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Theory of Critical Fluctuations

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A macroscopic system is subdivided into cells of identical size and shape arranged in a regular spatial array. The method of canonical ensembles would consider one of the cells, schematizing the rest into a "reservoir." The present "cellular method" treats the cells on an equal footing and is appropriate to deal with the fluctuations near the critical point for which the standard theory yields infinite results. Earlier theories dealing with the same problem appear as special cases of the present treatment. In particular, the critical points are defined generally enough to include the so-called λ-points in solids. The macroscopic system is invariant under the group of translations which displaces one cell into another. The macroscopic quantities (e.g., the thermodynamic parameters) are invariants of this group.

I. INTRODUCTION

THE role of fluctuations in statistical thermodynamics is primarily a negative one. Indeed, the very existence of thermodynamics can be said to be based on the fact that the fluctuations in the macroscopic thermodynamic variables are negligible compared to the mean values of these variables. The proof of this fact is essential in the statistical foundation of thermodynamics. The agreement in the results obtained from different statistical representations of a physical system is also a consequence of the negligible character of the fluctuations. Thus, whether one uses a microcanonical ensemble which corresponds to a completely closed system, or a canonical ensemble which corresponds to a system in contact with a reservoir, the results are the same since fluctuations can be neglected.

It is therefore of fundamental interest that fluctuations are not negligible at the so-called critical points of physical systems, of which the gas-liquid critical point is the best known case. As a matter of fact, if the fluctuations are calculated according to standard procedures, infinite results are obtained. Experimental results indicate that critical-point fluctuations, although finite, are orders of magnitude larger than usual and give rise to macroscopic phenomena, e.g., critical opalescence.

Several theories[1-4] have been proposed for treating the problem of critical-point fluctuations, each based on a different analysis of the physical situation. There are several reasons for our reconsidering the question. In the first place, the relation between the above-mentioned theories is rather obscure and none of them can claim general acceptance. In the second place, all of them appear to be too specialized. (In fact, one of the authors has recently shown[5] that critical points are of rather common occurrence, since the well-known λ-point phenomena observed in solids and some liquids may be considered as critical points.) The above-mentioned theories refer only to the gas-liquid critical points and to the critical mixing points in liquids. Finally, these theories are often based, in part, on rather special molecular models and do not really treat the basic statistical problem.

In Section II we sum up the results of the conventional theory of fluctuations in a form general enough for our purposes. The difficulties arising at the critical point are discussed in detail.

In Section III we introduce the "cellular method" which can be considered a refinement of the ordinary treatment of generalized canonical ensembles. This method allows one to treat the correlation of fluctuations in different volume elements, an effect which is of great importance at critical points and which is ignored by the standard method. The importance of these correlations was first pointed out by Ornstein and Zernike,[2] and our method is a development of their idea. This development, on its formal side, leads to a general criterion for the definition of macroscopic variables, i.e., those variables which can be used in discussing macroscopic phenomena.

In Section IV we present a calculation of fluctuations and their correlations.

Section V is devoted to a discussion of the relationships between our theory and those previously mentioned, as well as to some clarification of the relationships of these theories to each other. In particular, the question of critical opalescence is discussed.

II. FLUCTUATIONS AND CRITICAL POINTS

The thermodynamic properties of a closed system can be adequately described in terms of a so-called

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[1] M. V. Smoluchowski, Ann. d. Physik. **IV** (Folge) **25**, 205 (1908).

[2] L. Ornstein and F. Zernike, Proc. Amst. Akad. Sci. **17**, 793 (1914); **18**, 1520 (1916); **19**, 1321 (1917); Physik. Zeits. **19**, 134 (1918); **27**, 761 (1926).

[3] Y. Rocard, J. de phys. et rad. 4, 165 (1933).

[4] J. Yvon, Actualités Scientifiques et Industrielles, Nos. 542, 543 (Paris, 1937).

[5] L. Tisza, "General theory of phase transitions," National Research Council Conference on Phase Transformations in Solids, 1948 (to appear in book form).

fundamental equation

$$U=U(X_1, X_2, \cdots, X_{r+1}), \tag{1}$$

where U is the internal energy and X_1, X_2, $\cdots$, X_{r+1} are the extensive variables characterizing the system. (The X_i include volume, entropy, mole numbers, etc.) We shall assume our system to be spatially homogeneous on a macroscopic scale so that U is a first-order homogeneous function of its arguments. It is then most convenient to let $X_{r+1}=V$, the volume, and to define the "densities":

$$x_i=\frac{X_i}{X_{r+1}}; \quad u=\frac{U}{X_{r+1}}. \tag{2}$$

The fundamental equation can then be written

$$u=u(x_1, x_2, \cdots, x_r). \tag{3}$$

The generalized forces conjugate to X_k or x_k are

$$P_k=\partial U/\partial X_k=\partial u/\partial x_k. \tag{4}$$

In order to obtain the fluctuations of the quantities x_k about their mean values, we shall consider our system as a part of a large closed system, e.g., one cm^3 of a gas in a large container. We now have the possibility of processes in which the quantities X_k flow from the sub-system to the remainder of the system, called a "reservoir," and vice versa; these processes are subject only to the condition that there is no change in the value of X_k for the whole closed system. The assumed difference in size between the sub-system and the reservoir implies that these processes may lead to a noticeable change in the state of the sub-system while the quantities x_k and P_k are essentially unchanged in the reservoir.

