On the Statistical Mechanics of Change of State

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The nature of the pressure against density curve at constant temperature is investigated by the methods of the grand canonical ensemble for a system of identical molecules between which only short range forces act. It is shown that, except for surface effects, the total energy, entropy, etc., are proportional to the number of molecules in the system. The pressure is proven to be a non-decreasing function of the density which may have regions of constancy as a function of the density. This shows rather clearly the impossibility for any analytic equation of the Van der Waals' type being able to give a satisfactory account of condensation without *ad hoc* assumptions.

IT should be possible to understand the isothermal change of a vapor into a liquid in terms of the forces acting between the molecules. Since this change takes place for nearly every system of molecules, one would expect that the detailed nature of the forces is not important. Only such general considerations should enter, as whether the forces are attractive or repulsive, and their behavior for large distances of separation of the molecules.

We shall show for a system of molecules of one species between which only short range forces act that: (a) the pressure is a monotonically increasing function of the density at constant temperature, although there may be regions in which the pressure is independent of the density; (b) the energy, entropy, free energy, etc., are approximately proportional to the number of molecules present. It is only in the asymptotic approximation for a large number of molecules and where the dimensions of the space containing the molecules are large compared to the range of the molecular forces that (a) and (b) hold. The neglected terms may be regarded as giving rise to surface effects. It should not be implied that short range forces are necessary for (a) and (b), although we have been able to show that (a) and (b) are true only for this case.

The grand canonical ensemble will be used for the statistical description of the system because of its elegance and convenience. We will furthermore consider the system to obey the laws of classical mechanics. This has been shown by Kahn and Uhlenbeck[1] not to be an essential restriction. The appearance of Planck's constant in our equation is for dimensional purposes. It has no quantum mechanical implications.

The partition function of a classical grand canonical ensemble with generic phases is

$$e^{-\psi/\vartheta}=\sum_{N=0}^{\infty}\int\cdots\int\frac{\exp\left[-\dfrac{H(p_1,\cdots p_{3N};x_1,y_1,\cdots z_N)-\alpha N}{\vartheta}\right]}{h^{3N}N!}dp_1\cdots dp_{3N}dx_1\cdots dz_N. \tag{1}$$

In terms of the function, ψ, the pressure, average number of particles in the system, and the mean square fluctuations in the number of particles are:

$$p=-\partial\psi/\partial V, \tag{2}$$

$$(N)_{Av}=-\partial\psi/\partial\alpha, \tag{3}$$

$$\langle[N-(N)_{Av}]^2\rangle_{Av}=-\vartheta\partial^2\psi/\partial\alpha^2. \tag{4}$$

Equations (2) and (3) do not insure the existence of an equation of state. For a general ψ the pressure is not necessarily a function of the temperature and particle density only. To investigate the conditions under which an equation of state exists we write

$$\psi=-V\varphi,\qquad \beta=\ln V. \tag{5}$$

[1] B. Kahn and G. E. Uhlenbeck, Physica **5**, 399 (1938).

Then Eqs. (2) and (3) take the form

$$p=\varphi+(\partial\varphi/\partial\beta), \tag{6}$$

$$\rho=(N)_{Av}/V=\partial\varphi/\partial\alpha, \tag{7}$$

where ρ is the particle density.

The necessary and sufficient condition that the pressure may be written as a function of the density and temperature independent of the volume is that the Jacobian

$$\begin{vmatrix} \frac{\partial p}{\partial\alpha} & \frac{\partial\rho}{\partial\alpha} \\ \frac{\partial p}{\partial\beta} & \frac{\partial\rho}{\partial\beta} \end{vmatrix} = \begin{vmatrix} \frac{\partial\varphi}{\partial\alpha}+\frac{\partial^2\varphi}{\partial\alpha\partial\beta} & \frac{\partial^2\varphi}{\partial\alpha^2} \\ \frac{\partial\varphi}{\partial\beta}+\frac{\partial^2\varphi}{\partial\beta^2} & \frac{\partial^2\varphi}{\partial\alpha\partial\beta} \end{vmatrix} = 0. \tag{8}$$

