

## Black-Body Radiation Results in the Activation Theory

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Activation energy ( $AV$ ) is regarded as a requirement for an energy-conserved process or reaction to initiate atomic exchanges. Stimulation of this kind, with the requirement of such an extra type of energy, occurs in many situations. We give a simple review with emphasis on hydrogen chemisorption on a solid surface. We attribute the extra energy as being used to activate the atom or molecule to pass through an  $AV$  static barrier. In a statistical approach, we find that  $XV$  can exist only if there are tunnelling states.  $AV$  is calculated to have discrete increases as the temperature increases. We conclude that for high temperatures, black-body radiation occurs for this atomic desorption.

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In the theory of chemical reaction, a formalism of potential-energy-surface in terms of relative distances between reactant atoms is accepted for an interpretation of the reaction path. On such a potential-energy-surface, we discuss the activated complex on a plot in which the maximum energy on the reaction path is the activation energy ( $AV$ ). This  $AV$  is an energy in nature. In our opinion, it is a kind of thermodynamic potentials. Some conclusions based on the theoretical criteria on the potential-energy-surfaces are made in Ref. [1]. They are given as follows. Because the usual treatment of  $AV$  is an *ab initio* calculation, it usually does not provide potential energies including  $AV$ . When we investigate the dynamics or thermodynamics of chemical reactions, the explicit calculation of all kinds of energies at every point is rarely feasible. They are interesting for computation but not realistic in theory. What we can obtain effectively are the global surfaces. Furthermore, these surfaces are known only to “chemical accuracy”, which is about a few tens of meV (say 0.05 eV).

In this paper, we investigate  $AV$  from a statistical approach. We find that we need a combination of the tunnelling mechanism and a static  $AV$  barrier. This kind of approach was developed and applied to many physical problems by Azbel [2]. We believe that our

results have rather good reliability for a global understanding of the problems in systems of atoms, small molecules, and large global clusters, etc.

For simplicity, we consider a system of vibrating ad-hydrogen-atoms on a surface. For single-atomic adsorption, the standard electron configuration can be found for H/Al(111) in Borisov's paper [3]. The electron distribution is continuous 'from far-from-the-surface to near-surface'. This is a typical chemisorption case. When the coverage of ad-H-atoms increases, the energy-band structure is finally formed [4,5] for H/Cu(110), etc. In these references, the authors call it the "protonic" two-dimensional energy band; the reason being obvious from the above chemisorption description. They also describe the phenomenon as H "quantum delocalization". Another interesting paper is Ref. [6], in which quantum fluid is formed from ad-H-atoms. The coverage problem was studied. A further step in the study of the vibrational and phonon effects on core-levels can be found in Refs. [7,8] for Si(III)-(1 x 1):H etc. For the H/W-surface, core level shifts in W can be found in Ref. [9]. An investigation resembling the inner-shell electron promotion study of the bombardment atom can be found in Ref. [10]. Hydrogen-elimination reactions (in parallel to desorption cases) with low AV for amorphous silicon are reported by Sato et al. [11]. For the case of GaAs heterostructures, AV was reported in Ref. [12]. On the other hand, for collisions of an H-atom with an Al(111)-surface, we have H<sup>-</sup> formation which exhibits a charge transfer [3]. The detachment dissociation for H-atom(s) from an Al(110)-surface has been reported in Ref. [13]. Many have considered only the initial and final energies, together with momenta at most. From only energy considerations, the potential diagram is shown in Fig. 1 [14]. If we do not take the initial and final states into account, or if we concentrate on the dynamical process, we have an AV  $E_{act}$  as shown in Fig. 2. In Lüth's opinion [14], this AV comes from the recombination of two H-atoms to form an H<sub>2</sub>-molecule. Actually, if we consider the chemical physics point of view, the activated complex in the theory of the potential-energy-surface must be introduced. Then this part of the recombinative contribution is not all that we must consider. There are very active recent developments in the same spirit with Hamiltonians without the kinetic energy, e.g., the Hubbard model investigations for electrons are in this category. The kinetic energy measurements in the processes of interest in this paper use the time-of-flight technique. A report of Si<sup>+</sup> from Si(100) is given by Liu and Wu [15]. This report includes a charge transfer process. Their experimental results also exhibit the strength of bonding, where we have the surface dangling bond of the Si/Si-surface. For H from W(211), the mechanism of thermally activated vibrational motions is discussed in Ref. [16]. AV of Si on a solid surface was also investigated and recently a measurement was attempted in Ref. [17]. The recombination to form H<sub>2</sub> molecules is also an active topic. In a paper of Eenshuistra et al. [18], the "wall" recombination of H<sub>2</sub> molecules from the tungsten wall is observed to have

