Theory of Monolayer. II. Vibration of Molecule in the Monolayer Normal to the Surface.

By Hiroshi HOTTA

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The author assumed in the previous paper(1) the equality of the vibrational term of the partition function of the molecule normal to the surface in both gaseous and liquid states of the monolayer. In the present paper, we shall criticise this propriety as a problem of the dynamics of material points and derive the relation between frequency and intermolecular distance or potential energy.

This vibration should be, of course, independent of the surface area per molecule in the region, where the mutual interaction between the surface molecules is negligible. Therefore, we now consider the system with mutual interaction. As a model of such a system we imagine a molecule vibrating normal to the surface, which is connected with n surrounding fixed molecules by springs, the strength of which is equal to the mutual potential energy, u, as shown in Fig. 1. The mass of the molecule is m.

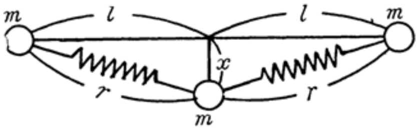

Fig. 1.

The mutual potential energy between any pair of the vibrating molecule and the surrounding one, U, is generally expressed in the form

$$U=nu=\frac{a}{r^6}-\frac{b}{r^k}, \tag{1}$$

and

$$r^2=l^2+x^2, \tag{2}$$

where r is the distance between two neighboring molecules, l the distance between them at equilibrium position, x the displacement normal to the surface, k the constant which is generally taken within a range of $12\geqq k\geqq 9$. The obtained value from the experimental data, as found in the previous paper,(1) was not u but U. Hence, the force normal to the surface, F, is as usual

$$F=-\frac{dU}{dr}\frac{dr}{dx}=\left(\frac{6a}{r^7}-\frac{kb}{r^{k+1}}\right)\frac{x}{r} \tag{3}$$

from (1) and (2). Since the equation of motion is

$$m\frac{d^2x}{dt^2}+F=0, \tag{4}$$

which may be rewritten as

$$m\frac{d^2x}{dt^2}+y^2x=0, \tag{5}$$

inserting (3) into (4) and comparing this with (5),

$$y^2=\frac{6a}{(l^2+x^2)^4}-\frac{kb}{(l^2+x^2)^{\frac{k}{2}+1}}$$
$$=\left(\frac{6a}{l^8}-\frac{kb}{l^{k+2}}\right)+\left[\frac{k\left(\frac{k}{2}+1\right)b}{l^{k+4}}-\frac{24a}{l^{10}}\right]x^2+\cdots\cdots. \tag{6}$$

First Approximation

If we neglect the second term in (6), viz., $l\gg x$,

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(1) H. Hotta, This Bulletin, **25**, 398 (1952).

according to well-known treatment, the frequency ν is expressed by

$$\nu=\frac{1}{2\pi}\sqrt{\frac{1}{m}\left(\frac{6a}{l^8}-\frac{kb}{l^{k+2}}\right)}$$
$$=\frac{1}{2\pi l^4}\sqrt{\frac{a}{m}\left(6-k\cdot\frac{b}{a}\cdot\frac{1}{l^{k-6}}\right)}. \tag{7}$$

If we define

$$U^e=\frac{a}{l^6}, \tag{8}$$

the equation (7) is rewriteen as

$$\nu=\frac{1}{2\pi l}\sqrt{\frac{6U^e}{m}}. \tag{9}$$

On the other hand, if we define

$$U^c=\frac{a}{l^6}-\frac{b}{l^k}, \tag{10}$$

the equation (7) is rewritten as

$$\nu=\frac{1}{2\pi l}\sqrt{\frac{6U^c}{m}\left(1-\frac{k-6}{k}\cdot\frac{b}{a}\cdot\frac{1}{l^k}\cdot\frac{1}{U^c}\right)}. \tag{11}$$

Since the mutual potential energy in the liquid expanded film near the vaporization point may be approximately expressed in the form (8) as shown in the previous paper,⁽¹⁾ the equations (7) and (9) are rewritten as the limiting form

$$\nu^e=\frac{1}{2\pi l^4}\sqrt{\frac{6a}{m}} \tag{12}$$
$$=\frac{1}{2\pi l}\sqrt{\frac{6U^e}{m}}, \tag{13}$$

where ν^e is the frequency corresponding to (8). It is shown by (12) that ν^e is inversely proportional to the fourth power of the intermolecular distance or the square of the surface area per molecule.

