystal, calculations are carried out of the mean-square displacement of an atom in a thin film of L layers bounded by two free (001) surfaces. The results are compared with those for a semi-infinite crystal bounded by a single free (001) surface for atoms at the same distance from the surface. The conditions under which the two sets of results are in essential agreement are established.

I. INTRODUCTION

Although the calculation of the mean-square displacements of atoms in the surface layers of a semi-infinite crystal has a long history,[1] such calculations have acquired a particular significance in recent years due to the important role played by mean-square atomic displacements in theoretical calculation of low-energy-electron-diffraction intensities.[2]

At the present time the most detailed calculations of the mean-square displacements of atoms at crystal surfaces[3] are carried out by representing a semi-infinite crystal in the form of a thin film, or slab, of a comparatively small number of atomic layers (of the orders of 20). The normal-mode frequencies and the corrresponding polarization vectors for such a crystal film can be obtained by purely numerical methods on a high-speed computer, and are then combined to yield the mean-square displacements as functions of the distance into the film from the surface according to well-known expressions.[4]

The number of layers in a crystal film used in such calculations is determined primarily by the length and cost of the computational effort involved in obtaining the normal mode frequencies and polarization vectors for the film, and in the subsequent calculations of the mean-square displacements. Nevertheless, it is generally felt that the film thicknesses employed in these calculations are large enough that effects due to the finite thickness of the film are unimportant. Put another way, it has been felt that the approach of the mean-square displacement toward its limiting bulk value with increasing distance into the crystal from its surface is so rapid, occurring within a distance of the order of half a dozen or so atomic layers, that by the time a film is of the order of 20 layers thick the influence of the second surface on what is happening in the vicinity of the first is negligible.

That this may in fact not be the case is suggested by the results of two recent calculations of the mean-square displacements of atoms in a semi-infinite crystal; the first carried out by the methods of lattice dynamics,[5] the second by continuum mechanics.[6] Both of these calculations agree in showing that the mean-square displacement approaches its limiting bulk value very slowly: The surface correction to the limiting bulk value decreases as only the first power of the inverse distance into the crystal from the surface. The existence of this long "tail" to the single surface contribution to the mean-square displacement suggests that the presence of a second surface on a film may affect the values of the mean-square displacement for atoms in the vicinity of the first surface in a quantitatively non-negligible way.

In fact, in actual calculations of the mean-square displacements by the slab method, where the results are intended to represent mean-square displacements in a semi-infinite crystal, the rate of approach of the mean-square displacement to its bulk value with increasing distance into the crystal from the surface is accelerated by suitably adjusting the ratio of the lateral extent of the crystal to its thickness.[7] This is done through the choice of the values of the two-dimensional wave vector in the plane of the surfaces that serves as a partial label for the normal modes of the slab, since their density is related to the lateral dimensions of the slab through periodic boundary conditions on the atomic displacements in directions parallel to the surface. How this is done and why it works will be clear from the analysis presented in this paper.

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In this paper we obtain the variation of the mean-square displacement across a thin film of a crystal as a function of the number of atomic layers in the film and compare the results with those for a semi-infinite crystal. In this way we can answer such qualitative questions as the nature of the difference between the mean-square displacement of an atom in a thin film and an atom in a semi-infinite crystal, and such quantitative questions as the condition under which calculations based on a film can yield results approximating those for a semi-infinite crystal, with a specified error.

In order to make this kind of comparison most accurately it is desirable, perhaps even necessary, that the calculations be carried out analytically. This requirement demands in turn the use of a rather simple crystal model in our calculations. We have chosen to use the so-called Montroll-Potts model of a simple cubic crystal with nearest-neighbor, central, and noncentral force interactions between atoms.[8] This model is well known not to satisfy the conditions imposed by the requirements of infinitesimal rotational invariance[9]; it does not give rise to Rayleigh surface waves on a (001) surface such as we consider here.[10] A film based on it also does not possess the plate modes in the long-wavelength limit predicted by continuum theory.[11] Nevertheless, these deficiencies of the model are unimportant for the physical properties we are considering, for which the existence of Rayleigh waves and plate modes is inessential.

The only related work of which we are aware is that of Corciovei and Berlinde,[12] who also studied the mean-square displacement of an atom in a thin film of a Montroll-Potts crystal bounded by (001) free surfaces. These authors, however, averaged this quantity over the thickness of the film and calculated the resulting average as a function of the thickness of the film. In contrast, we obtain the mean-square displacement at any lattice site within the film.

In Sec. II we will obtain the dynamical Green's function for a thin film of a Montroll-Potts crystal, bounded by a pair of (001) free surfaces. This result is used in Sec. III in a calculation of the mean-square displacement of a typical atom in the film in the classical, or high-temperature, limit. The results of this calculation are discussed in Sec. IV.

II. DYNAMICAL GREEN'S FUNCTION FOR A CRYSTAL FILM

In this section we obtain the dynamical Green's function for a thin film of a simple cubic crystal with nearest-neighbor, central, and noncentral force interactions between atoms. The film, which consists of L layers, is bounded by a pair of (001) surfaces.

We construct the film in the following way. We begin with an infinitely extended simple cubic crystal whose lattice translation vectors are given by

$$\vec{x}(l)=a_0(l_1,l_2,l_3)\ , \tag{2.1}$$

where a_0 is the lattice parameter, and l_1,l_2,l_3 are any three integers, positive, negative, or zero, which we denote collectively by l. We then excise a film of L layers by equating to zero all interactions between atoms in the plane $l_3=0$ and atoms in the plane $l_3=1$ and between atoms in the plane $l_3=L$ and atoms in the plane $l_3=L+1$, and then restricting l_3 to assume only the values $1\le l_3\le L$.