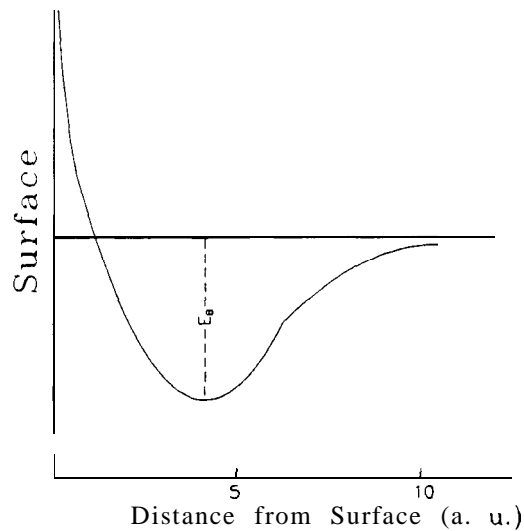


FIG. 1. A schematic plot of the potential energy of an atom or molecule in front of a solid surface when only the initial and final states are taken into account.  $E_B$  stands for the binding energy which has a magnitude on the order of 1 eV. The distance from the surface is estimated from Ref. [3] for the embedded H-atom on an Al(111) surface. But from Ref. [14], the scale of the distance is smaller approximately by a factor of 1/7.

vibrational levels up to  $\nu=5$ , which is usually  $\nu=3$ . Another report [19] gives the wall recombination of  $H_2$  molecules from a stainless steel wall with  $\nu$  up to  $\nu=9$  (the usual Boltzmann distribution value near 3000 K is  $\nu=3$ ). A calculation by Müller [20] shows that the H-H bond is weakened for recombinative desorption of  $H_2$  from a Pt surface. All of these experimental and computational results hint that in the final state after the formation of  $H_2$  molecules from a recombinative desorption process, the H-H bond is weakened by the assumption that it is formed. In the author's opinion, recombinations of this kind can hardly occur near the surface. They can be excluded from the standard surface processes because the desorbed H-atoms have to move far enough outside the "surface region" before the recombination process occurs. Particularly, we consider a local region of the vibration mechanism. Apart from the surface system, this problem has been also studied using clusters [21]. Vibrational excitations are ensured for  $H_3^+$  in this process. The collapse of surfaces and clusters is studied in Refs. [11,22-26]. Also, influences of the bonding of H-atoms, and thus its AV in chemical reactions have been reported in Ref. [27]. Consequently, we have to temporarily neglect many processes such as the recombination process, etc. in this paper in our theoretical considerations. We still keep in mind the activation, such as