If we insert the value of U^e of myristic acid at 14°C. obtained in the previous paper⁽¹⁾ into (13), the frequency normal to the surface under the condition metioned above becomes

$$\nu^e=1.2\times10^{11}\ \text{sec.}^{-1} \tag{14}$$

On the other hand, if the frequency of the vibration on the surface, ν^S, can be defined, according to the harmonic oscillator model,⁽²⁾ by

$$\nu^S=\sqrt{\frac{kT}{2\pi m A_f}}, \tag{15}$$

where A_f is the molecular free surface as defined by equation (18) in the previous paper.⁽¹⁾ By inserting the numerical value corresponding to (14) into (15), we obtain

$$\nu^S=1.6\times10^{11}\ \text{sec.}^{-1}. \tag{16}$$

Next, since the vibration in the gaseous film may be the thermal agitation, the corresponding frequency, ν^G, is given, according to the cage model,⁽³⁾ by

$$\nu^G=\frac{1}{4r^G}\sqrt{\frac{2kT}{\pi m}}, \tag{17}$$

which is one-third of the three-dimensional frequency, where r^G is the radius of a cage. Therefore, we obtain also

$$\nu^G=\frac{2\times10^{11}}{r^G}\quad\text{sec.}^{-1} \tag{18}$$

by inserting the numerical value to (17), where r^G is in the A. unit. If we suppose that the maximum displacement of the centre of a surface molecule in the gaseous film, viz., r^G, may be at the most a few Angstroms, the ratio of ν^L to ν^G in the equation (9) in the previous paper should be nearly equal to unity, and the contribution to the heat of surface vaporization negligible.

These three frequencies are nearly equal. This shows that the effect of the mutual potential energy to the vibration should be negligible at the surface vaporization point. And these orders of magnitude of the frequencies may be plausible, compared with the experimental results in the other branches of science, e. g., rheology and microwave, etc.⁽⁴⁾

Since we must consider the repulsion term as in (10) in the more compact film, the frequency must be given by (11). If we define

$$z=\frac{b}{l^k}\cdot\frac{1}{U^c}, \tag{19}$$

which means the fraction of the repulsion term, then the equation (11) is transformed into the form

$$\nu^c=\frac{1}{2\pi l}\sqrt{\frac{6U^c}{m}\left(1-\frac{k-6}{6}z\right)}, \tag{20}$$

where ν^c is the frequency corresponding to (10). Müller⁽⁵⁾ has calculated the van der Waals potential and the lattice energy of an n-hydrocarbon molecule in a paraffin crystal. Since z is supposed to be at the most one- or two-tenths even in the liquid condensed film from his estimation, if we neglect the effect of the head group, the contribution of the term $(k-6)z/6$ to the frequency

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(2) Fowler and Guggenheim, "Statistical Thermodynamics," 1939, p. 325.

(3) Ibid., p. 530.

(4) M. Toda, "Ekitai-Kozo-ron" (The theory of liquid structure) (in Japanese). Chap. VIII; C. V. Raman and C. S. Venkateswaran, *Nature*, **143**, 798 (1939); C. P. Smyth et al., *J. Am. Chem. Soc.*, **70**, 4102 (1948); ibid., **72**, 3447 (1950).

(5) A. Müller, *Proc. Roy. Soc.*, A **154**, 628 (1936)

may be small, when k is within the range of $12 \geqq k \geqq 9$. Therefore, the equations (13) and (20) are generalized in the form,

$$\nu = \frac{1}{2\pi l}\sqrt{\frac{6U}{m}} \tag{21}$$

within the error mentioned above.

But, since the steric hindrance should be considered in the compact film, the model at the beginning must be modified suitably.

Second Approximation

When the equation of motion is expressed as

$$m\frac{d^2x}{dt^2} + y^2x + \beta x^3 = 0, \tag{22}$$

the corresponding frequency is approximately

$$\nu \doteqdot \frac{1}{2\pi}\sqrt{\frac{1}{m}\left(y^2 + \frac{3}{4}\beta C^2\right)}, \tag{23}$$

where C is the amplitude.(6) Therefore, when we consider the second term in (6), the frequency becomes

$$\nu = \frac{1}{2\pi l} \times \sqrt{\frac{1}{m}\left[\left(\frac{6a}{l^6} - \frac{kb}{l^k}\right) - \frac{3}{4}\left(\frac{C}{l}\right)^2\left(\frac{24a}{l^6} - \frac{k\left(\frac{k}{2}+1\right)b}{l^k}\right)\right]}$$

$$= \frac{1}{2\pi l} \times \sqrt{\frac{6U}{m}\left[\left(1 - \frac{k-6}{6}z\right) - 3\left(\frac{C}{l}\right)^2\left(1 - \frac{k\left(\frac{k}{2}+1\right) - 24}{24}z\right)\right]} \tag{24}$$

using (1) and (19). When the amplitude is small against intermolecular distance, *viz.*, $l \gg C$, the equation (24) becomes similar to (7).

Summary

The author has assumed in the previous paper that the vibrational term of the partition function of the molecule normal to the surface is equal in both gaseous and liquid films. This assumption was verified at the surface vaporization point in the present paper with the dynamics of material points. The derived relation between frequency and intermolecular distance or potential energy is (12) or (13).

In conclusion, the author wishes to express his sincere thanks to Prof. T. Isemura for his kind advice and encouragement.

Iustitute of Scientific and Industrial Research,
Osaka University, Osaka

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(6) T. Tsuboi, "Shindo-ron" (Theory of Vibration) (in Japanese), p. 255.