The time-independent equations of motion of the infinite crystal perturbed by the annulment of the interactions between the layers $l_3=0$ and $l_3=1$ and between the layers $l_3=L$ and $l_3=L+1$ can be written in the form

$$(\underline{L}^{(0)}-\delta\underline{L}^{(1)}-\delta\underline{L}^{(2)})\vec{u}=0\ , \tag{2.2}$$

where the elements of the matrices $\underline{L}^{(0)}$, $\delta\underline{L}^{(1)}$, and $\delta\underline{L}^{(2)}$ are given by

$$\begin{aligned}L^{(0)}_{\alpha\beta}(ll';\omega^2)=\delta_{\alpha\beta}[&M\omega^2\delta_{l_1l_1'}\delta_{l_2l_2'}\delta_{l_3l_3'}+\gamma(\delta_{l_1l_1'-1}\delta_{l_2l_2'}\delta_{l_3l_3'}+\delta_{l_1l_1'+1}\delta_{l_2l_2'}\delta_{l_3l_3'}\\&+\delta_{l_1l_1'}\delta_{l_2l_2'-1}\delta_{l_3l_3'}+\delta_{l_1l_1'}\delta_{l_2l_2'+1}\delta_{l_3l_3'}+\delta_{l_1l_1'}\delta_{l_2l_2'}\delta_{l_3l_3'-1}\\&+\delta_{l_1l_1'}\delta_{l_2l_2'}\delta_{l_3l_3'+1}-6\delta_{l_1l_1'}\delta_{l_2l_2'}\delta_{l_3l_3'})]\ ,\end{aligned} \tag{2.3a}$$

$$\delta L^{(2)}_{\alpha\beta}(ll')=-\delta_{\alpha\beta}\gamma\delta_{l_1l_1'}\delta_{l_2l_2'}(\delta_{l_30}-\delta_{l_31})(\delta_{l_3'0}-\delta_{l_3'1})\ , \tag{2.3b}$$

$$\delta L^{(2)}_{\alpha\beta}(ll')=-\delta_{\alpha\beta}\gamma\delta_{l_1l_1'}\delta_{l_2l_2'}(\delta_{l_3L}-\delta_{l_3L+1})(\delta_{l_3'L}-\delta_{l_3'L+1})\ , \tag{2.3c}$$

where M is the mass of an atom in the crystal, and γ is the nearest-neighbor force constant. To simplify the Montroll-Potts model further, we have assumed that the central and noncentral force constants are all equal. In these expressions α and β label the Cartesian axes. The matrix $\underline{L}^{(0)}$ describes the vibrations of the infinitely extended crystal; $\delta\underline{L}^{(1)}$ subtracts the interactions between the planes $l_3=0$ and $l_3=1$; $\delta\underline{L}^{(2)}$ subtracts the interactions between the planes $l_3=L$ and $l_3=L+1$.

We now define three Green's functions, $G_{\alpha\beta}(ll';\omega^2)$, $G^{(S)}_{\alpha\beta}(ll';\omega^2)$, and $U_{\alpha\beta}(ll';\omega^2)$ as the solutions of the equations

$$\underline{L}^{(0)}\underline{G}=\underline{I} \tag{2.4a}$$

$$(\underline{L}^{(0)}-\delta\underline{L}^{(1)})\underline{G}^{(S)}=\underline{I} \tag{2.4b}$$

$$(\underline{L}^{(0)}-\delta\underline{L}^{(1)}-\delta\underline{L}^{(2)})\underline{U}=\underline{I}\ . \tag{2.4c}$$

In each case $\underline{I}$ is a unit matrix with elements $\delta_{\alpha\beta}\delta_{ll'}$. The Green's function G is that for an infinitely extended crystal; $\underline{G}^{(S)}$ is the Green's function for a semi-infinite crystal occupying the region $l_3\geq 1$; $\underline{U}$ is the Green's function for the film defined by $1\leq l_3\leq L$.

To solve Eq. (2.4a) we represent $G_{\alpha\beta}(ll';\omega^2)$ in the form

$$G_{\alpha\beta}(ll';\omega^2)=\frac{\delta_{\alpha\beta}}{N^2}\sum_{\vec{k}_{||}}G(\vec{k}_{||}\omega\,|\,l_3l_3')e^{i\vec{k}_{||}\cdot[\vec{x}_{||}(l)-\vec{x}_{||}(l')]}\ , \tag{2.5}$$

which reflects the periodicity our system retains in directions parallel to the surfaces about to be introduced. In this expression $\vec{x}_{||}(l)=a_0(l_1,l_2,0)$ is a two-dimensional position vector parallel to the surface, and $\vec{k}_{||}=\hat{x}_1k_1+\hat{x}_2k_2$ is a two-dimensional wave vector parallel to the surface, where $\hat{x}_1,\hat{x}_2$ are unit vectors in the 1 and 2 directions. We assume periodic boundary conditions in the 1 and 2 directions, with the periodicity element being a square with edges of length Na_0 along each of these directions. The N^2 allowed values of the wave vector $\vec{k}_{||}$ are therefore given by

$$\vec{k}_{||}=\frac{2\pi}{Na_0}(m_1,m_2,0),\quad -\frac{N}{2}+1\leq m_1,m_2\leq\frac{N}{2} \tag{2.6}$$

where m_1 and m_2 are integers. The area swept out by the allowed values of $\vec{k}_{||}$ is the two-dimensional first Brillouin zone for this problem.

When we substitute Eq. (2.5) into Eq. (2.4a) and use Eq. (2.3a) we find that the Fourier coefficient $G(\vec{k}_{||}\omega\,|\,l_3l_3')$ satisfies the finite difference equation

$$G(\vec{k}_{||}\omega\,|\,l_3+1l_3')-2\zeta G(\vec{k}_{||}\omega\,|\,l_3l_3')+G(\vec{k}_{||}\omega\,|\,l_3-1l_3')=\frac{1}{\gamma}\delta_{l_3l_3'}\ , \tag{2.7a}$$

$$\zeta=3-\cos k_1a_0-\cos k_2a_0-\frac{M}{2\gamma}\omega^2\ , \tag{2.7b}$$

which has the solution

$$G(k_{||}\omega\,|\,l_3l_3')=\frac{1}{4\pi\gamma}\int_{-\pi}^{\pi}d\theta\frac{e^{i(l_3-l_3')\theta}}{\cos\theta-\zeta+i\epsilon}=\frac{1}{\gamma}\frac{t^{|l_3-l_3'|+1}}{t^2-1}\ , \tag{2.8}$$

where

$$t=\begin{cases}\zeta-(\zeta^2-1)^{1/2}, & \zeta>1 & (2.9a)\\ \zeta+i(1-\zeta^2)^{1/2}, & -1<\zeta<1 & (2.9b)\\ \zeta+(\zeta^2-1)^{1/2}, & \zeta<-1. & (2.9c)\end{cases}$$

We have introduced a positive infinitesimal imaginary part $i\epsilon$ into the denominator of the integrand in Eq. (2.8) to define the manner of treating the pole that it would otherwise have on the real axis.