If φ is independent of β it is evident that (8) will be satisfied. There are, of course, many other functions which would satisfy (8). It is, however, the only form for which total energy, entropy, etc., are proportional to the number of particles. Thus our task of showing (a) and (b) is reduced to the problem of showing that φ is asymptotically independent of β for large dimensions. The truth of (a) follows readily from Eqs. (4), (6), and (7) for φ independent of β. For this condition we find

$$p=\varphi(\alpha), \tag{9}$$

$$\rho=\frac{\partial\varphi(\alpha)}{\partial\alpha}>0, \tag{10}$$

$$\langle[N-(N)_{Av}]^2\rangle_{Av}/\vartheta V=\frac{\partial^2\varphi(\alpha)}{\partial\alpha^2}>0, \tag{11}$$

where these derivatives exist. The inequality in (10) is obvious because the particle density is positive, and similarly that in (11) because the mean square fluctuations in the number of particles is certainly positive. Equation (10) tells us the pressure is an increasing function of α. Equation (11) shows that the density is an increasing function of α. This relation may be inverted to read that α is an increasing function of the density. The fact that α is an increasing function of the density and that the pressure is an increasing function of α implies that the pressure is an increasing function of the density.

However, if $\varphi(\alpha)$ is a continuous function of α with a discontinuity in slope at some point, say $\alpha=\alpha_0$, then the slope of $\varphi(\alpha)$, which is the density, may be considered as taking on all values between the limiting values of the slope from the left and from the right. We now see that this value of $\alpha=\alpha_0$ leads to a region of values of the density in which pressure is independent of the density. Such a point in the curve corresponds to a region in which there are two or more phases present.

The next stage in our development will be to show for systems for which the molecular forces are short range that $\varphi(\alpha, V)$ is asymptotically independent of the dimensions of the system, and that it may have the character indicated in the preceding paragraph. The method by which we do this is based on a power series development for $\varphi(\alpha, V)$ in terms of certain characteristic integrals of the interactions between the molecules and $e^{\alpha/\vartheta}$. Returning to expression (1) for $e^{-\psi/\vartheta}$ we can immediately evaluate the integrals over momentum space, for a Hamiltonian of the form

$$H(p_1, p_2, \cdots, p_{3N}; x_1, y_1, \cdots, z_N) = \frac{1}{2m}\sum_{k=1}^{3N} p_k^2+U(x_1, y_1, \cdots, z_N), \tag{12}$$

in which $U(x_1, y_1, \cdots, z_N)$ is the potential energy of N molecules. We now have

$$e^{-\psi/\vartheta}=\sum_{N=0}^{\infty}\frac{1}{N!}\left\{\frac{(2\pi m\vartheta)^{\frac{3}{2}}}{h^3}e^{\alpha/\vartheta}\right\}^N \times\int\cdots\int dx_1\cdots dz_N \times\exp\left[\frac{-U(x_1, y_1, \cdots, z_N)}{\vartheta}\right]. \tag{13}$$

To obtain the power series indicated above we define the following sequence of functions by the recursion relationships

$$\begin{aligned} W(1)&=S(1)\equiv 1, \\ W(1, 2)&=S(1, 2)+S(1)S(2), \\ W(1, 2, 3)&=S(1, 2, 3)+S(1)S(2, 3)+S(2)S(1, 3)+S(3)S(1, 2)+S(1)S(2)S(3), \\ W(1, 2, 3, 4)&=S(1, 2, 3, 4)+\cdots, \end{aligned} \tag{14}$$

where

$$W(1, 2, \cdots, N) = \exp\left[-U(x_1, \cdots, z_N)/\vartheta\right].$$

The general law of formation, (14), for the functions $S(k_1, k_2, \cdots)$ is as follows. Partition all of the particles numbered 1 to N into sets such that each particle appears in one and only one set. For each set write the symmetric function $S(k_1, k_2, \cdots)$ for the particles appearing in that set. For each partition form the product of the S's for that partition, and sum over all possible partitions of the numbers 1 to N. This sum we set equal to $W(1, 2, \cdots, N)$. It is clear that this operation defines $S(1, 2, \cdots, N)$ in terms of $W(1, 2, \cdots, N)$ and other S's containing fewer than N particles, and consequently, in terms of all of the W's for the particles 1 to N which contain N and fewer of these particles.