in Fig. 2, but the formation concept is not attributed to  $\text{H}_2$  recombination. There are also many other interesting views about the sequential dynamics of adsorption [28]. A paper of Tsong [29] states that, for a tip near a metal, AV comes from the superposition of potentials from two sides. In the sense of magnetism [30] of ferromagnets, from a statistical viewpoint, the potential diagram should be like Fig. 2 with an electromagnetic polarizability. This assignment is of course, a physical continuation of the oscillating dipole-dipole interaction which implies that the van der Waals force is its time average. Hence it is a kind of electromagnetic interaction, a derived coulombic interaction, and subject to electromagnetic symmetries. Close to atomic systems, the oscillating emission of Us-clusters etc. was studied in Ref. [31]. For the magnetic effect, the surface barrier was found by Watanabe and Iwata [32]. This point is different from the kinetic-less potential-energy-surface mentioned above. On the contrary, kinetic energy-emphasized studies can also be found for  $\text{H}$  reactive collisions induced by solid-liquid transitions on targets [26]. Other research on the vibration and oscillating dipoles for  $\text{H}/\text{Si}(111)$  can be found in Refs. [34,35]. For noble metals and inert gases, the physisorption implies that adatoms may be taken into account individually, each atom by itself. For chemisorption such as the  $\text{H}$ -atom adsorptions mentioned above [3], charge transfers can be a dominating factor, or at least an influential part when the

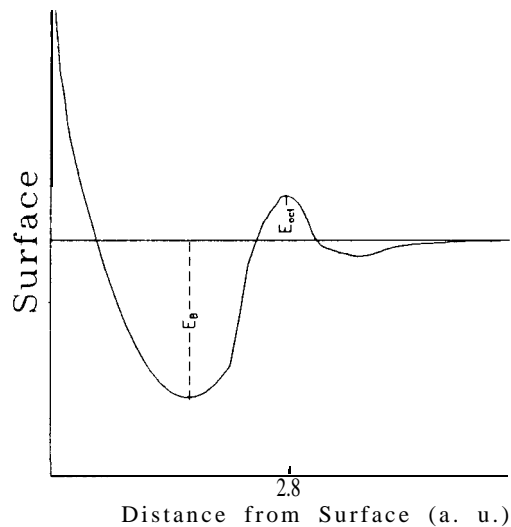


FIG. 2. A schematic plot of the potential energy of an atom or molecule in front of a solid surface when the dynamical process is considered. For the barrier,  $E_{act}$  denotes the activation energy which is calculated in this paper and for the well,  $E_B$  denotes the binding energy which has a magnitude on the order of 1 eV. The distance from the surface is estimated from Ref. [37] for  $E_{act}$ .

whole H-atom is desorbed. The charge transfer must then be involved in the process [3,15,36]. Of course, for far-surface distances, it is understood that the final state of nearby atoms is exerted by the van der Waals forces, of the same nature as those for intermolecular interactions. Therefore the initial and final momentum and energy considerations are not able to give us the physical picture of the adsorption and desorption processes. Thermal activation has been studied in superconducting junctions [36]. Abstracting, all of the above results lead us to the conclusion that AV is a potential barrier in front of the surface.

Recent developments regarding molecules on surfaces include many resonance tunnelling processes. For electrons, there are rather complete theoretical results and for atomic or molecular tunnellings, we can also find some reports. Here we assume that we have a set of oscillator states in which the ad-atoms or molecules occupy. This consideration is equivalent to approximating the potential well right in front of the surface by a harmonic potential as shown in Fig. 2. To find the dynamical configuration we count the number of tunnelling states with energies below the AV. We also find the AV as a discrete function of temperatures similar to Ya. Azbel's results [2]. Further we conclude that the magnitude of the AV is determined by the *vibration frequency*. Starting with the Arrhenius-type law for the rate constant in chemical reactions

$$k = Ae^{-E_{act}/kT},$$

where  $A$  is the preexponential factor and  $E_{act}$  is the AV. For our system of ad-hydrogen-atoms, a chemical reaction helps us to understand