The solution for $G_{\alpha\beta}(ll';\omega^2)$ just obtained enables us to solve for $G^{(S)}_{\alpha\beta}(ll';\omega^2)$. We rewrite Eq. (2.4b) as an integral equation for this Green's function:

$$G^{(S)}_{\alpha\beta}(ll';\omega^2)=G_{\alpha\beta}(ll';\omega^2)+\sum_{l''\gamma}\sum_{l'''\gamma}G_{\alpha\beta}(ll'';\omega^2)\delta L^{(1)}_{\gamma\delta}(l''l''')G^{(S)}_{\delta\beta}(l'''l';\omega^2)\ . \tag{2.10}$$

To solve this equation we expand $G^{(S)}_{\alpha\beta}(ll';\omega^2)$ in the form

$$G^{(S)}_{\alpha\beta}(ll';\omega^2)=\frac{\delta_{\alpha\beta}}{N^2}\sum_{\vec{k}_{||}}G^{(S)}(\vec{k}_{||}\omega\,|\,l_3l_3')e^{i\vec{k}_{||}\cdot[\vec{x}_{||}(l)-\vec{x}_{||}(l')]}\ , \tag{2.11}$$

and exploit the separable nature of the matrix $\delta L^{(1)}_{\alpha\beta}(ll')$ to obtain the equation satisfied by the Fourier coefficient $G^{(S)}(\vec{k}_{||}\omega\,|\,l_3l_3')$:

$$G^{(S)}(\vec{k}_{||}\omega \mid l_3 l_3') = G(\vec{k}_{||}\omega \mid l_3 l_3') - \gamma[G(\vec{k}_{||}\omega \mid l_3 0) - G(\vec{k}_{||}\omega \mid l_3 1)][G^{(S)}(\vec{k}_{||}\omega \mid 0 l_3') - G^{(S)}(\vec{k}_{||}\omega \mid 1 l_3')] \, . \tag{2.12}$$

This equation is readily solved with the result that

$$G^{(S)}(\vec{k}_{||}\omega \mid l_3 l_3') = G(\vec{k}_{||}\omega \mid l_3 l_3') - \gamma \frac{[G(\vec{k}_{||}\omega \mid l_3 0) - G(\vec{k}_{||}\omega \mid l_3 1)][G(\vec{k}_{||}\omega \mid 0 l_3') - G(\vec{k}_{||}\omega \mid 1 l_3')]}{1 + 2\gamma[G(\vec{k}_{||}\omega \mid 00) - G(\vec{k}_{||}\omega \mid 10)]} \, . \tag{2.13}$$

If we now restrict l_3 and l_3' by the condition $l_3, l_3' \geq 1$ we can simplify this result considerably. We substitute the result given by Eq. (2.8) into Eq. (2.13) and obtain the simple result that

$$G^{(S)}(\vec{k}_{||}\omega \mid l_3 l_3') = \frac{1}{\gamma} \frac{t^{|l_3 - l_3'| + 1}}{t^2 - 1} + \frac{1}{\gamma} \frac{t^{l_3 + l_3'}}{t^2 - 1} \tag{2.14a}$$

$$= G(\vec{k}_{||}\omega \mid l_3 l_3') + G(\vec{k}_{||}\omega \mid l_3 - 1, -l_3') \, , \tag{2.14b}$$

a result first obtained by Dobrzynski and Mills.[13]

We come finally to the Green's function $U_{\alpha\beta}(ll';\omega^2)$. Its defining equation, Eq. (2.4c) can be rewritten as an integral equation with the aid of Eq. (2.4b):

$$U_{\alpha\beta}(ll';\omega^2) = G^{(S)}_{\alpha\beta}(ll';\omega^2) + \sum_{l''\gamma} \sum_{l'''\delta} G^{(S)}_{\alpha\beta}(ll'';\omega^2) \delta L^{(2)}_{\gamma\delta}(l''l''') U_{\delta\beta}(l'''l';\omega^2) \, . \tag{2.15}$$

We expand this Green's function according to

$$U_{\alpha\beta}(ll';\omega^2) = \frac{\delta_{\alpha\beta}}{N^2} \sum_{\vec{k}_{||}} U(\vec{k}_{||}\omega \mid l_3 l_3') e^{i\vec{k}_{||} \cdot [\vec{x}_{||}(l) - \vec{x}_{||}(l')]} \, . \tag{2.16}$$

The equation satisfied by the Fourier coefficient $U(\vec{k}_{||}\omega \mid l_3 l_3')$ is

$$U(\vec{k}_{||}\omega \mid l_3 l_3') = G^{(S)}(\vec{k}_{||}\omega \mid l_3 l_3') - \gamma[G^{(S)}(\vec{k}_{||}\omega \mid l_3 L) - G^{(S)}(\vec{k}_{||}\omega \mid l_3 L + 1)][U(\vec{k}_{||}\omega \mid L l_3') - U(\vec{k}_{||}\omega \mid L + 1 l_3')] \, , \tag{2.17}$$

and its solution is

$$U(\vec{k}_{||}\omega \mid l_3 l_3') = G^{(S)}(\vec{k}_{||}\omega \mid l_3 l_3') - \gamma \frac{[G^{(S)}(\vec{k}_{||}\omega \mid l_3 L) - G^{(S)}(\vec{k}_{||}\omega \mid l_3 L + 1)][G^{(S)}(\vec{k}_{||}\omega \mid L l_3') - G^{(S)}(\vec{k}_{||}\omega \mid L + 1 l_3')]}{1 + \gamma[G^{(S)}(\vec{k}_{||}\omega \mid LL) - 2G^{(S)}(\vec{k}_{||}\omega \mid L L + 1) + G^{(S)}(\vec{k}_{||}\omega \mid L + 1 L + 1)]} \, . \tag{2.18}$$

If we now use Eq. (2.8) and restrict l_3 and l_3' by the conditions $l_3, l_3' \leq L$, we can simplify Eq. (2.18) considerably. We obtain finally the result that

$$U(\vec{k}_{||}\omega \mid l_3 l_3') = \frac{1}{\gamma} \frac{t^{|l_3 - l_3'| + 1}}{t^2 - 1} + \frac{1}{\gamma} \frac{t^{l_3 + l_3'}}{t^2 - 1} + \frac{1}{\gamma} \frac{t}{t^2 - 1} \frac{t^{2L}}{1 - t^{2L}} (t^{-l_3 - l_3' + 1} + t^{-l_3 + l_3'} + t^{l_3 - l_3'} + t^{l_3 + l_3' - 1}) \, . \tag{2.19}$$

We now proceed to utilize this result for the determination of the mean-square displacement of an atom in the film.

