The Effect of External Force on Surface Stability by the Self-Consistent Einstein Model

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Effects of an external force on the surface lattice dynamics, such as anharmonic surface vibration, surface relaxation of the lattice constant and thermal stability of the surface, are studied by the use of the one-dimensional self-consistent Einstein model with emphasis on material strength. A new numerical method to solve the basic equations revealed surface instability phenomena. Above a critical temperature determined by the external force, the mean square displacements and the lattice constants satisfying the basic equations are not found. Under a tensile force, the system is unstable and will fracture when the force is stronger than a critical one which is considerably lower than the ideal strength.

§ 1. Introduction

The thermal stability of surfaces of solids subjected to an external force seems to be an interesting problem. For example, the thermal motion of constituent elements, atoms or molecules, at a crack tip in a mechanically loaded solid must play an important role in the growth of the crack. A recent study by one of the authors suggested that the molecular motion at a crack tip enhanced by the stress and the environment is essential to environmental stress cracking in polymers. 1

The study of the lattice dynamics of surfaces has made much progress. The experiments by the LEED and others have revealed the surface-softening-phenomena, that is, that the thermal vibration of atoms on surfaces of metal crystals is much smaller in frequency than that of interior atoms. Several investigations 2–10 have proved the phenomena by using the self-consistent Einstein model (SCEM) which is a simplified version of the self-consistent phonon model. 10 The finding leads us further to an expectation that the surface-softening-phenomena are affected by an external force and that they may be closely related to the cracking phenomena. Apart from the problems, the external force effect must be important in itself and in relation to the melting or other phenomena in fine particles 10 under stress.

In this paper, the effect of an external force upon the surface stability is studied by using the SCEM with emphasis on material strength. As the first step of our approach, the treatment is confined to a one-dimensional system. It is expected implicitly that the essential feature of the effect will be observable even
in the one-dimensional system. The fault intrinsic in the one-dimensional system, that is, its crystalline order is excluded in the thermodynamic limit, is avoided by using the SCEM. The procedure of deriving the basic equations follows much the same way proposed by Matsubara et al., except in replacing their free energy term by the Gibbs free energy to include the external force. The method of numerical calculation in solving the equations is newly arranged so as to clarify what happens on and near the surface.

§ 2. Basic equations by the self-consistent Einstein model

Let us study a system of linearly arranged \((N+1)\) particles each with mass \(M\). Its Hamiltonian is given by

\[
H = \frac{M}{2} \sum_{n=1}^{N} \left( \frac{d u_n}{dt} \right)^2 + \sum_{n=1}^{N} v(u_n - u_{n+1} + \sum_{i=1}^{n} a_i),
\]

where \(v(x)\), \(u_n\), and \(a_i\) are the pair potential, the displacement of the \(n\)-th particle from its thermal average and the thermal equilibrium distance between the \((l-1)\)-th and \(l\)-th particles, respectively. Following Matsubara et al., we employ a function

\[
H_{tr} = \frac{M}{2} \sum_{n=1}^{N} \left( \frac{d u_n}{dt} \right)^2 + \sum_{n=1}^{N} \frac{\phi_n}{2} u_n^2
\]

as a trial Hamiltonian, which represents a linear crystalline system composed of the Einstein oscillators. When the particles at both the ends are exerted by an external force \(P\), the free energy \(G\) is defined by

\[
G = \langle H \rangle - \langle H_{tr} \rangle - kT \ln \text{Tr} \left[ \exp \left( -\frac{H_{tr}}{kT} \right) \right] + P \langle x_N - x_0 \rangle,
\]

where \(x_l\) \((l=0, \ldots, N)\) is the coordinate of the \(l\)-th particle, and the thermal average of a physical quantity \(X\), \(\langle X \rangle\), is defined by

\[
\langle X \rangle = \frac{\text{Tr} \left[ X \exp \left( -\beta H_{tr} \right) \right]}{\text{Tr} \left[ \exp \left( -\beta H_{tr} \right) \right]}, \quad (\beta = 1/kT)
\]