We shall call these functions, S, cluster functions because all of them, except those containing only one particle, vanish if we take any one of the particles in them sufficiently far away from the remaining particles so that its interaction energy with them disappears. For short range forces this means that each particle of a particular S must be close to at least one other particle of this S if they are to contribute to the integrals in (13). This fact is quite evident for the case of an S containing only two particles, since $W(1, 2)$ equals one if the two particles are separated far enough. We prove the above for a general S by mathematical induction. Suppose that for $N>2$ the first particle is far away from the remaining ones. Then $W(1, 2, \cdots, N) = W(2, 3, \cdots, N)$. Now separate the right-hand side of (14) into three parts: the single terms $S(1, 2, \cdots, N)$ containing all of the particles; the sum of all the terms with $S(1)$ as a factor, which is $W(2, 3, \cdots, N)$; the sum of the remaining terms in each of which the first particle appears with at least one other particle, and no more than $N-2$ other particles, and each of which is zero by hypothesis. Thus we obtain $W(1, 2, \cdots, N) = W(2, 3, \cdots, N) + S(1, 2, \cdots, N)$ or $S(1, 2, \cdots, N) = 0$.

We define

$$b_l(V) = \frac{1}{Vl!}\int \cdots \int S(1, 2, \cdots, l)\,dx_1 dy_1 \cdots dz_l. \tag{15}$$

In terms of the functions, $b_l(V)$, (13) may now be written

$$e^{-\psi/\vartheta} = \prod_{l=1}^{\infty} \sum_{n_l=0}^{\infty} \frac{1}{n_l!}\left\{\left[\frac{(2\pi m\vartheta)^{\frac{3}{2}} e^{\alpha/\vartheta}}{h^3}\right]^l V b_l(V)\right\}^{n_l}. \tag{16}$$

On carrying out the sums indicated in (16) there results

$$\psi = -\vartheta V \sum_{l=1}^{\infty}\left[\frac{(2\pi m\vartheta)^{\frac{3}{2}}}{h^3} e^{\alpha/\vartheta}\right]^l b_l(V). \tag{17}$$

A comparison of (17) and (5) shows us that

$$\varphi = \vartheta \sum_{l=1}^{\infty}\left[\frac{(2\pi m\vartheta)^{\frac{3}{2}}}{h^3} e^{\alpha/\vartheta}\right]^l b_l(V). \tag{18}$$

A necessary condition that $\varphi(\alpha, V)$ be asymptotically independent of the size of the system is the asymptotic independence of the $b_l(V)$ of V. The independence of the $b_l(V)$ of the volume for large dimensions is a consequence of the fact that the S's vanish unless the particles form a cluster. For any value of l we shall now show that one can find dimensions of the system sufficiently large so that the effect of a given change in the size of the system is as small as one could wish. Consider now the integral which defines $b_l(V)$. Take the coordinates of all of the particles except the first one to be fixed. The value of the integral over the coordinates of the first particle will then depend only upon the relative coordinates of the remaining $(l-1)$ particles except when these particles are near some boundary of the system because the integrand of (15) vanishes unless the first particle is in the neighborhood of the remaining particles. Similarly integrate over the coordinates of the first $(l-1)$ particles. For short range forces the value of this integral is independent of the position of the lth particle unless it is near to a boundary of the system because the value of the integrand of (15) will vanish if any one of the other particles is too far from the lth one and because the integrand depends only upon the relative coordinates of the particles. The distance which we must keep the lth particle from the boundary, in order that the integrals over the remaining particles be independent of the position of the lth particle, will increase as l increases. We now see that the integral over the lth particles will give a factor

proportional to the volume of the system provided the dimensions of the system are so large that the last particle is near the boundary of the system for only a small fraction of the range of integration for which it is far from the boundary. In fact, the difference between the actual factor and the volume is roughly proportional to the surface area of the boundary with a proportionality factor which depends upon l. Thus, $b_l(V)$ may be written approximately as the sum of a term which is a function of l only plus a term proportional to the boundary area divided by the volume. The neglect of the part which depends upon the boundary is not uniform as a function of l, therefore the $b_l(V)$ are asymptotically independent of the volume and boundary.