III. THE MEAN-SQUARE DISPLACEMENT OF AN ATOM IN A THIN FILM

The results of the preceding section enable us to obtain the mean-square displacement of an atom in a thin film. Our starting point is the relation between the mean square displacement and the Green's function[14] $U_{\alpha\beta}(ll' \mid \omega^2)$:

$$\langle u_\alpha^2(l)\rangle = -k_B T \sum_{n=-\infty} U_{\alpha\alpha}(ll \mid -\Omega_n^2) , \quad (3.1)$$

where $\Omega_n = (2\pi n/\beta\hbar)$, and $\beta = (k_B T)^{-1}$, with k_B Boltzmann's constant and T the absolute temperature. In the high-temperature, or classical, limit, which is the only one we consider in this paper, the only nonvanishing contribution to the sum on the right-hand side of Eq. (3.1) comes from the term with $n=0$:

$$\langle u_\alpha^2(l)\rangle = -k_B T U_{\alpha\alpha}(ll \mid 0), \quad T\to\infty . \quad (3.2)$$

With the aid of Eq. (2.16) we can rewrite Eq. (3.2) as

$$\langle u_\alpha^2(l)\rangle = -\frac{k_B T}{N^2}\sum_{\vec{k}_{\parallel}} U(\vec{k}_{\parallel} 0 \mid l_3 l_3) . \quad (3.3)$$

From the form of $U(\vec{k}_{\parallel}\omega \mid l_3 l_3')$ given by Eq. (2.19) we see that we can write $\langle u_\alpha^2(l)\rangle$ as the sum of three contributions:

$$\langle u_\alpha^2(l)\rangle = \langle u_\alpha^2(l)\rangle_B + \langle u_\alpha^2(l)\rangle_{1S} + \langle u_\alpha^2(l)\rangle_{2S} . \quad (3.4)$$

The first term is the bulk contribution to the mean-square displacement, i.e., the mean-square displacement in an infinitely extended crystal. The second term is the correction to the bulk contribution to the mean-square displacement that arises from the presence of a single, planar surface bounding a semi-infinite crystal. The last contribution represents the effect on $\langle u_\alpha^2(l)\rangle$ of the presence of a second, planar bounding surface, parallel to the first, creating a film of L atomic layers. We consider each contribution in turn.

We replace the summation over $\vec{k}_{\parallel}$ by an integration, and make the changes of variables

$$k_1 a_0 = \theta_1, \quad k_2 a_0 = \theta_2, \quad -\pi \le \theta_1, \theta_2 \le \pi . \quad (3.5)$$

Then on substituting the first term on the right-hand side of Eq. (2.19) into Eq. (3.3) we obtain for $\langle u_\alpha^2(l)\rangle_B$ the expression

$$\langle u_\alpha^2(l)\rangle_B = \frac{k_B T}{\gamma\pi^2}\int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \frac{t}{1-t^2} , \quad (3.6)$$

where now

$$t = \zeta - (\zeta^2-1)^{1/2} , \quad \zeta = 3-\cos\theta_1-\cos\theta_2 \ge 1 . \quad (3.7)$$

We now use the facts that

$$\frac{t}{1-t^2} = \frac{1}{2(\zeta^2-1)^{1/2}} \quad (3.8)$$

and

$$\frac{1}{\pi}\int_0^\pi d\theta_3 \frac{\cos l\theta_3}{\zeta-\cos\theta_3} = \frac{[\zeta-(\zeta^2-1)^{1/2}]^{|l|}}{(\zeta^2-1)^{1/2}} , \quad (3.9)$$

to rewrite Eq. (3.6) as

$$\langle u_\alpha^2(l)\rangle_B = \frac{k_B T}{2\gamma}\frac{1}{\pi^3}\int_0^\pi\int_0^\pi\int_0^\pi \frac{d\theta_1 d\theta_2 d\theta_3}{3-\cos\theta_1-\cos\theta_2-\cos\theta_3} = (0.505\,46)\frac{k_B T}{2\gamma} , \quad (3.10)$$

since the triple integral is recognized as the third of the three famous Watson integrals.[15]

The contribution $\langle u_\alpha^2(l)\rangle_{1S}$ can be written in the form

$$\langle u_\alpha^2(l)\rangle_{1S} = \frac{k_B T}{\gamma\pi^2}\int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \frac{t^{2l_3}}{1-t^2} . \quad (3.11)$$

With the aid of Eqs. (3.8) and (3.9) we can rewrite this expression in the form

$$\langle u_\alpha^2(l)\rangle_{1S} = \frac{k_B T}{2\gamma}\frac{1}{\pi^3}\int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \int_0^\pi d\theta_3 \frac{\cos(2l_3-1)\theta_3}{3-\cos\theta_1-\cos\theta_2-\cos\theta_3} . \quad (3.12)$$

The values of this integral for the first two values of l_3 are

$$\langle u_\alpha^2(l)\rangle_{1S}=\frac{k_BT}{2\gamma}(0.172\,13),\quad l_3=1 \tag{3.13a}$$

$$=\frac{k_BT}{2\gamma}(0.055\,09),\quad l_3=2\,. \tag{3.13b}$$

It is shown in the Appendix that the integral

$$I(l)=\frac{1}{\pi^2}\int_0^\pi d\theta_1\int_0^\pi d\theta_2\frac{t^l}{1-t^2},\quad l>0 \tag{3.14}$$

in the limit of large l has the asymptotic expansion

$$I(l)\sim\frac{1}{4\pi}\frac{1}{l-1}+\frac{1}{16\pi}\frac{1}{(l-1)^3}+O((l-1)^{-5})\,. \tag{3.15}$$

It follows, therefore, that in the limit of large l_3

$$\langle u_\alpha^2(l)\rangle_{1S}\sim\frac{k_BT}{4\pi\gamma}\left[\frac{1}{(2l_3-1)}+\frac{1}{4(2l_3-1)^3}+\cdots\right], \tag{3.16}$$

a result obtained previously by Dobrzynski and Lajzerowicz.[5]

It should be pointed out that the result given by Eq. (3.16) which has been obtained under the assumption that $2l_3-1$ is large, is quite accurate even for the smallest values of l_3, viz., $l_3=1,2$. Indeed we obtain from Eq. (3.16) the results that

$$\langle u_\alpha^2(l)\rangle_{1S}\sim\begin{cases}\dfrac{k_BT}{2\gamma}(0.198\,94),\quad l_3=1 & (3.17a)\\ \dfrac{k_BT}{2\gamma}(0.054\,53),\quad l_3=2\,. & (3.17b)\end{cases}$$

The first value is in error by 15.5%; the second is in error by only 1%.