The last term on the right-hand side of Eq. (2.3) expresses the external force effect which is introduced in the present paper. When \(P\) is positive, the force is compressive, and when negative it is tensile. The method of the SCEM is to choose the variational parameters \(\phi_n\) and \(a_n\) so as to minimize the free energy \(G\) by the equations,

\[
\frac{\delta G}{\delta \phi_n} = 0, \quad n = 0, 1, \ldots, N
\]

and
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\[ \frac{\delta G}{\delta a_n} = 0, \quad n = 1, 2, \cdots, N. \] (2.6)

The pair potential is assumed hereafter as the one given by the Morse function

\[ v(x) = D \left[ \exp \left\{ -2\alpha (x - r_0) \right\} - 2\exp \left\{ -\alpha (x - r_0) \right\} \right]. \] (2.7)

The introduction of the nearest neighbor interaction and the high temperature approximation\(^7\) derives the following relations (2.8) and (2.9) from Eqs. (2.5) and (2.6) for a semi-infinite system (\( N \to \infty \)):

\[ \phi_n = \phi''_{n_0}(a_1), \]
\[ \phi_n = \phi''_{n-1}(a_n) + \phi''_{n+1}(a_{n+1}), \quad n = 1, 2, \cdots \] (2.8)

and

\[ \phi'_{n-1}(a_n) + P = 0, \quad n = 1, 2, \cdots, \] (2.9)

where a prime indicates \( d/dx \) and \( \phi_{mx} \) (\( m > n \)) is the average potential defined by

\[ \phi_{mx}(x) = \langle v(x + u_m - u_n) \rangle = D_{mn} \left[ \exp \left\{ -2\alpha (x - r_{mn}) \right\} - 2\exp \left\{ -\alpha (x - r_{mn}) \right\} \right]. \] (2.10)

Here quantities \( D_{mn} \) and \( r_{mn} \) are

\[ D_{mn} = D \exp \left\{ -\frac{\alpha^2}{\beta} \left( \frac{1}{\phi_m} + \frac{1}{\phi_n} \right) \right\} = D \exp \left( -\lambda_m - \lambda_n \right) \] (2.11)

and

\[ r_{mn} = r_t + \frac{3\alpha}{2\beta} \left( \frac{1}{\phi_m} + \frac{1}{\phi_n} \right) = r_t + \frac{3}{2\alpha} \left( \lambda_m + \lambda_n \right), \] (2.12)

respectively, and \( \lambda_m \) is the reduced mean square displacement

\[ \lambda_m = \frac{\alpha^2}{\beta \phi_m} = \alpha^2 \langle u_m \rangle. \] (2.13)

Equations (2.8) tell us that the Einstein frequencies are determined by the curvature of the average potentials at equilibrium positions and Eq. (2.9) means that the equilibrium positions are determined by the balance between the external force and the interparticle force derived from the average potential.

From Eq. (2.10), Eq. (2.9) is rewritten by

\[ a_n = r_0 + \frac{3}{2\alpha} \left( \lambda_{n-1} + \lambda_n \right) - \frac{1}{\alpha} \ln \Pi_{s-1,n}, \quad n = 1, 2, \cdots, \] (2.14)

where

\[ \Pi_{s-1,n} = \frac{1}{2} \left\{ 1 + \sqrt{1 + \frac{2P}{\alpha D} \exp \left( \lambda_{s-1} + \lambda_n \right)} \right\}. \] (2.15)
The minus sign in front of the root in Eq. (2.15) was discarded because it gives infinite interparticle distances at \( P=0 \). From Eqs. (2.10) and (2.14), Eqs. (2.8) become

\[
\begin{align*}
\lambda_b &= \frac{kT}{2D} \exp \left( \frac{\lambda_b + \lambda_i}{2} \right) \frac{1}{\Pi_{\alpha}(2\Pi_{\alpha} - 1)}, \\
\lambda_n &= \frac{kT}{2D} \exp \left( \frac{\lambda_{n+1} - \lambda_n + \lambda_{n-1}}{2\Pi_{n-1,n}} \right) \exp \left( \frac{\Pi_{n-1,n}(2\Pi_{n-1,n} - 1)}{\Pi_{n,n+1}} \right) \exp \left( \frac{\Pi_{n,n+1}(2\Pi_{n,n+1} - 1)}{\Pi_{n,n+1}} \right), \\
n &= 1, 2, \ldots.
\end{align*}
\]