which is modelled in one-dimension as is done in chemical physics. On the left hand side, we have the para-hydrogen molecule while on the right hand side we have the ortho-hydrogen molecule. In this reaction we can see that the system conserves its energy. If we disregard the nuclear spins, no reaction has actually occurred. Furthermore it is kinetically possible, analogous to the well-known three equal mass ball collision in elementary physics. But we need to add an AV of only  $3.9 \times 10^{-2}$  eV per molecule to initiate the reaction. The dissociation energy of  $H_2$  is  $44.75 \times 10^{-2}$  eV. It seems that the formation of a neutral  $H_3$  cluster as the first step is not feasible for this reaction. We hesitate to apply the collapse of clusters mentioned above to this case [11,23]. Furthermore, the AV is less than 1/10 of the dissociation energy of  $H_2$ . Thus we are sure that the reaction occurs before or more often statistically than the dissociation and recombination processes take place, but because of the conservation of energy, Eq. (1) is in equilibrium so that no extra energies are necessary. All the energies are in balance. The necessity of the addition of this extra "involvement energy" for initiating the reaction is what we need to investigate. Furthermore (1) occurs inside the equilibrium gas in a non-controlled condition; all the

atoms and molecules behave as particles in the kinetic theory of gases. The kinetic energy of the incident atoms, such as the H-atom in (1), is actually in the form of equipartition energy. Referred to an equilibrium condition with energy conservation, this energy is the only extra energy available to initiate the reaction. Therefore we must conclude that the extra available energy during this reaction is the equipartition energy, The equipartition energy for each degree of freedom is the main subject. Furthermore the degrees of freedom are closely related to the dimensionality. In surface processes, here in particular the atomic desorptions, the dimensionality is a subject of investigations. The results of the degrees of freedom investigation are used to study the dimensionality of the process in modelling.

The Arrhenius-type law is given in the form of a Boltzmann factor with mono-energy,  $AV, E_{act}$ . We can easily see that  $E_{act}$  is a *modelled value* with the conjectured form of an exponential function among the bulk energy distributions. This form of the law has been applied to many quantities or observables. In this paper, we simplify the Arrhenius-type law as a statistical average by modelling

$$e^{-\beta E_{act}} \equiv \langle e^{-\beta E} \rangle$$

and study the influences of tunnelling. We shall show that without tunnellings, there are no activations. For the reactive collision of hydrogen atoms above, for the energy concerned, we propose that

$$e^{-\beta E_{act}} = \frac{\int e^{-\beta E} P(E) dE}{\int P(E) dE}, \quad (2)$$

for a certain statistical distribution  $P(E)$ . As pointed out in a paper of Su [38], we are really not able to have one single distinct atom incident in our experiments; we must treat the incident atom as an atom inside an atomic (or molecular) beam with a planar incidence, when an atomic adsorption process occurs in front of a surface. Similar to a plane-wave incident on a surface, we can decompose the space into (2+1)-dimensions. The plane of the "wave-front" has certain arbitrariness. We may think that the dynamics is "essentially one-dimensional", particularly with or without the charge and dipole inductions inside the surfaces. We resolve this puzzle, i.e. the mathematical dimensionality of the system, by using Boltzmann statistics as follows. The Boltzmann distribution can be expressed as

$$\begin{aligned} P(E) dE &= e^{\beta(\mu-E)} D(E) dE, \\ e^{\beta\mu} &= \lambda^3 N/V; \quad D(E) \equiv \text{density of states}, \\ \lambda &= \frac{\hbar}{(2\pi M kT)^{1/2}}, \end{aligned} \quad (3)$$

for  $\lambda$  the thermal de Broglie wavelength of a molecule. Here the chemical potential  $\mu$  is calculated from the three-dimensional case. As is well-known in the statistical theory of

semiconductor heterostructures etc., the dimensionality of the phase space is relevant to results of the density of states. For instance, for the two-dimensional case without edge effects

$$D(E_{2D}) = 2\pi k_f \frac{dk_{\parallel}}{dE_{2D}} = \frac{2m}{\hbar^2},$$

$$D(E_{2D}) = \text{constant } C / \text{Area} \times \text{Energy Range}.$$

For an atom incident on a surface, we use this result. Since we obtain black-body radiation as our final result, this choice does have a certain physical meaning. Here to verify our conjecture above, we calculate