We come finally to the contribution $\langle u_\alpha^2(l)\rangle_{2S}$. This can be written in the form

$$\langle u_\alpha^2(l)\rangle_{2S}=\frac{k_BT}{\gamma\pi^2}\times\int_0^\pi d\theta_1\int_0^\pi d\theta_2\frac{t}{1-t^2}\frac{t^{2L}}{1-t^{2L}}\times(t^{-2l_3+1}+2+t^{2l_3-1})\,. \tag{3.18}$$

The integrand in this expression has a singularity in the vicinity of the point $\theta_1=\theta_2=0$. This is characteristic of the integrand in the expression for the mean-square displacement of an atom in a thin film.[7] We deal with this by excluding from the integration over θ_1 and θ_2 a circular region centered at the origin whose radius ϵ is of the order of the magnitude of the smallest allowed wave vector $\vec{k}_{||}$. The physical reason for this exclusion is that the three normal modes of vibration of a film at the point $\vec{k}_{||}=0$ ($\theta_1=\theta_2=0$), whose frequencies vanish by infinitesimal translational invariance, describe a rigid-body displacement of the film as a whole. Such a displacement should be exlcuded from a calculation of the mean-square displacement of an atom, since this dynamical property is properly associated with the oscillatory, not translational, motion of the atom about its rest position. Since the mean-square displacement is given by a sum over the values of the wave vector $\vec{k}_{||}$ allowed by periodic boundary conditions [see Eqs. (3.3) and (2.6)], we can effect this exclusion by omitting from the sum in Eq. (3.3) the term with $\vec{k}_{||}=0$. However, since we are approximating this sum by an integral, in view of the dense distribution of the allowed values of $\vec{k}_{||}=0$ throughout the two-dimensional first Brillouin zone, this exclusion is equivalent to removing from the region of integration a square of edge $(2\pi/Na_0)$ centered at the point $\vec{k}_{||}=0$. For simplicity, we replace this square by a circle. If the area of the excluded circle were to equal that of the excluded square, its radius in $\vec{\theta}$ space would be $\epsilon=2\pi^{1/2}/N$. It is this value we will assume for ϵ. We now rewrite Eq. (3.18) as

$$\langle u_\alpha^2(l)\rangle_{2S}=\frac{k_BT}{\gamma\pi^2}\sum_{n=1}^\infty{}'\int_\epsilon^\pi d\theta_1\int_\epsilon^\pi d\theta_2\frac{1}{1-t^2}(t^{2nL-2l_3+2}+2t^{2nL+1}+t^{2nL+2l_3})$$

$$=\frac{k_BT}{\gamma}\sum_{n=1}^\infty[I_\epsilon(2nL-2l_3+2)+2I_\epsilon(2nL+1)+I_\epsilon(2NL+2l_3)]\,, \tag{3.19}$$

where the primes indicate that the integrals run from $(\theta_1^2+\theta_2^2)^{1/2} > \epsilon$, and $I_\epsilon(l)$ is the integral that results when a circle of radius ϵ centered at $\theta_1 = \theta_2 = 0$ is excluded from the domain of integration in the integral on the right-hand side of Eq. (3.19). It is shown in the Appendix that the asymptotic form of $I_\epsilon(l)$ in the limit of large l is

$$I_\epsilon(l) \sim e^{-\epsilon(l-1)} \left[\frac{1}{4\pi(l-1)} + \frac{1}{16\pi(l-1)^3}[1+\epsilon(l-1)+\tfrac{1}{2}\epsilon^2(l-1)^2+\tfrac{7}{24}\epsilon^3(l-1)^3] + O\left[\frac{P_6(\epsilon(l-1))}{(l-1)^5}\right]\right], \tag{3.20}$$

where $P_6(x)$ is a sixth-degree polynomial in x.

When the result given by the first term on the right-hand side of Eq. (3.20) is substituted into Eq. (3.19) we obtain the result that

$$\langle u_\alpha^2(l)\rangle_{2S}^{(1)} = \frac{k_B T}{4\pi\gamma} \sum_{n=1}^{\infty} \left[\frac{e^{-\epsilon(2nL-2l_3+1)}}{2nL-2l_3+1} + 2\frac{e^{-\epsilon 2nL}}{2nL} + \frac{e^{-\epsilon(2nL+2l_3-1)}}{2nL+2l_3-1} \right]. \tag{3.21}$$

These sums diverge unless ϵ is kept nonzero, reflecting the singularity in the integrand in Eq. (3.18). To simplify the notation, let us introduce the definition

$$a = \frac{l_3 - \frac{1}{2}}{L}, \tag{3.22}$$

so that $0 < a < 1$. Then Eq. (3.21) takes the form

$$\langle u_\alpha^2(l)\rangle_{2S}^{(1)} = \frac{k_B T}{8\pi\gamma L} \sum_{n=1}^{\infty} \left[\frac{e^{-n(2\epsilon L)}}{n-a} e^{(2\epsilon L)a} + 2\frac{e^{-n(2\epsilon L)}}{n} + \frac{e^{-n(2\epsilon L)}}{n+a} e^{-(2\epsilon L)a} \right]. \tag{3.23}$$

We rewrite this as

$$\langle u_\alpha^2(l)\rangle_{2S}^{(1)} = \frac{k_B T}{8\pi\gamma L} \left[-2\ln(1-e^{-2\epsilon L}) + \int_{2\epsilon L}^{\infty} du \frac{e^{-(1-a)u}}{1-e^{-u}} + \int_{2\epsilon L}^{\infty} du \frac{e^{-(1+a)u}}{1-e^{-u}} \right], \tag{3.24}$$

where we have used the integral representation

$$\frac{1}{x} = \int_0^\infty dt e^{-xt}, \tag{3.25}$$

valid for real, positive x.