It is well known[6] that the probability of finding the sub-system in a state $x_{1\alpha}$, $x_{2\alpha}$, $\cdots$, $x_{r\alpha}$, which may differ from the equilibrium state x_1, $\cdots$, x_r, is given by a generalized canonical distribution function:

$$p_\alpha=w_\alpha \exp 1/kT\left[\psi-E_\alpha+\sum_{k=2}^{r}P_k x_{k\alpha}\right]. \tag{5}$$

Here p_α is the probability of finding a state of the system described by the index α, w_α is the statistical weight (degeneracy) of this state, E_α its energy, and $x_{k\alpha}$ the value of the variable x_k in this state. The index k runs from 2 to r omitting x_1 which is the entropy density. The function ψ is the thermodynamic potential

$$\psi=U-\sum_{k=1}^{r}P_k x_k. \tag{6}$$

We can put the expression for p_α into a more symmetrical form as follows. Let us define:

$$S_\alpha=k \ln w_\alpha.^{\text{a}} \tag{7}$$

Then:

$$p_\alpha=\exp\frac{\left[U-E_\alpha-\sum_{k=1}^{r}P_k(x_k-x_{k\alpha})\right]}{kT}, \tag{8}$$

where the summation now goes from 1 to r (including the entropy term). We can also write:

$$p_\alpha=\exp\frac{[\psi-\psi_\alpha]}{kT} \tag{9}$$

where:

$$\psi_\alpha=E_\alpha-\sum_{k=1}^{r}P_k x_{k\alpha}. \tag{10}$$

This "microscopic free energy" ψ_α will be of interest to us subsequently.

The physical meaning of $\psi-\psi_\alpha$ is the minimum work required to bring about the state α. Hence Eq. (9) expresses the well-known principle of Boltzmann. Let us introduce the notation:

$$\delta x_k=x_{k\alpha}-x_k. \tag{11}$$

If we expand E_α as a function of the δx_k, we obtain

$$E_\alpha=\bar{E}_\alpha+\sum_{k=1}^{r}\left(\frac{\partial E_\alpha}{\partial x_k}\right)_0\delta x_k+\frac{1}{2}\sum_{k,\,l=1}^{r}\left(\frac{\partial^2 E_\alpha}{\partial x_k\partial x_l}\right)_0\delta x_k\delta x_l, \tag{12}$$

keeping second-order terms. Now $\bar{E}_\alpha=U$, $(\partial E_\alpha/\partial x_k)_0=P_k$; and we can define

$$\left(\frac{\partial^2 E_\alpha}{\partial x_k\partial x_l}\right)_0=u_{kl}=\frac{\partial^2 U}{\partial x_k\partial x_l}. \tag{13}$$

Then to this approximation we find

$$p_\alpha=c\exp\left\{\frac{-\frac{1}{2}\sum_{k,\,l=1}^{r}u_{kl}\delta x_k\delta x_l}{kT}\right\}, \tag{14}$$

where c is a normalization constant which is needed because Eq. (14) is only an approximation to Eq. (8).

In terms of this Gaussian distribution, one can immediately write down the fluctuations in which we are interested:

$$\langle\delta x_k\delta x_l\rangle_{\text{Av}}=\left\{\frac{\int(\delta x_k)(\delta x_l)p_\alpha d(\delta x_1)\cdots, d(\delta x_r)}{\int p_\alpha d(\delta x_1)\cdots, d(\delta x_r)}\right\}$$

$$=kTv_{kl}, \tag{15}$$

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[6] E. A. Guggenheim, J. Chem. Phys. 7, 103 (1939).

[a] S_α is the entropy one assigns to a system known to be in a state α of statistical weight w_α.

where the matrix $\|v_{kl}\|$ is the inverse of the matrix $\|u_{kl}\|$. These matrices have been called stiffness $\|u_{kl}\|$ and compliance $\|v_{kl}\|$ matrices.[5]

The smallness of kT compared to the internal energy of macroscopic systems assures us that the relative fluctuations are small, hence the microcanonical and canonical methods are essentially equivalent. Speaking more physically, the behavior of the sub-system is the same whether it is isolated from the rest by a real wall or isolated only in imagination.