$$e^{-\beta E_{act}} = \frac{\int_0^{\infty} C e^{\beta(\mu-2E)} dE}{\int_0^{\infty} C e^{\beta(\mu-E)} dE} = \frac{1}{2}; \quad (4)$$

$$E_{act} = \beta^{-1} \ln 2 = \frac{1.38}{2} kT.$$

We see that  $E_{act}$  is the equipartition energy of approximately one degree of freedom which confirms our one-dimensional conceptions. Here we have self-consistently demonstrated that our conjecture is verified by calculations. Of course, we need to adjust it as follows. From the concept of AV, it is a barrier in the potential-energy-surface. The particle energy in the reaction path must be larger than the AV so that the formation of products is possible. Consequently, we can picture that only part of the energy  $E > E_{act}$  is able to pass over the activation complex and make measurable or effective collisions or proceed in a reaction. From the probability idea in (3) we must have a cutoff at  $E_{act}$  if there are no tunnellings. This restriction is a classical condition with which a particle with energy less than the barrier is not able to pass the barrier. To generalize our calculations, we use the quantum theory which includes tunnelling. We propose to use Boltzmann statistics with a cutoff to calculate the AV together with some tunnellings. Similar to (3) we use the distribution

$$P_1(E) dE = C e^{\beta(\mu-E)} \theta(E - E_{act}) dE. \quad (5)$$

Then the AV becomes

$$e^{-\beta E_{act}} = \frac{\int_{E_{act}}^{\infty} e^{-\beta E} P_1(E) dE + \text{tunnelling}(E_t < E_{act})}{\int_{E_{act}}^{\infty} P_1(E) dE + \text{tunnelling}(E_t < E_{act})}, \quad (6)$$

with both sides functions of the AV. For tunnellings, we assume that we have a set of discrete quantized tunnelling states with a set of eigen-energies  $\{E_t\}$ . Therefore the AV can be obtained from

$$e^{-\beta E_{act}} = \frac{\int_{E_{act}}^{\infty} e^{-\beta E} P_1(E) dE + C e^{\beta\mu} T_2}{\int_{E_{act}}^{\infty} P_1(E) dE + C e^{\beta\mu} T_1}, \quad (7)$$

$$T_1 \equiv \sum_t e^{-\beta E_t}; \quad T_2 \equiv \sum_t e^{-2\beta E_t},$$

which leads to

$$e^{-\beta E_{act}} = e^{-\beta E_{act}} \frac{1/2 + \beta T_2 e^{2\beta E_{act}}}{1 + \beta T_1 e^{\beta E_{act}}}. \quad (8)$$

For the one-dimensional case, we must obtain from (8)

$$E_{act} = \frac{1}{2} kT;$$

$$T_2 = \frac{1}{2e} kT + \frac{T_1}{\sqrt{e}}$$

for  $e = 2.718281\dots$ , the natural base number. Here the functional relation between  $T_1, T_2$  and the temperature is given; the definition of the  $T$ 's are given in (7). It is noted that for exactly one degree of freedom, this condition is extra so that no parameter can be used as an unknown to be determined. The proper solution for (8) is

$$e^{\beta E_{act}} = \frac{1}{2T_2} \left( T_1 + \sqrt{T_1^2 + \frac{2T_2}{\beta}} \right). \quad (9)$$