This asymptotic independence of the $b_l(V)$ of the volume may be supplemented by a rough integration which will suffice to determine the behavior of $b_l(V)$. Integrate over the coordinates of the first particle. We get a contribution to the value of the integral roughly proportional to the cube of the range of the molecular interaction for each of the remaining particles, and consequently, a factor $(l-1)v$, where v is an appropriately defined interaction volume. Similarly, integrating over the coordinates of the second, third, etc., particles we would obtain factors $(l-2)v$, $(l-3)v$, $(l-4)v$, etc. We see that we obtain[2]

$$b_l(V)=f(l,\ V)v^{l-1}, \tag{19}$$

where $|f(l,\ V)|$ is a function of l which varies more slowly than an exponential. If we write

$$z=v\frac{(2\pi m\vartheta)^{\frac{3}{2}}e^{\alpha/\vartheta}}{h^3}$$

and place this expression in Eq. (18) then

$$\varphi(z,\ V)=\frac{\vartheta}{v}\sum_{l=1}^{\infty}f(l,\ V)z^l. \tag{20}$$

The asymptotic independence of the $b_l(V)$ of V is not sufficient to guarantee the asymptotic independence of $\varphi(z,\ V)$ of V. For this, one needs uniform convergence of the power series (20) as a function of V. We define

$$B_l=\frac{1}{Vl!}\int\cdots\int|S(1,2,\cdots,l)|\,dx_1dy_1\cdots dz_l, \tag{21}$$

in which we integrate the variables x_1, y_1, $\cdots$, z_{l-1} over all space, and $x_ly_lz_l$ over V, The B_l are independent of V and also

$$|b_l(V)|\leq B_l. \tag{22}$$

A crude estimation for B_l would show that

$$B_l=F(l)v_0{}^{l-1}, \tag{23}$$

with v_0 constant and $F(l)$ a slow varying function. Let

$$f(l,\ V)=f^0(l)+f'(l,\ V), \tag{24}$$

where $\lim_{V\to\infty}f'(l,\ V)=0$ and $f^0(l)$ is independent of V. Now write

$$\varphi(z,\ V)=\frac{\vartheta}{v}\Big[\sum_{l=1}^{N}f^0(l)z^l+\sum_{l=1}^{N}f'(l,\ V)z^l+\sum_{l=N+1}^{\infty}f(l,\ V)z^l\Big]. \tag{25}$$

Equations (22) and (23) give us

$$\Big|\sum_{l=N+1}^{\infty}f(l,\ V)z^l\Big|\leq\sum_{l=N+1}^{\infty}F(l)\Big\{\frac{v_0}{v}|z|\Big\}^l. \tag{26}$$

For $z<v/v_0$ the series on the right side of (26) converges. Therefore, there exists an N such that

$$\Big|\sum_{l=N+1}^{\infty}f(l,\ V)z^l\Big|<\frac{\epsilon}{2}, \tag{27}$$

with ϵ any positive quantity. For this fixed N there exists a sufficiently large V such that

$$\Big|\sum_{l=1}^{N}f'(l,\ V)z^l\Big|<\frac{\epsilon}{2}. \tag{28}$$

This implies that

$$\lim_{V\to\infty}\varphi(z,\ V)=\varphi(z) \tag{29}$$

exists, which is all that is required. The uniform convergence[3] of the series (20) enables us to

[2] This form for the $b_l(V)$ is also given by Mayer and Mayer, *Statistical Mechanics* (John Wiley and Sons, 1940), p. 298.