This situation is different, however, at the so-called critical point where $\|u_{ik}\|$ is positive semidefinite ($\mathrm{Det}\|u_{ik}\|=0$) and where the matrix elements v_{ik} and hence the fluctuations become infinite.[5] Actually, the experimentally observed fluctuations become extremely high at the critical point, as manifested in the phenomenon of critical opalescence, for example. The fluctuations are, however, finite and our formalism must be improved, so as to provide a finite result.

The weak point in the above discussion, which is essentially the same as the standard discussion of fluctuations, is in the use of the canonical ensemble to represent the behavior of a sub-system of our whole system while idealizing the remainder by treating it as a reservoir. When the fluctuations are large, as in the vicinity of a critical point, the microcanonical and canonical ensembles no longer give the same results, and it is essential to treat the system as a whole in a proper manner. This will involve a modification of the usual canonical ensemble which will be carried out in the next section. At this stage, we merely need to point out that such a modification is necessitated by the large critical-point fluctuations which indicate a breakdown of the usual approach discussed above.

Before going on to examine the statistical problem in more detail, it seems convenient to simplify the definition of the critical point. As presented above, it appears as a result of the "co-operation" of all extensive variables $x_1, x_2, \cdots, x_r$. Instead, we can choose $P_1, P_2, \cdots, P_{r-1}, x_r$ as independent variables, and introduce the corresponding free energy

$$A(x_r)=u-\sum_{k=1}^{r-1}P_kx_k. \tag{16}$$

(A is a function of $P_1, P_2, \cdots, P_{r-1}$ as well as x_r, but it is the latter dependence which will interest us.) It can be shown[5] that a critical point may also be defined as follows:

$$\frac{\partial^2 A}{\partial x_r^2}=0,\quad \frac{\partial^3 A}{\partial x_r^3}=0,\quad \frac{\partial^4 A}{\partial x_r^4}>0. \tag{17}$$

The advantage of this formulation is that it refers explicitly to a single independent variable. Of course, this can be chosen to be any of the $x_1, x_2, \cdots, x_r$. The various formalisms arising are not identical, but lead to the same conclusions.

III. THE CELLULAR METHOD

We generalize the concept of a canonical ensemble by introducing what we call the cellular method. Instead of concentrating our attention on a sub-system and schematizing the rest into a "reservoir," we divide the whole system into cells which we treat on an equal footing. We choose these cells as identical in size and shape and arranged in a regular spatial array. If we are dealing with a fluid system, we can choose a simple cubic array of cubical cells. If we deal with a crystalline system, it will be natural to let our array have the symmetry of the crystal; the individual cells can then consist either of single unit cells of the crystal or of groups of contiguous unit cells. To avoid the necessity of introducing the reciprocal lattice, we shall work with a cubic array, but our considerations can easily be transcribed so as to apply to the general case.

The position of any cell is then specified by a vector k:

$$k=k_1j_1+k_2j_2+k_3j_3, \tag{18}$$

where k_1, k_2, k_3 are integers between 0 and $M-1$ if there are M^3 cells, and j_1, j_2, j_3 are the unit vectors defining the primitive translations of our array. (In the rest of the paper the symbols k, l, m, j_1, j_2, and j_3 designate vectors, whereas k_1, k_2, k_3, l_1, l_2, l_3, m_1, m_2, and m_3 are integers.)

In the previous section, we pointed out that if one works with the appropriate thermodynamic potential $A(x_r)$, the conditions for a critical point can be expressed in terms of the one variable x_r. We are now interested in considering states of our large system specified by the set of values x_{rk}, where k varies over all the M^3 cells; x_{rk} is the value of x_r in the cell k. (We take the variables $P_1, P_2, \cdots, P_{r-1}$ as fixed for our system.)

By applying an argument similar to that used in the preceding section, one can easily show that the probability of finding a state $\{x_{rk}\}$, is given by:

$$p=C\exp\left(-\frac{1}{2}\sum_{kl}a_{kl}z_kz_l\right), \tag{19}$$

where[b]

$$a_{kl}=\frac{1}{kT}\left(\frac{\partial^2 A}{\partial x_{rk}\partial x_{rl}}\right)_0=\frac{1}{kT}\left(\frac{\partial^2 A}{\partial z_k\partial z_l}\right)_0; \tag{20}$$

$$z_k=x_{rk}-\bar{x}_r. \tag{21}$$

In spite of the great formal similarity between Eq. (14) and Eq. (19), one must be very careful to distinguish between the two quadratic forms appearing in the exponential in these two equations. The first, Eq. (14), refers to a set of different thermodynamic variables $x_1\cdots, x_r$; the second, Eq. (19), refers to the set of values x_{rk} of one thermodynamic variable x_r in the different cells k of the whole system. Both quadratic

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[b] It is necessary to average over all of the "internal coordinates" of the system, e.g., thermal vibration coordinates; in other words, we preserve only the dependence on the set of variables z_k.

forms express the minimum work necessary to carry the system from its equilibrium state to one deviating from equilibrium.