Since $\epsilon = 2\pi^{1/2}/N$, we have that

$$2\epsilon L = 4\pi^{1/2} L/N \equiv \delta << 1, \tag{3.26}$$

because N can be of the order of 10^8 for a physical film, while L might range from 10 to 10^3. We therefore evaluate the right hand side of Eq. (3.24) only to the leading nonzero order in δ. To this end we write

$$\langle u_\alpha^2(l)\rangle_{2S}^{(1)} = \frac{k_B T}{8\pi\gamma L} \left[-2\ln\delta + \delta + O(\delta^2) + 2E_1(\delta) + \int_\delta^\infty du \left[\frac{e^{-(1-a)u}}{1-e^{-u}} - \frac{e^{-u}}{u} \right] + \int_\delta^\infty du \left[\frac{e^{-(1+a)u}}{1-e^{-u}} - \frac{e^{-u}}{u} \right] \right], \tag{3.27}$$

where $E_1(\delta)$ is the exponential integral. For small δ we have the expansion[16]

$$E_1(\delta)=-\ln(C\delta)+\delta-\frac{\delta^2}{4}+O(\delta^3)\,, \tag{3.28}$$

where $C=1.781072...$ is Euler's constant. We can replace the lower limits on the integrals by zero, with an error of the order of δ. In this way we obtain the result that

$$\langle u_\alpha^2(l)\rangle_{2S}^{(1)}=\frac{k_BT}{8\pi\gamma L}[-4\ln(C^{1/2}\delta)-\psi(1-a) -\psi(1+a)+O(\delta)]\,, \tag{3.29}$$

where $\psi(z)$ is the psi (digamma) function.[17] The recurrence formula[17]

$$\psi(1+z)=\psi(z)+1/z \tag{3.30}$$

enables us to rewrite this result finally in the form

$$\langle u_\alpha^2(l)\rangle_{2S}^{(1)}=-\frac{k_BT}{4\pi\gamma}\frac{1}{(2l_3-1)} +\frac{k_BT}{8\pi\gamma L}[-4\ln(C^{1/2}\delta) -\psi(1-a)-\psi(a)]\,, \tag{3.31}$$

with an error of the order of δ/L.

With the second term on the right-hand side of Eq. (3.20) is substituted into Eq. (3.19), we can set $\epsilon=0$ directly in the reslting sum with an error of $O(\delta/L^3)$. We do so and obtain

$$\langle u_\alpha^2(l)\rangle_{2S}^{(2)}=\frac{k_BT}{128\pi\gamma L^3}\sum_{n=1}^{\infty}\left[\frac{1}{(n-a)^3} +\frac{2}{n^3}+\frac{1}{(n+a)^3}\right] =\frac{k_BT}{128\pi\gamma L^3}[2\zeta(3)-\tfrac{1}{2}\psi^{(2)}(1-a) -\tfrac{1}{2}\psi^{(2)}(1+a)]\,, \tag{3.32}$$

where $\psi^{(2)}(z)$ is a polygamma function.[18] The recurrence formula[19]

$$\psi^{(2)}(1+z)=\psi^{(2)}(z)+2/z^3 \tag{3.33}$$

enables us to write Eq. (3.32) finally as

$$\langle u_\alpha^2(l)\rangle_{2S}^{(2)}=-\frac{k_BT}{16\pi\gamma}\frac{1}{(2l^3-1)^3} +\frac{k_BT}{128\pi\gamma L^3}[2\zeta(3)-\tfrac{1}{2}\psi^{(2)}(1-a) -\tfrac{1}{2}\psi^{(2)}(a)]\,, \tag{3.34}$$

with an error of the order of (δ/L^3).

Combining the results of Eqs. (3.31) and (3.34) we find that

$$\langle u_\alpha^2(l)\rangle_{2S}\sim-\frac{k_BT}{4\pi\gamma}\frac{1}{(2l_3-1)}-\frac{k_BT}{16\pi\gamma}\frac{1}{(2l_3-1)^3}-\cdots+\frac{k_BT}{8\pi\gamma L}[-4\ln(C^{1/2}\delta)-\psi(a)-\psi(1-a)] +\frac{k_BT}{128\pi\gamma L^3}[2\zeta(3)-\tfrac{1}{2}\psi^{(2)}(a)-\tfrac{1}{2}\psi^{(2)}(1-a)]+\cdots\,. \tag{3.35}$$

We have therefore obtained the result that the mean-square displacement of an atom in a thin film of L layers is given in the classical limit by

$$\langle u_\alpha^2(l)\rangle_{\rm film}=(0.505\,46)\frac{k_BT}{2\gamma}+\frac{k_BT}{8\pi\gamma L}[-4\ln(C^{1/2}\delta)-\psi(a)-\psi(1-a)] +\frac{k_BT}{128\pi\gamma L^3}[2\zeta(3)-\tfrac{1}{2}\psi^{(2)}(a)-\tfrac{1}{2}\psi^{(2)}(1-a)]+\cdots,\ 0<a<1\,. \tag{3.36}$$

This result is manifestly symmetric about the point $a=\frac{1}{2}$, which corresponds to the midpoint of the film, as would be expected.

For comparison the mean-square displacement of an atom in a semi-infinite crystal is given in the classical limit by

$$\langle u_\alpha^2(l)\rangle_{\text{semi}} = (0.505\,46)\frac{k_BT}{2\gamma} + \frac{k_BT}{8\pi\gamma L}\frac{1}{a} + \frac{k_BT}{128\pi\gamma L^3}\frac{1}{a^3} + \cdots, \quad a<1 \tag{3.37}$$

in the same notation.

We conclude this section by presenting the result for the mean-square displacement of an atom in the surface layer ($l_3=1$) of a thin film of L layers. In this case we have that $a = 1/2L << 1$. We use the small-z expansions[17,18]

$$\psi(1+z) = -\ln C + \zeta(2)z - \zeta(3)z^2 + \cdots, \tag{3.38a}$$

$$\psi^{(2)}(1+z) = -[2\zeta(3) - 6\zeta(4)z + 12\zeta(5)z^2 - \cdots] \tag{3.38b}$$

in Eqs. (3.29) and (3.32) to obtain

$$\langle u_\alpha^2(l)\rangle_{2S} = -\frac{k_BT}{2\pi\gamma}\frac{\ln\delta}{L} + \frac{3k_BT\zeta(3)}{32\pi\gamma L^3} + \cdots. \tag{3.39}$$

When this result is added to the sum of Eqs. (3.10) and (3.13a) we obtain for the mean-square displacement of an atom in the surface layer of a thin film of L layers

$$\langle u_\alpha^2(l)\rangle_{\text{film}} = \frac{k_BT}{2\gamma}(0.677\,59) - \frac{k_BT}{2\pi\gamma}\frac{\ln\delta}{L} + \frac{3k_BT}{32\pi\gamma}\frac{\zeta(3)}{L^3} + \cdots, \tag{3.40}$$

in the classical limit. The first term gives the corresponding result for a semi-infinite crystal.