Equations (2.14) and (2.16) giving \( \{\lambda_n\} \) and \( \{a_n\} \) are basic ones for investigating the anharmonic surface vibration and the surface relaxation of the lattice constant. They reduce to the ones by Matsubara et al.\(^a\) when \( P=0 \). To get their analytical solutions is a very difficult task. A way to solve the equations is the iteration method by Matsubara et al.\(^a\). The method being laborious at a high temperature, to pursue the surface stability which is the main concern of this study is difficult. An alternative method has been developed in this study to overcome it and will be discussed in \( \S \) 4.

\section*{\S 3. Bulk properties}

At first, properties far from the surface, i.e., bulk properties, are examined. Physical quantities \( a_b \) and \( \lambda_b \) which are defined as

\[
\begin{align*}
\lim_{n \to \infty} a_n &= a_b \quad \text{and} \quad \lim_{n \to \infty} \lambda_n = \lambda_b
\end{align*}
\]

satisfy the following equations,

\[
\begin{align*}
a_b &= r_0 + \frac{3}{\alpha} \lambda - \frac{1}{\alpha} \ln \Pi, \\
kT &= \lambda_b \exp \left( -2\lambda_b \Pi_b (2\Pi_b - 1) \right),
\end{align*}
\]

where

\[
\Pi_b = \frac{1}{2} \left[ 1 + \sqrt{1 + \frac{2P}{\alpha D} \exp (2\lambda_b)} \right].
\]

Let us solve Eq. (3.3) graphically with respect to \( \lambda_b \) for a given pair of \( P \) and \( T \). The curves \( \lambda_b \) versus \( kT/4D \) with several values of \( P/\alpha D \) calculated by Eq. (3.3) are plotted in Fig. 1.

(i) When \( P/\alpha D \geq P_{\text{so}}/\alpha D \) \( (P_{\text{so}}/\alpha D = 0.11) \), we have, at any temperature, a solution \( \lambda_b \) which goes to zero continuously as \( T \) tends to zero.

(ii) For each \( P/\alpha D \) in the range \(-0.5 \sim P_{\text{so}}/\alpha D \), there is a critical temperature
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Fig. 1. The bulk reduced mean square displacement $\Delta^2$ vs the temperature $kT/4D$. The numbers attached to the curves are the values of $P/\alpha D$.

$T_{mc}$ above which the equation has no physical solution. Below $T_{mc}$, there is one physical solution which goes to zero continuously as $T$ tends to zero. As $T$ tends to $T_{mc}$ from lower temperature side, there is a singularity

$$\lim_{T \to T_{mc}^-} \frac{d\Delta^2}{dT} \to +\infty .$$

(3.5)

Other solutions, if exist, are unphysical and should be discarded.

(iii) When $P/\alpha D = -0.5$, the equation is satisfied by one solution $\Delta^2 = 0$ at $kT/4D = 0$.

(iv) When $P/\alpha D < -0.5$, Eq. (3.3) has no longer any solution.

The system is unstable at a temperature above $T_{mc}$. The temperature $T_{mc}$ may be regarded as the melting point of the system, which varies with the external force. Under a tensile force, the unstable state will not be able to support the force and fracture. The force may be regarded as the ideal strength of the perfect crystal at that temperature. The tensile force $P/\alpha D = -0.5$ is the strength at $T = 0$ and corresponds to the maximum attractive force of the Morse potential. The ideal strength versus the temperature

Fig. 2. The ideal strength of the perfect crystal $P/\alpha D$ vs the temperature $kT/2D$.  

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is shown in Fig. 2.

The surface instability, however, affects the bulk properties and lowers the critical temperature as will be discussed in the next section. The melting point and the strength obtained here thus should be regarded as the upper bounds.