We should point out an important restriction on the values of the z_k, the deviations of x_{rk} from its average value x_r; namely, we must have:

$$\sum_k z_k=0. \tag{22}$$

This expresses the fact that our whole system is closed, so there can be no net fluctuation in x_r if we sum over all cells.

The eigenvalues and eigenvectors of this form are of considerable interest, so we shall now determine them. This is simple, if we notice that the set of coefficients a_{kl} for fixed k, l varying over all cells, is just a permutation of the set $a_{k'l}$ for any other fixed k'. This expresses the fact that the interactions (as measured by a_{kl}) of any cell with its neighbors of all orders are independent of the particular cell considered. (We impose periodic boundary conditions on our whole system, so that the cells near the boundary "surfaces" need not be considered separately.)

The eigenvalues λ_m and eigenvectors ξ_{lm} must satisfy

$$\sum_l a_{kl}\xi_{lm}=\lambda_m\xi_{km}; \tag{23}$$

(k, m varying over all cells, i.e., $m=m_1j_1+m_2j_2+m_3j_3$, $m_i=0, 1, \cdots, M-1$). The solutions to Eq. (23) are:

$$\lambda_m=\sum_l a_{kl}\exp\left[\frac{2\pi i}{M}m\cdot(l-k)\right], \tag{24}$$

$$\xi_{lm}=\frac{1}{M^{\frac{3}{2}}}\exp\left[\frac{2\pi i}{M}l\cdot m\right], \tag{25}$$

where

$$\sum_k \xi_{km}\xi_{km'}{}^*=\delta(m-m'). \tag{26}$$

Since a_{kl} depends only on $l-k$, λ_m is actually independent of k as it must be.

The eigenvalues can be written in a simpler form if we note that it is sufficient to take only two distinct values of the a_{kl}:

$$\begin{array}{lll} a_{kk}=a_0;\quad a_0>0 & \text{(all } k\text{)}, & \\ a_{kl}=a_1 & (k, l \text{ nearest neighbors}), & (27) \\ a_{kl}=0 & \text{(otherwise).} & \end{array}$$

The first of these conditions states that all cells are equivalent. The second condition, nearest-neighbor "interactions" only, is not necessary for most of the following work but simplifies the form of the equations to some extent.

The eigenvalues are now:

$$\lambda_m=a_0+2a_1\sum_{i=1}^{3}\cos\frac{2\pi}{M}m_i;\quad (m=m_1j_1+m_2j_2+m_3j_3). \tag{28}$$

The eigenvector corresponding to $\lambda_0(\lambda_0=\lambda_{M(j_1+j_2+j_3)}=a_0+6a_1)$ is of especial significance. It is

$$\xi_0=\frac{1}{M^{\frac{3}{2}}}(1, 1, \cdots, 1).$$

This is the only eigenvector which does not involve phase differences between the different cells. Now, while the eigenvalues λ_m depend on the properties of the quadratic form of Eq. (19), the eigenvectors really furnish an appropriate and flexible coordinate system, as it were, for describing our physical system.

We may use the unique character of the eigenvector ξ_0 to suggest a characterization of those variables of our system which can be handled in a macroscopic discussion; namely, only variables which transform like ξ_0, i.e., which are the invariants of the translation group, can qualify as macrovariables, since all others involve unobservable phase differences as one goes from cell to cell.

The variables which satisfy this criterion are of two rather different kinds. In the first class, we have thermodynamic variables such as magnetic moment per unit volume, average particle density, etc. The additional characteristic feature of these variables is that their conjugate "forces" exist and, consequently, the values of these variables are subject to the control of the experimenter. In the second class are variables which might be called quasi-thermodynamic ones, such as the atomic coordinates in a crystal and the long-range order in alloys, etc. Here there are no conjugate forces, so the variables in question cannot be controlled freely. Nevertheless, they are of a macronature in the sense described above and, correspondingly, are subject to measurement—by their coherent x-ray scattering, for example.

The variables which do not behave like ξ_0 are perhaps typified by the thermal vibrations or phonons which essentially involve phase differences between cells and must always be averaged over in macroscopic treatments.

Let us finally apply our study of the eigenvalues to the case of the critical point. This is now redefined as the point where:

$$\frac{1}{2}\sum_{k,l}a_{kl}z_kz_l,$$

becomes positive semidefinite, i.e., one of its eigenvalues must vanish. It is not difficult to see that the eigenvalue which vanishes (the others remaining positive) is λ_0. Thus, at the critical point,

$$\lambda_0=a_0+6a_1=0. \tag{29}$$

This result is, of course, to be expected in the light of the above discussion, but it can be proved directly and, therefore, is an example in support of the arguments advanced.