Several direct evidences follow from (8) and (9). (i) There is no possibility to have AV without tunnelling states because if both  $T_1$  and  $T_2$  are zero, (8) is not able to be satisfied. (ii) From the solution (9), we see that the AV is determined by the tunnelling energies. (iii) There is no possibility to have an infinite number of states for the tunnellings such as hydrogen-like states. Otherwise both  $T_1$  and  $T_2$  are infinities. From (9) the AV is again undetermined. On the other hand, if the system is modelled with  $N$  degrees of freedom, then for a generally continuous  $N$

$$E_{act} = \frac{N}{2} kT,$$

$$N = 2 \left[ \ln \left( \frac{T_1}{T_2} \right) - \ln 2 + \ln \left( 1 + \sqrt{1 + \frac{2T_2}{\beta T_1^2}} \right) \right],$$

which gives a solution of  $N$  as a function of the temperature. Because the modeling of a reaction is current interest [39], and since we may have the reduction of dimensionalities, the dimensionality of modeling the system is actually very relevant. This kind of modeling has already been done in the above reaction (1). It is manifest that (1) is one-dimensional and interpreted as "most stable".

For the declined well right in front of the surface as shown in Fig. 2, we approximate it as a harmonic well since we already have had the harmonic vibrations of the adsorbates there. Thus adatoms start their vibrations and detach from the surface for large vibrations after energy gains. Therefore these adatoms are able to be described by simple harmonic oscillators with energy eigenvalues  $(n+1/2)\hbar\omega$ . The number of possible oscillation modes below the activation maximum, i.e.  $E_{act}$ , is our number of tunnelling states. First, we consider only one tunnelling level,



$$\frac{3}{2}\hbar\omega > E_{act} > \frac{1}{2}\hbar\omega \quad (10)$$

so that  $T_1 = \exp(-\beta\hbar\omega/2)$ ;  $T_2 = \exp(-\beta\hbar\omega)$ . We obtain in the final solution from (9)

$$E_{act} = \frac{1}{2}\hbar\omega + kT \ln[(1 + \sqrt{1 + 2kT})/2], \quad (11)$$

$$\text{for } \hbar\omega > kT \ln \frac{1 + \sqrt{1 + 2kT}}{2}. \quad (12)$$

From (11) we see that it is not exactly any number of degrees of freedom. The variation of the AV with  $kT$  is shown in Fig. 3. Essentially there is no problem for this AV. To understand the result, we study the exact one degree of freedom case

$$\begin{aligned} E_{act} &= \frac{1}{2}kT; \\ \hbar\omega &= kT \left( 1 - 2 \ln \frac{1 + \sqrt{1 + 2kT}}{2} \right), \end{aligned} \quad (12a)$$

in which the frequency  $\omega$  becomes negative if  $kT$  is larger than 2.1353. For these high temperatures, one degree of oscillation is not possible. Whereas from (11) we can obtain more realistic results and find the thermodynamic determination of the AV for certain temperatures. Recently Peksa *et al.* tried to determine the AV of desorption for a metal surface [40]. For chemical reactions, we may have a negative AV as reported by Hernandez *et al.* [39] with a reduced-dimensionality model. For such possibilities, we need further study. It is interesting that here the first term of the AV is the energy eigenvalue of the oscillator which is determined by the oscillation mechanism. The second term is determined totally by the temperature. Therefore *for a different system or mechanism, we have different AV's*. In other words, we have shown that AV is not a quantity determined by dynamical configurations. The tunnelling character, here only the one tunnelling state, determines the whole statistical nature, the activation. In other words, *the vibration frequency, such as  $\omega$  above determines the AV*. Condition (12) gives us the determination of the tunnelling character. This equation determines the inclusion of the number of tunnelling states, i.e. for higher temperatures we have to include two or more tunnelling states. This uncertainty can make the definition of AV ambiguous. In general, if we get  $n$  tunnelling states, we have the condition

$$\left( n + \frac{1}{\alpha} \right) \hbar\omega > E_{act}^{(n)} > \left( (n-1) + \frac{1}{\alpha} \right) \hbar\omega. \quad (13)$$