§ 4. Surface properties and discussion

The values of \( \{r_n\} \) and \( \{a_n\} \) near the surface were numerically evaluated by the following procedure. Works were restricted to the case of a low external force for simplicity and Eqs. (2.14) and (2.16) were linearized with respect to \( P \). The validity of the method is, however, not limited by the restriction. The linearized forms are

\[
a_n = r_0 + 3 \left( \frac{\lambda_{n-1} + \lambda_n}{2\alpha} \right) - \frac{P}{2\alpha^2 D} \exp(\lambda_{n-1} + \lambda_n), \quad n = 1, 2, \ldots
\]

and

\[
kT = k_0 \left\{ \exp(-\lambda_0 - \lambda_1) + \frac{3P}{2\alpha D} \right\},
\]

\[
kT = k_0 \left\{ \exp(-\lambda_{n-1} - \lambda_n) + \exp(-\lambda_n - \lambda_{n+1}) + \frac{3P}{\alpha D} \right\}, \quad n = 1, 2, \ldots
\]

Further Eq. (3.3) becomes

\[
kT = k_0 \left\{ 2 \exp(-2\lambda_2) + \frac{3P}{\alpha D} \right\}.
\]

This approximation is known to be fairly well in the range studied here, \(|P/\alpha D| \leq 0.05\).

As \( n \) increases, \( \lambda_n \) approaches \( \lambda_0 \) very quickly, i.e., \( \lambda_n \) is very close to \( \lambda_0 \) even at \( n = 2 \) or 3 as shown below. Thus we define \( \varepsilon_n \) by

\[
\lambda_n = \lambda_0 + \varepsilon_n,
\]

and linearize Eq. (4.2) with respect to \( \varepsilon_n \) for \( n \geq 2 \). The final result is

\[
e_n = \frac{1}{2} \left( \varepsilon_n + \varepsilon_{n+1} \right), \quad n = 2, 3, \ldots
\]

where

\[
e = \frac{1}{\lambda_0} \left\{ 1 - \lambda_0 + \frac{3P}{2\alpha D} \exp(2\lambda_0) \right\}.
\]

The exact solution of Eq. (4.5) is given by \( k \)

\[
\varepsilon_n = \varepsilon_1 \exp\{-k(n-2)\}, \quad n = 2, 3, \ldots
\]
where

\[ \kappa = \text{arccosh } c = \ln (c + \sqrt{c^2 - 1}) \tag{4.8} \]

The procedure for solving Eqs. (4·2) with respect to \( \{\lambda_n\} \) for a given pair of \( P/\alpha D \) and \( \lambda_0 \) is composed of the following steps.

1. Assume an appropriate value for \( \lambda_0 \).
2. Determine \( kT/2D \) from Eq. (4·3) by the use of \( \lambda_0 \) in (1).
3. Determine \( \lambda_i \) from Eq. (4·2) by the use of \( kT/2D \) in (2).
4. Determine \( \lambda_i \) (\( i = 2 \) and \( 3 \)) from Eq. (4·2) by the use of \( \lambda_{i-1} \) and \( kT/2D \) in (2).
5. Determine \( \kappa \) from Eqs. (4·6) and (4·8) by the use of \( \lambda_0 \) in (1).
6. Determine \( \lambda_0 \) from Eqs. (4·4) and (4·7) by the use of \( \lambda_0, \kappa \) and \( \lambda_0 \) in (1), (5) and (4), respectively.
7. Compare the \( \lambda_i \)'s in (4) and (6), and repeat the steps (1) \( \sim \) (7) by using another \( \lambda_0 \) until two \( \lambda_i \)'s coincide.
8. Determine \( \lambda_n \) (\( n \geq 4 \)) from Eqs. (4·4) and (4·7) by the use of the final value for \( \lambda_0 \).
9. Write down the solutions \( \lambda_n (n \geq 0) \).

The essential point of the above procedure is that Eqs. (4·2) are used in a region near the surface, while Eqs. (4·4) and (4·7) are used in an inner region, and \( \lambda_0 \) is selected so that the two \( \{\lambda_n\} \)'s are matched smoothly at the boundary of the two regions. (Here, the boundary has been set between \( n = 2 \) and \( 3 \).)

To use the linearized equations for particles on and near the surface, as Naya et al. did, should be avoided, because nonlinear effect is crucial there as will be seen below.