[3] The uniform convergence of series (20) follows if a series of the form $\sum_{l=1}^{\infty}B_lz^l$ has a finite radius of convergence.

consider the $b_l(V)$ to be independent of the dimensions of the system as long as they are sufficiently large.

For a slowly varying $f(l)$, the nearest singularities of $\varphi(z)$ are on the unit circle. At sufficiently low temperatures, and if the forces have regions where they are attractive, then it is true that the b_l are positive.[4] The only question which remains before us is whether a convergent power series can represent a function which for real z is continuous at $z=1$ with a discontinuity in slope.

We will show this by constructing a function with these properties. Take the function defined by the integral

$$g(z)=\frac{z-1}{2}\int_0^{\theta_0}h(\theta)\left[\frac{1}{z-e^{i\theta}}+\frac{1}{z-e^{-i\theta}}\right]d\theta, \quad (30)$$

in which θ_0 is less than π, and where $h(\theta)$ is a continuous positive function possessing derivatives of at least the third order, where $h'(0)<0$, and where $h(\theta)$ has a contact of at least the third order at $\theta=\theta_0$. This function, $g(z)$, is continuous at $z=1$, and for real z there is a discontinuity in the first derivative at this point. For $|z|<1$, $g(z)$ can be expanded into a convergent power series, $g(z)=\sum c_n z^n$, all of whose coefficients, c_n, except finitely many are positive. This defect in $g(z)$ could be readily remedied by the addition of an appropriate polynomial to the integral. The coefficients of z^n are, except for the first term,

$$c_n=\int_0^{\theta_0}h(\theta)[\cos n\theta-\cos(n+1)\theta]d\theta. \quad (31)$$

Integrating by parts three times we obtain

$$c_n=-h'(0)\left[\frac{2n+1}{n^2(n+1)^2}\right]-\int_0^{\theta_0}h'''(\theta)\left[\frac{\sin n\theta}{n^3}-\frac{\sin(n+1)\theta}{(n+1)^3}\right]d\theta. \quad (32)$$

[4] Reference 2, pp. 305–308.

It is clear that since the first term of c_n is positive and of order $-h'(0)/n^3$, and the second term, the integral, is of order $1/n^4$ or smaller, only finitely many of the c_n can be negative. To such a function $g(z)$ an appropriate entire function can be added so that the sum has the properties shown in Eqs. (10) and (11).

The fact that we have been able to construct a function possessing the appropriate properties is no guarantee that the functions defined by the power series (20) will have these properties. We must distinguish several possible cases for functions defined by power series such as (20):

(a) The functions $\varphi(z, V)$ do not have analytic continuations for real $z>1$.

(b) They do have an analytic continuation for real $z>1$, but for these z the $\lim_{V\to\infty}\varphi(z, V)$ does not exist. This means that the $\varphi(z, V)$ are not uniformly bounded for real $z>1$.

(c) The analytic continuation of the $\varphi(z, V)$ exists for real $z>1$ and $\varphi(z, V)$ approaches a limit as V tends to infinity. In this case the continuation of the function $\varphi(z)$ defined by (29) will exist and is the same as the $\lim_{V\to\infty}\varphi(z, V)$ for real $z>1$.

If conditions (a) or (b) hold, then one can only say that the grand canonical ensemble may not be used for the description of condensed systems. If (c) holds then all of our previous conclusions are valid. We would then be at considerable variance with the conclusions of K. Fuchs.[5] In his work the volume dependence of the cluster integrals was used to explain the vapor pressure curve between a solid and a gas. Also, in our development surface effects appear in a very general manner from the term in $b_l(V)$ which is proportional to the boundary area divided by the volume. This is quite different from the case where one uses the canonical ensemble where they appear in terms of very special properties assumed for the $b_l(V)$.[6]

[5] K. Fuchs, Proc. Roy. Soc. **179**, 194–301 (1941).
[6] Reference 2, p. 313.