IV. DISCUSSION

The results obtained in this paper apply to two physically distinct situations, and the discussion of these results is somewhat different in each of these cases. The first of these is when the thin film we have studied is a representation of a physical thin film whose lateral dimensions are large compared with its thickness. The second is when, for computational purposes, a film is used as an approximation to a semi-infinite crystal. We consider each of the situations in turn.

There may be experimental situations in which it is the mean-square displacements of atoms in a thin film of a solid that are required. In such situations the computational methods employed at the present time for the calculation of these quantities, based as they are on the use of a thin film, would appear to be appropriate and accurate.

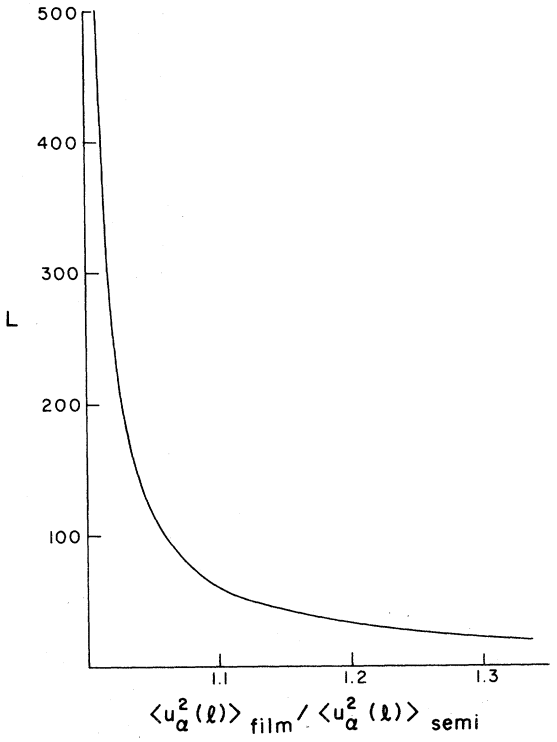

FIG. 1. The mean-square value of the atomic displacement in the midplane of a film of thickness L layers divided by the mean-square value in the semi-infinite case for an atom $L/2$ layers below the surface is plotted versus L.

However, if the results of a calculation based on a thin film are intended to provide an approximation to the mean-square displacements of atoms in a semi-infinite crystal, the results of this paper show that rather thicker films, by at least an order of magnitude, have to be employed than have been used in such calculations to date, if good accuracy is to be achieved.

In Fig. 1 we have plotted a curve of $\langle u_\alpha^2(l)\rangle_{\text{film}}/\langle u_\alpha^2(l)\rangle_{\text{semi}}$ as a function of L for $a=\frac{1}{2}$, $N=10^8$. From this figure we see that the film has to be at least 600-layers thick, before the value of the mean-square displacement at its midplane is within 1% of the value of the mean-square displacement at the same depth in a semi-infinite crystal.

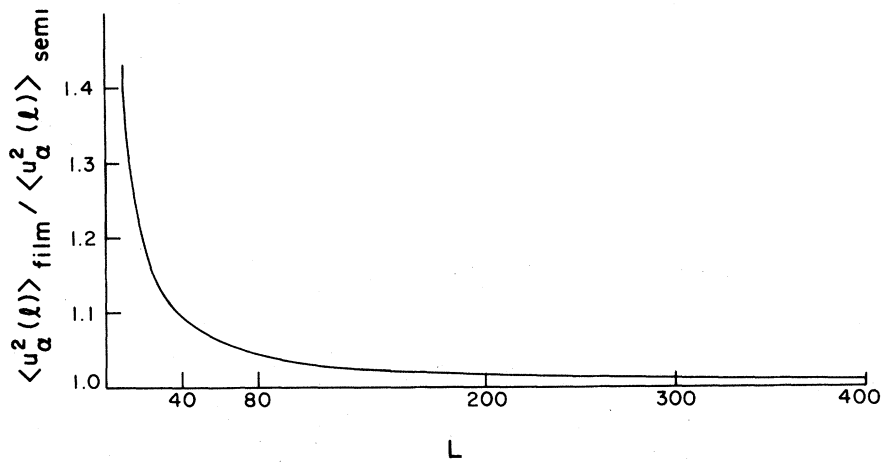

FIG. 2. The mean-square value of the atomic displacement of an atom on the surface of the film divided by the mean-square value of an atom on the surface in the semi-infinite case is plotted versus the number of layers L in the film.

In Fig. 2 we have plotted a curve of $\langle u_\alpha^2(l)\rangle$ film divided by $\langle u_\alpha^2(l)\rangle_{\text{semi}}$ versus L for an atom on the surface ($l_3 = 1$). Again, choosing $N = 10^8$, we see from the figure that L has to be at least 400 before the result for a thin film is within 1% of that for a semi-infinite crystal.

Although the main body of the paper has dealt with the case $L << N$, i.e., a thin film, we would like to make a final comment concerning the case that $L \approx N$. In the latter case, of course, we are dealing not with a thin film, but with a cubical volume of the crystal. Allen and deWette[7] suggested that $\langle u_\alpha^2(l)\rangle$ approaches the semi-infinite value very quickly as one moves into the interior of the crystal from the surface in the case when $L = N$. It is easy to see why this is so in our calculation, since it follows directly from Eqs. (3.4), (3.24), and (3.37). Setting $L = N$ and $a = \frac{1}{2}$ and ignoring terms proportional to L^{-3} we obtain

$$\frac{\langle u_\alpha^2(l)\rangle_{\text{film}}}{\langle u_\alpha^2(l)\rangle_{\text{semi}}} \approx 1 + \frac{1}{4\pi L}\frac{-2\ln(1-e^{-4\sqrt{\pi}}+2e^{-2\sqrt{\pi}}+\frac{4}{3}e^{-6\sqrt{\pi}})}{0.505\,46+1/2\pi L} = 1+\frac{0.009}{L}+O(L^{-2})\,. \tag{4.1}$$

When $L = N$, the right-hand side of Eq. (4.1) equals 1.0009, which shows that fewer than ten layers are required in order that the mean-square displacements calculated for the cube ($L = N = 10$) and for a semi-infinite solid agree to within 1% for atoms at the midplane. In conclusion, we emphasize that for a physical film ($L << N$), L must be at least 600 in order to obtain the same accuracy.