Results obtained by the above procedure for \( P/\alpha D = \pm 0.02 \) are tabulated in Table I. The values of \( \{\alpha_n\} \) obtained from Eq. (4·1) by the use of \( \{\lambda_n\} \) are also listed in Table I. Here the values of the parameters \( \alpha \) and \( r_0 \) employed are

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Fig. 3. Schematic representation of the temperature dependence of the reduced mean square displacement. \( T_s \) is the critical temperature above which no physical solution \( \lambda \) exists.
Table 1. (a) A measure of the thickness incorporating the surface phenomena, $1/\kappa$, the reduced mean square displacements, $\lambda$, and the lattice constants, $a$, near the surface under the compressive force $P/aL=0.02$ and at various temperatures $kT/2D$. Here the parameters of the Morse function are $\alpha=1.883$ Å$^{-1}$ and $r_m=3.733$ Å.

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Table I. (b) A measure of the thickness incorporating the surface phenomena, $1/k$, the reduced mean square displacements, $\lambda$, and the lattice constants, $a$, near the surface under the tensile force $P/aD = -0.02$ and at various temperatures $kT/2D$. Here the parameters of the Morse function are $\alpha = 1.1836 \text{Å}^{-1}$ and $r_0 = 3.733 \text{Å}$.

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1.1836 Å⁻¹ and 3.733 Å, respectively, which correspond to Pb. The obtained results are shown in Figs. 3–10.

The temperature dependence of the solution is schematically shown in Fig. 3 where the solution exhibited by the broken curve is unphysical and has been dis-

![Graph](https://example.com/graph1.png)

Fig. 4. Temperature dependence of the reduced mean square displacements of the 0-th and 1-st particles normalized by the bulk one under the external forces $P/aD = -0.05, -0.02, 0, 0.02$ and 0.05 from left to right.

![Graph](https://example.com/graph2.png)

Fig. 5. Temperature dependence of the reduced mean square displacements of the 1-st and 2-nd particles normalized by the bulk one under the external forces $P/aD = -0.05, -0.02, 0, 0.02$ and 0.05 from left to right.
The Effect of External Force on Surface Stability

In Fig. 4, \( \lambda_0/\lambda_0 \) and \( \lambda_i/\lambda_0 \) are plotted as the functions of \( kT/2D \) for several values of \( P/\alpha D \). Similar plots for \( \lambda_0/\lambda_0 \) and \( \lambda_i/\lambda_0 \) are shown in Fig. 5. Note the difference in the vertical axis scales between Figs. 4 and 5. The quantities \( \lambda_0/\lambda_0 \), etc. are omitted here for simplicity. The values in cases \( P/\alpha D = \pm 0.02 \) are tabulated in Table I. There is a temperature \( T_c \) above which no physical solutions of \( \lambda \) exist for each applied force \( P/\alpha D \). Noticeable points are that \( T_c \) is lower than \( T_b \) and that as \( T \) tends to \( T_c \) from lower temperature side,

\[
\frac{d\lambda_n}{dT} \rightarrow +\infty, \quad n = 0, 1, \ldots. \tag{4.9}
\]

The critical temperature \( kT_c/2D \) is depicted against \( P/\alpha D \) in Fig. 6. \( T_c \) is an increasing function of \( P \) and vanishes when the external force is compressive and stronger than a critical value \( P_0 (> P_{\alpha D}) \). The precise value of \( P_0 \) will be reported elsewhere.

As is known from Eq. (4.7), \( 1/\kappa \) is a measure of the thickness incorporating the surface phenomena. In Fig. 7, \( 1/\kappa \) versus \( kT/2D \) is shown for several values of \( P/\alpha D \). See also Table I. Note that the quantity \( 1/\kappa \) is finite in the temperature range \( 0 \leq T \leq T_c \).