In fact, we notice that if $a_0+6a_1=0$, all other λ_m are positive; but if $\lambda_m=0$, $m\neq 0$, then some $\lambda_m<0$, contradicting our requirement that the quadratic form be positive semidefinite. In the absence of correlations $a_1=0$ and Eq. (29) reduces to the previous definition of critical points.

IV. FLUCTUATIONS WITH CORRELATIONS

We can now turn to the calculations of the mean-square fluctuation in the value of x_r in cell k and the correlations of the fluctuations in different cells. We shall use the approach of the preceding section.

We have already written in Eq. (19) the expression for the probability of finding a state of the system characterized by a given set of values of the x_{rk}. It has also been pointed out that there is a restriction, Eq. (22), on the values of the set of variables z_k, because our system is closed. We now want to calculate

$$\langle z_k z_l\rangle_{\mathrm{Av}}=\frac{\displaystyle\int z_k z_l \exp\left[-\frac{1}{2}\sum_{k,\,l} a_{kl} z_k z_l\right] d\tau'}{\displaystyle\int \exp\left[-\frac{1}{2}\sum_{k,\,l} a_{kl} z_k z_l\right] d\tau'}, \tag{30}$$

where $d\tau'$ means that we integrate over the M^3-1 dimensional space of the z_k, subject to the restriction of Eq. (22).

In order to take into account this restriction in the simplest way, we go over to the coordinate system determined by the eigenvectors of the matrix $\|a_{kl}\|$. The calculation is given in the Appendix; we quote only the result here:

$$\langle z_k z_l\rangle_{\mathrm{Av}}=\frac{1}{M^3}\sum_p{}' \frac{\cos(2\pi/M)p\cdot(k-l)}{\lambda_p}. \tag{31}$$

The primed summation means that we sum over all p except $p=0$, i.e., that the eigenvalue λ_0 does not appear in the sum. This follows immediately from the restriction of Eq. (22), as is shown in the Appendix.

Let us first analyze this result for the case $k=l$. Introducing the explicit expressions for the eigenvalues, we have

$$\langle z_k{}^2\rangle_{\mathrm{Av}}=\frac{1}{M^3}\sum_{p_1,\,p_2,\,p_3}{}' \times\frac{1}{a_0+2a_1[\cos(2\pi/M)p_1+\cos(2\pi/M)p_2\cos(2\pi/M)p_3]}. \tag{32}$$

Now, far from the critical point, where the interactions between cells should not be important, this reduces to the conventional result. For, in this case, it follows from Eq. (29) that

$$a_0 \gg -6a_1, \tag{33}$$

and, therefore,

$$\lambda_p \simeq a_0, \tag{34}$$

$$\langle z_k{}^2\rangle_{\mathrm{Av}}\simeq\frac{1}{a_0}=\frac{kT}{(\partial^2 A/\partial x_r{}^2)_{P_1,\,\ldots,\,P_{r-1}}} \tag{35}$$

which is the result obtained by the method of Section II in this particular case (one variable).

Closer to the critical point, we can transform the sum in Eq. (32) into an integral, since M is as large as we please;

$$\langle z_k{}^2\rangle_{\mathrm{Av}}=\frac{1}{a_0}\frac{1}{(2\pi)^3}\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} \times\frac{dq_1dq_2dq_3}{\{1+(2a_1/a_0)[\cos q_1+\cos q_2+\cos q_3]\}}. \tag{36a}$$

Equation (36a) shows that the fluctuations become larger as we approach the critical point. At the critical point, where $(2a_1/a_0)=-\frac{1}{3}$, the integral still converges[c] and can even be evaluated exactly. Thus

$$\begin{aligned}\langle z_k{}^2\rangle_{\mathrm{Av}}&=\frac{1}{a_0}\frac{3}{\pi^3}\int_0^{\pi}\int_0^{\pi}\int_0^{\pi}\frac{dq_1dq_2dq_3}{3-(\cos q_1+\cos q_2+\cos q_3)}\\&=\frac{3}{a_0}(18+12\sqrt{2}-10\sqrt{3}-7(6)^{\frac{1}{2}})\left(\frac{2K_2}{\pi}\right)^2,\end{aligned} \tag{36b}$$

where K_2 is the complete elliptic integral of modulus $(2-\sqrt{3})(\sqrt{3}-\sqrt{2})$. Numerically:

$$\langle z_k{}^2\rangle_{\mathrm{Av}}=1.5164/a_0, \tag{36c}$$

at the critical point.

Let us now analyze the physical meaning of our results. In the first place we know that at the critical point $a_0=-6a_1\neq 0$. Since thermodynamics assures us that $a_0>0$, it follows that $a_1<0$ at and near the critical point. This means that a fluctuation in any cell increases the probability of a fluctuation of like sign in the neighboring cells. This is most readily seen from Eq. (40) below.