We must have the restriction

$$\hbar\omega > kT \ln \frac{e^{-\beta(n-1/2)\hbar\omega} T_1^{(n)}}{2 T_2^{(n)}} \left( 1 + \sqrt{1 + \frac{2}{\beta} \frac{T_2^{(n)}}{(T_1^{(n)})^2}} \right)$$

otherwise we must jump from  $n$  to  $n + 1$  for  $T_1^{(n)}$  and  $T_2^{(n)}$  as the temperature is increased. The results are obtained as

$$\begin{aligned} e^{\beta E_{act}} &= \frac{1}{2} \left( \frac{T_1}{T_2} \right) \left( 1 + \sqrt{1 + \frac{2}{\beta} \frac{T_2}{T_1^2}} \right), \\ T_1^{(n)} &\equiv \sum_{\ell=0}^{n-1} e^{-\beta(\ell+\frac{1}{2})\hbar\omega}; \\ T_2^{(n)} &\equiv \sum_{\ell=0}^{n-1} e^{-2\beta(\ell+\frac{1}{2})\hbar\omega}. \end{aligned} \quad (14)$$

We obtain the quantities

$$T_1^{(n)} = e^{-\beta\hbar\omega/2} \frac{1 - e^{-n\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} = e^{-\frac{n}{2}\beta\hbar\omega} \frac{\sinh(n\beta\hbar\omega/2)}{\sinh(\beta\hbar\omega/2)}, \quad (14a)$$

$$T_2^{(n)} \equiv T_1^{(n)}(\beta \rightarrow 2\beta) = e^{-n\beta\hbar\omega} \frac{\sinh(n\beta\hbar\omega)}{\sinh(\beta\hbar\omega)},$$

$$e^{\beta E_{act}^{(n)}} = \frac{1}{2} \frac{\cosh(\frac{1}{2}\beta\hbar\omega)}{e^{-\frac{n}{2}\beta\hbar\omega} \cosh(\frac{n}{2}\beta\hbar\omega)} \left( 1 + \sqrt{1 + \frac{2}{\beta} \tanh\left(\frac{1}{2}\beta\hbar\omega\right) \coth\left(\frac{n}{2}\beta\hbar\omega\right)} \right), \quad (14b)$$

$$\begin{aligned} E_{act}^{(n)} &= \left( (n-1) + \frac{1}{2} \right) \hbar\omega + kT \\ &\times \ln \left[ \frac{\cosh(\frac{1}{2}\beta\hbar\omega)}{e^{\frac{(n-1)}{2}\beta\hbar\omega} \cosh(\frac{n}{2}\beta\hbar\omega)} \frac{\left( 1 + \sqrt{1 + \frac{2}{\beta} \tanh(\frac{1}{2}\beta\hbar\omega) \coth(\frac{n}{2}\beta\hbar\omega)} \right)}{2} \right] \end{aligned} \quad (14c)$$

$$\rightarrow \frac{1}{2} \hbar\omega \text{ as } T \rightarrow 0 \text{ for all } n. \quad (14d)$$

Intuitively the above limit is a simple one-dimensional harmonic oscillator at zero temperature physically, and the AV coincides with the oscillator ground state energy. The limiting result may lead us to the wrong conclusion, that we have only one degree of freedom. Because of the condition (13)

$$\hbar\omega > kT \times \ln \left[ \frac{\cosh(\frac{1}{2}\beta\hbar\omega)}{e^{\frac{(n-1)}{2}\beta\hbar\omega} \cosh(\frac{n}{2}\beta\hbar\omega)} \frac{\left( 1 + \sqrt{1 + \frac{2}{\beta} \tanh(\frac{1}{2}\beta\hbar\omega) \coth(\frac{n}{2}\beta\hbar\omega)} \right)}{2} \right] \quad (15)$$

we have a maximum temperature restriction on the  $n$ -states configuration. We list this maximum temperature for a given  $n$  in Table I for  $n = 1 - 6$ . Further we have plotted the AV for various temperatures for  $n = 1 - 6$  in Fig. 3. In Fig. 3, the unit of  $h\nu$  is  $h\nu \equiv \hbar\omega$  of the oscillator. Values of the AV show discreteness. Every jump from  $n$  to  $n + 1$  shows a discontinuity and includes one more state with energy below the AV.