Let us examine the surface relaxation of the lattice constant. In Fig. 8, the \( (a_i/r_0 - 1)'s \) under several values of \( P/\alpha D \) are plotted against \( kT/2D \). Similar plots for \( (a_i/a_0 - 1) \) and \( (a_2/a_0 - 1) \) are shown in Figs. 9 and 10, respectively. Note the difference in the vertical axis scales between Figs. 9 and 10. The quantities \( (a_i/a_0 - 1) \), etc. are omitted here for simplicity. The temperature depend-

![Fig. 6. The critical temperature \( kT_c/2D \) vs the external force \( P/\alpha D \).](https://example.com/figure6)

![Fig. 7. A measure of the thickness incorporating the surface phenomena \( 1/\kappa \) vs the temperature \( kT/2D \) under the external forces \( P/\alpha D = -0.05, -0.02, 0, 0.02 \) and 0.05 from left to right.](https://example.com/figure7)
Fig. 8. Temperature dependence of the bulk lattice constant normalized by \( r_0 \) under the external forces \( P/\alpha D = -0.05, -0.02, 0, 0.02 \) and 0.05 from left to right. Here the parameters of the Morse function are \( \alpha = 1.1836 \text{ Å}^{-1} \) and \( r_0 = 3.733 \text{Å} \).

Fig. 9. Temperature dependence of the lattice constant between the 0-th and 1-st particles normalized by the bulk one under the external forces \( P/\alpha D = -0.05, -0.02, 0, 0.02 \) and 0.05 from left to right. Here the parameters of the Morse function are \( \alpha = 1.1836 \text{Å}^{-1} \) and \( r_0 = 3.733 \text{Å} \).

Fig. 10. Temperature dependence of the lattice constant between the 1-st and 2-nd particles normalized by the bulk one under the external forces \( P/\alpha D = -0.05, -0.02, 0, 0.02 \) and 0.05 from left to right. Here the parameters of the Morse function are \( \alpha = 1.1836 \text{Å}^{-1} \) and \( r_0 = 3.733 \text{Å} \).
The Effect of External Force on Surface Stability

The change of the lattice constant is similar to that of the reduced mean square displacement. As $T$ tends to $T_e$ from lower temperature side,

$$\frac{da_n}{dT} \rightarrow +\infty, \quad n=1,2,\ldots$$

(4·10)

We have found the critical temperature $T_e$ which is lower than $T_\infty$. At the temperature $T_e$, the surface of the system becomes unstable and, in due course, the stability of the whole system will be faded away. The melting of the system, promoted by the surface effect, starts at this temperature. Under a tensile force $P$ and at a temperature $T$, the system will fracture when $P<P_e(T)<0$. (See Fig. 6.) The bond between particles near the surface will first break. The critical force $P_e(T)$ is considerably weaker than the ideal strength described in §3. Actually, the strength is also affected by other factors such as crystalline defects. Here our attention is not there but focused on the effects of the thermal motion.

Detailed properties of the system at a temperature above $T_e$ are obscure at present, but we can say at least that the trial function in the form of the Einstein model becomes inadequate near the surface. Kristensen et al. have found a diffusive motion of atoms on surfaces of fine particles above a certain temperature by a molecular dynamical computer experiment. A possible way to extend the study beyond $T_e$ is to use a trial function incorporating the diffusive surface motion. Here we will not discuss this problem any further and leave it as a future problem.

§5. Conclusion

The external force effects on the anharmonic surface vibration, the surface relaxation of the lattice constant, the thermal stability of the surface and other related phenomena have been studied in detail by using the SCEM. A new numerical method of solving the basic equations by the SCEM has revealed a temperature range in which the equations give meaningful lattice vibrations, and found singularities at the boundary of the range $T_e(P)$. Above the critical temperature $T_e(P)$, the equations have no physical solution suggesting the instability of the crystalline phase. An investigation of the physical properties of the system at this temperature range is, however, remained in future. The mechanical strength of the system under a tensile force has also been discussed. The surface instability is related to the fracture of the system near the surface. The softening of the surface lattice vibration considerably lowers the strength.

So far we have confined ourselves to the phenomena of the one-dimensional system. Similar phenomena can be expected in a higher dimensional system. The SCEM was applied by Matsubara et al. to an FCC lattice without the external force. To see whether the difference in the dimension may induce a noticeable
effect in the result is a next problem and will be reported elsewhere in future.

In preparing the manuscript, the authors have noticed the paper by Pietronero and Tosatti in which they claimed that melting is a surface initiated process and the unstable surface proceeds into the bulk.

References

5) See, for example,
6) For the studies of fine particles under no external force by the SCEM, see,
7) An extension of the theory to the lower temperature side is studied in the last one of Ref. 6).