Secondly, we see that the fluctuations are kept finite by the physical requirement that the entire system be closed with respect to the thermodynamic variable x_r whose fluctuations we are considering. This entered our formalism in the restriction of Eq. (22) which automatically led to the omission of the term in λ_0 from the sum of Eq. (32). Thus the convergence of the integral in Eq. (36b) and the closure of our whole system lead to finite critical fluctuations.

Considering now the case $k\neq l$, i.e., the correlation of the fluctuations in different cells, we may make several remarks. In the first place, it is clear that, in the limit of vanishing interaction between cells, all $\langle z_k z_l\rangle_{\mathrm{Av}}$ are

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[c] The proof of convergence and the more difficult evaluation of the integral are due to G. N. Watson, Quart. J. Math. (Oxford) **10**, 266 (1939).

We should like to express our sincere thanks to Dr. Elliott Montroll for informing us of this reference.

zero ($k \neq l$). For, in this case, $\lambda_p = a_0$ and the phase factors cancel out.[d] Second, as $|k-l|$ increases the cancellation between successive terms increases and $\langle z_k z_l \rangle_{\text{Av}}$ becomes small.

This point can be brought out more clearly by another method which we now discuss. This method is of interest in itself and it establishes the connection between our work and that of Ornstein and Zernike[2] (see Section V). The essential point is to derive an equation relating the correlation coefficient of the fluctuations in different cells to the basic coefficients a_{kl} which are derivatives of the free energy and thus express the forces within our system.

The correlation coefficient g_{kl} is defined[7] by

$$g_{kl} = \frac{\langle z_k z_l \rangle_{\text{Av}}}{(\langle z_k^2 \rangle_{\text{Av}} \langle z_l^2 \rangle_{\text{Av}})^{\frac{1}{2}}} \tag{37}$$

Instead of using the expressions given above for these quantities, it is more convenient to evaluate them in terms of the minors of the determinant of $\|a_{kl}\|$. Let A be the determinant of $\|a_{kl}\|$ and A_{kl} be the co-factor (with its appropriate sign) of a_{kl} in A. Then[8]

$$\langle z_k z_l \rangle_{\text{Av}} = \frac{\displaystyle\int z_k z_l \exp\left[-\frac{1}{2}\sum_{k,l} a_{kl} z_k z_l\right] d\tau}{\displaystyle\int \exp\left[-\frac{1}{2}\sum_{k,l} a_{kl} z_k z_l\right] d\tau} = \frac{A_{kl}}{A}. \tag{38}$$

Since $A_{kk} = A_{ll}$ for all k, l as a result of the properties of $\|a_{kl}\|$, we have

$$g_{kl} = A_{kl}/A_{ll}. \tag{39}$$

Let us define

$$f_{kl} = -a_{kl}/a_{kk}. \tag{40}$$

The quantity f_{kl} is the average of z_k when $z_l = 1$ and all other variables are zero (linear regression coefficient).[7] We see that f_{kl} is a direct index of the "energetic" interaction between cells k and l, and vanishes under our assumptions unless k and l are nearest neighbors. Using Eqs. (39) and (40), one can easily show[e] that

$$g_{kl} = f_{kl} + \sum_{m \neq k,l} f_{km} g_{ml}. \quad (k \neq l) \tag{41}$$

Equation (41) has a simple interpretation: it states that the correlation coefficient g_{kl} (which measures the statistical effect of cell l on cell k) is equal to the sum of two terms. The first is the direct interaction f_{kl}, present only for nearest neighbors; the second is the sum giving the effect g_{ml} of cell l on all other cells m which have a non-vanishing interaction f_{km} with cell k.

We need consider the set of Eqs. (41) only for some definite value of l, since the set g_{kl} for this l value is the same, except for permutation, as any other set g_{km}. Hence we shall fix l and, with this understanding, drop it from our notation. We then have, as our final result,

$$g_k = f_k + \sum_{m \neq k} f_{km} g_m. \tag{42}$$

V. DISCUSSION

In this section, we shall point out the connections between the theory presented in this paper and the earlier work done on this problem, particularly with respect to the theory of critical opalescence.

It was shown in Section II that the customary statistical treatment of fluctuations leads to infinite critical-point fluctuations. The physical reason for this was that the minimum work necessary to produce such a fluctuation vanishes at the critical point in the usual approximation. It is clear from the nature of the problem that any additional contribution to the work, usually neglected, will limit the fluctuations to finite values at the critical point. A number of theories have been advanced which have this result, and it is our purpose to point out the nature of the additional term in each case and to discuss the interrelations of these theories in the light of our own.