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APPENDIX

In this Appendix we obtain the asymptotic form of the integral

$$I(l) = \frac{1}{\pi^2}\int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \frac{t^l}{1-t^2} \tag{A1}$$

in the limit of large l (> 0), where t is defined by Eq. (3.7). We use Eqs. (3.7) and (3.8) to rewrite this integral as

$$I(l)=\frac{1}{2\pi^2}\int_0^{\pi}d\theta_1\int_0^{\pi}d\theta_2\frac{[\zeta-(\zeta^2-1)^{1/2}]^{(l-1)}}{(\zeta^2-1)^{1/2}}\ . \tag{A2}$$

In view of the fact that $0<t<1$ we can write this integral in the form

$$I(l)=\frac{1}{2\pi^2}\int_0^{\pi}d\theta_1\int_0^{\pi}d\theta_2\frac{e^{(l-1)\ln[\zeta-(\zeta^2-1)^{1/2}]}}{(\zeta^2-1)^{1/2}}\ . \tag{A3}$$

We also note that $\ln[\zeta-(\zeta^2-1)^{1/2}]$ can be expanded in the form

$$\ln[\zeta-(\zeta^2-1)^{1/2}]=-2\left[\left(\frac{\zeta-1}{\zeta+1}\right)^{1/2}+\frac{1}{3}\left(\frac{\zeta-1}{\zeta+1}\right)^{3/2}+\frac{1}{5}\left(\frac{\zeta-1}{\zeta+1}\right)^{5/2}+\cdots\right]. \tag{A4}$$

It is easy to see that $\ln[\zeta-(\zeta^2-1)^{1/2}]$ assumes its largest value when $\theta_1=\theta_2=0$. In the limit of large $(l-1)$ we therefore expand the functions entering the integrand in powers of θ_1 and θ_2. We begin with the fact that

$$\zeta=1+\tfrac{1}{2}(\theta_1^2+\theta_2^2)-\tfrac{1}{24}(\theta_1^4+\theta_2^4)+\tfrac{1}{720}(\theta_1^6+\theta_2^6)-\cdots\ . \tag{A5}$$

We next transform to two-dimensional polar coordinates (r,θ) according to

$$\theta_1=r\cos\theta,\quad \theta_2=r\sin\theta \tag{A6}$$

and write ζ as

$$\zeta=1+\tfrac{1}{2}r^2-\tfrac{1}{24}r^4f_4(\theta)+\tfrac{1}{720}r^6f_6(\theta)-\cdots \tag{A7a}$$

with

$$f_{2n}(\theta)=\cos^{2n}\theta+\sin^{2n}\theta\ . \tag{A7b}$$

It follows that

$$(\zeta^2-1)^{-1/2}=\frac{1}{r}\left[1-\frac{r^2}{24}(3-f_4)+\frac{r^4}{5760}(135+30f_4+15f_4^2-8f_6)+O(r^6)\right] \tag{A8}$$

and

$$\ln[\zeta-(\zeta^2-1)^{1/2}]=-r+\frac{r^3}{24}(1+f_4)-\frac{r^5}{5760}(27+30f_4-5f_4^2+8f_6)+O(r^7)\ . \tag{A9}$$

When we substitute the expansions (A8) and (A9) into Eq. (A3) we can remove the upper limit on the integral on r to infinity, because the error committed in doing so is exponentially small in $(l-1)$ compared with the algebraically small result we obtain. Thus we obtain the result that

$$I(l)\sim\frac{1}{2\pi^2}\int_0^{\pi/2}d\theta\int_0^{\infty}dr\,e^{-(l-1)r}\left[1-\frac{r^2}{24}[3-f_4(\theta)]+(l-1)\frac{r^3}{24}[1+f_4(\theta)]+O(r^4,(l-1)r^5,(l-1)^2r^6)\right]$$

$$=\frac{1}{2\pi^2}\int_0^{\pi/2}d\theta\left[\frac{1}{(l-1)}+\frac{f_4(\theta)}{3(l-1)^3}+O((l-1)^{-5})\right] \tag{A10}$$

$$=\frac{1}{4\pi(l-1)}+\frac{1}{16\pi(l-1)^3}+O((l-1)^{-5})\ . \tag{A11}$$

For certain purposes in the text the asymptotic behavior of the integral

$$I_\epsilon(l)=\frac{1}{\pi^2}\int_0'^{\pi}d\theta_1\int_0'^{\pi}d\theta_2\frac{t^l}{1-t^2}\ , \tag{A12}$$

where the primes indicate that the integrals run from $(\theta_1^2+\theta_2^2)^{1/2}>\epsilon$, for large, positive l is required. The preceding analysis can be repeated, and yields the result that

$$I_\epsilon(l)\sim\frac{1}{2\pi^2}\int_0^{\pi/2}d\theta\int_\epsilon^\infty dr\,e^{-(l-1)r}\left[1-\frac{r^2}{24}[3-f_4(\theta)]+(l-1)\frac{r^3}{24}[1+f_4(\theta)]\right.$$
$$\left.+O(r^4,(l-1)r^5,(l-1)^2r^6)\right]$$
$$=\frac{1}{2\pi^2}e^{-\epsilon(l-1)}\int_0^{\pi/2}d\theta\left[\frac{1}{(l-1)}+\left[\frac{f_4(\theta)}{3(l-1)^3}+\epsilon\frac{f_4(\theta)}{3(l-1)^2}+\epsilon^2\frac{f_4(\theta)}{6(l-1)}+\epsilon^3\frac{1+f_4(\theta)}{24}\right]\right.$$
$$\left.+O\left[\frac{P_6(\epsilon(l-1))}{(l-1)^5}\right]\right], \tag{A13}$$

where $P_6(x)$ is a sixth-degree polynomial in x. We obtain finally the result that

$$I_\epsilon(l)\sim e^{-\epsilon(l-1)}\left[\frac{1}{4\pi(l-1)}+\frac{1}{16\pi(l-1)^3}[1+\epsilon(l-1)+\tfrac{1}{2}\epsilon^2(l-1)^2+\tfrac{7}{24}\epsilon^3(l-1)^3]\right.$$
$$\left.+O\left[\frac{P_6(\epsilon(l-1))}{(l-1)^5}\right]\right]. \tag{A14}$$

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