For the case where temperatures are extremely high, as a consequence of the above discussion, we must have an AV out of the range of consideration although the activation

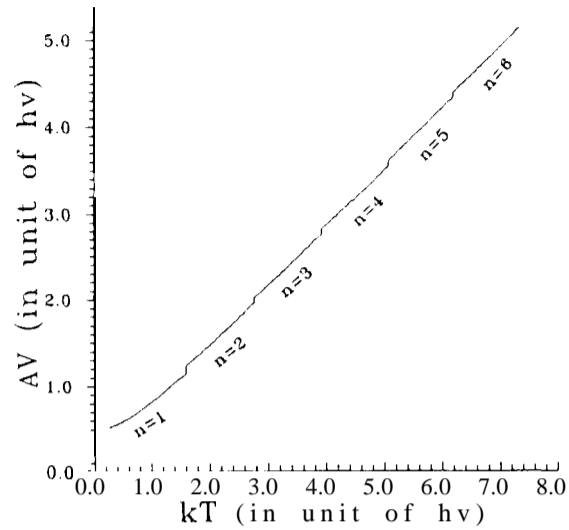


FIG. 3. The activation energy plot for various temperatures: it increases discretely at certain given maximum temperatures which are tabulated in Table I. Labels of  $n$  are the number of tunneling states. It is clear that as the temperature increases over each maximum temperature, it tends to include one more tunneling state. The scale of abscissa and ordinate are both in the unit of the vibration mode, i.e.  $h\nu = \hbar\omega$ .

TABLE I. For the number  $n$  of states below the activation energy, the value  $T_{max}$  gives the maximum temperature. Above this temperature the number of states is increased by one.

$n$	1	2	3	4	5	6
$kT_{max}$ (in $\hbar\omega$ )	1.607	2.780	3.930	5.071	6.216	7.355
$\beta_{min}$ (in $(\hbar\omega)^{-1}$ )	0.622	0.360	0.254	0.197	0.161	0.136

mechanisms, such as the activation complex etc., are still there. The adatom diffusion on a surface has been investigated by Chen and Ying [41]. It indicates that the quantum tunnelling regime at low temperatures may pass to the classical regime at high temperatures, for a H/Ni(100) system. We may assume that the motion along the perpendicular direction behaves with a similar mechanism. The statistical nature becomes that of black-body

radiation except that the chemical potential is not zero and the zero point energy exists. We have to neglect the statistical integral part and the distribution function becomes

$$P_2(\omega) \cong C \sum_{\ell=0}^{\infty} e^{\beta(\mu - (\ell + \frac{1}{2})\hbar\omega)} = C e^{\beta(\mu + \frac{1}{2}\hbar\omega)} \frac{1}{e^{\beta\hbar\omega} - 1}. \quad (16)$$

Mathematically we have an infinite AV. The expectation energy contributed from eigenfrequency  $\omega$  is

$$\begin{aligned} E_{P_2}(\omega) &= \frac{1}{2}\hbar\omega + \frac{C e^{\beta(\mu - \frac{1}{2}\hbar\omega)} \hbar\omega \sum_{\ell=1}^{\infty} \ell e^{-\beta\ell\hbar\omega}}{C e^{\beta(\mu - \frac{1}{2}\hbar\omega)} \sum_{\ell=0}^{\infty} e^{-\beta\ell\hbar\omega}} \\ &= \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}, \end{aligned} \quad (17)$$

where the ergodic distribution over  $\omega$  is assumed.

If the classical regime is adopted, we neglect the zero-point ground state

$$E'_{P_2}(\omega) = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}, \quad (18)$$

which is exactly the same as the black-body radiation case. Black-body radiation has a well-established theory. No further discussion is given here.

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