In the first place, it should be said that virtually all previous work on the subject has been concerned with the ordinary gas-liquid critical point of a pure substance or with the critical mixing point of a binary mixture of liquids. Our theory has been set up in such a manner as to be applicable to λ-points as well as critical points in the ordinary sense. For this reason, we shall be interested in discussing only those other theories which are capable, in principle, of such generalization. Hence we have not considered the mechanism proposed by Yvon,[4] who has pointed out that infinite fluctuations are avoided if one considers the effect of gravity. Briefly, near the ordinary critical point the compressibility is large and the gravitational field of the earth gives rise to a non-uniformity of density, "thickening" the gas-liquid interface into a layer. Although this effect undoubtedly exists, it seems to be special, insofar as it cannot be of importance in λ-points in solids, for example.

The original suggestion for obtaining finite critical-point fluctuations is due to Smoluchowski.[1] His proposal was to continue the expansion of the free energy to the next non-vanishing term (quartic term), at the critical point (see Eq. (12)). This insures a non-zero

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[d] The cancellation is not complete and $\langle z_k z_l \rangle_{\text{Av}} = (-1/a_0)(1/M^3)$ because we do not sum over the eigenvalue λ_0. This term is, of course, negligible for large M.

[7] H. Cramér, *Mathematical Methods of Statistics* (Princeton University Press, Princeton, 1946).

[8] The restriction of Eq. (22) has not been imposed here. It can be shown [M. J. Klein, Ph.D. thesis in physics, M.I.T. (1948)] that this restriction plays no important role in these considerations.

[e] For:

$$\sum_{m \neq k,l} f_{km} g_{ml} = -\sum_{m \neq k,l} \frac{a_{km} A_{ml}}{a_{kk} A_{ll}}$$

$$= -\frac{1}{a_{kk} A_{ll}} \left[\sum_m a_{km} A_{ml} - a_{kk} A_{kl} - a_{kl} A_{ll}\right]$$

$$= -\frac{A \delta_{kl}}{a_{kk} A_{ll}} + g_{kl} - f_{kl} = g_{kl} - f_{kl} \quad \text{as} \quad k \neq l.$$

minimum work and gives finite results. This method cannot be considered satisfactory because it is based on the consideration of one volume element with the remainder treated as a reservoir, and when the fluctuations are large (though finite) the difference of the states of neighboring volume elements and their correlations must be taken into account.

The first major attempt to give a more adequate treatment of critical-point fluctuations considering correlations is due to Ornstein and Zernike.[2] We have already mentioned that their papers served as a stimulus to the present work. Their chief contributions were the introduction of the idea of correlations and the development of an integral equation for determining the correlation coefficient in terms of the intermolecular forces. This integral equation, which they derived by other methods, follows from our Eq. (42) if one redefines f_k and g_k by dividing by the volume of one cell. Going over to the continuum, one then obtains

$$g(\mathbf{r})=f(\mathbf{r})+\int f(\mathbf{r}'-\mathbf{r})g(\mathbf{r}')d\mathbf{r}'. \tag{43}$$

They have shown that if $f(r)$ is a short-range isotropic function, one can transform Eq. (43) into a differential equation whose asymptotic solution is

$$g(r)\sim e^{-\kappa r}/r, \tag{44}$$

where

$$\kappa^2=\frac{2(1-F)}{E};\quad F=\int f(r)d\tau;\quad E=\frac{1}{3}\int r^2 f(r)d\tau. \tag{45}$$

This solution is instructive, since it shows that for $\kappa>0$ (above the critical point) $g(r)$, the correlation coefficient of the fluctuations, drops to zero exponentially as the distance increases. At the critical point where $\kappa=0$,[f] $g(r)\sim 1/r$, a long-range function, so that fluctuations make their influence felt over long distances.

Having indicated how the equations of Ornstein and Zernike follow from our work, under suitable approximations, we now turn to another important development, the theory of Rocard.[3] Rocard's starting point is the observation that the thermodynamic variable in question, our x_r (the density in his case), is actually a function of position in the system, due to the fact that fluctuations occur locally rather than over the system as a whole. Although this remark is in agreement with the theories given here and by Ornstein and Zernike, Rocard's method of working out its consequences is different. Since Rocard himself has stressed this difference, it is of interest that his equations also can be made to follow from our theory if certain approximations are made.

Rocard's method is to consider the modification in the effective "force," P_r (pressure in his case), due to the spatial variation of x_r. P_r is modified by an additive term proportional to the Laplacian of x_r, thus giving rise to a corresponding term in the minimum work. This latter term does not vanish at the critical point and, thus, finite fluctuations are obtained.

We shall now show how our theory can be made to give results of this form. The effective force P_{rk} (or simply P_k) in the cell k is given by

$$P_k=\frac{\partial}{\partial z_k}\left[\frac{1}{2}\sum_{k,\,l}a_{kl}z_k z_l\right]=\sum_l a_{kl}z_l, \tag{46}$$

since the quadratic form expresses the minimum work. Applying the nearest-neighbor approximation of Eq. (27) we obtain:

$$\begin{aligned}P_k=a_0z_k+a_1(z_{k+j_1}+z_{k-j_1}+z_{k+j_2}+z_{k-j_2}+z_{k+j_3}\\+z_{k-j_3})\simeq(a_0+6a_1)z(k)+a_1\nabla^2 z(k),\end{aligned} \tag{47}$$

where we have gone over to a continuous position vector k and we have approximated

$$z(k+j_1)+z(k-j_1)-2z(k)\text{ by }\frac{\partial^2 z(k)}{\partial x^2},\text{ etc.}$$

It is seen that Eq. (47) is essentially equivalent to Rocard's assumptions, since the first term gives rise to a vanishing work at the critical point where $a_0+6a_1=0$, and the second term is Rocard's additional term. It is worth pointing out that Rocard's approach does not take full account of the correlation effects since, after setting up an equivalent to Eq. (47), he considers only one cell and not its interactions with its neighbors.

The last theory to be considered is that of Yvon.[4] His fundamental approach is essentially similar to ours, but his method of treating the system as a whole is based on a rather different viewpoint. Our theory is based on treating the system as an assembly of interacting cells whose basic properties we do not compute but in terms of which we work. Yvon attempts a completely molecular description of the system (liquid in his case); he works in terms of an Ursell development but, due to the complexity of his method, he is able to handle only the terms corresponding to "binary clusters" of molecules when it comes to making explicit calculations. Since there is no reason to believe that this limitation is plausible in the neighborhood of the critical point, we do not think this method is fruitful in practice although it is probably correct in principle.

Let us conclude by comparing the predictions of the various theories discussed so far as critical opalescence[9–11] is concerned. We have not made here an explicit calculation of our own, but we have indicated that both the Ornstein-Zernike and the Rocard theories are, in a sense, special cases of ours.

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[f] $F=\sum_l f_{kl}=-6a_1/a_0$; hence $F=1$ at the critical point and $\kappa=0$.

[9] H. A. Stuart and H. G. Trieschmann, "Lichtzerstreuung," Hand und Jahrbuch d. Chem. Phys. Bd. 8, Abschn. II (Leipzig, 1936).

[10] J. Cabannes and Y. Rocard, *La Diffusion Moléculaire de la Lumière* (Les Presses Universitaires de France, Paris, 1929).

[11] G. Oster, Chem. Rev. **43**, 319 (1948).

Our interest is only in the dependence on wave-length and the angular distribution.

The Smoluchowski theory predicts

$$I/I_0 \propto 1/\lambda^4(1+\cos^2\theta)\beta, \tag{48a}$$

$$I/I_0 \propto 1/\lambda^4(1+\cos^2\theta)(\gamma)^{\frac{1}{2}}. \tag{48b}$$

Here I/I_0 is the ratio of scattered to incident intensity of light of wave-length λ observed in the direction θ; β is the compressibility,

$$\beta = -1/V(\partial V/\partial P)_T,$$

and $\gamma = \partial^3 V/\partial P^3$. The expression (48a) is valid away from the critical point, and (48b) at the critical point, in this theory.

Ornstein and Zernike's theory predicts

$$\frac{I}{I_0} \propto \frac{1}{\lambda^4}(1+\cos^2\theta)\frac{1}{\{1/\beta + d^2[\sin(\theta/2)/\lambda]^2\}}. \tag{49}$$

The constant d^2 is a measure of the radius of the intermolecular forces and is proportional to E defined in Eq. (45). The additional term in the denominator arises from the correlation of fluctuations in different volume elements giving rise to a $1/\lambda^2$ dependence and an enhancement of the forward scattering at the critical point. The result is not quite complete as it stands, since it makes I/I_0 infinite for $\theta=0$ at the critical point. Placzek[12] has shown that taking the finite volume of the scattering medium into account introduces a factor preserving the finiteness without modifying the result for experimentally realizable situations.

Rocard's theory predicts

$$\frac{I}{I_0} \propto \frac{1}{\lambda^4}(1+\cos^2\theta)\frac{1}{[(1/\beta)+c]}, \tag{50}$$

where c is a constant arising from the additional term in the pressure ($\propto \nabla^2\rho$).

The predictions of the Ornstein-Zernike and Rocard theories differ in two ways: the wave-length dependence, which becomes $1/\lambda^2$ at the critical point in the former theory, and the angular distribution, which is preferentially forward at the critical point in this theory. The two effects must go together here, as can be seen from the derivation of Eq. (49). (The theory of Yvon gives a wave-length dependence $\sim A\lambda^{-4} - B\lambda^{-6}$ where A, B are positive. We discuss this no further for reasons given above.)

Experimental work on critical opalescence has not settled the question in any clear fashion. The results of Andant[13] and Battacharya[14] show a change in wave-length dependence in the immediate vicinity of the critical point. Both find a dependence on $1/\lambda^2$ at the critical point and Andant has studied the change in exponent in (λ^{-n}) quite carefully. On the other hand, Rousset,[15] working with fluid mixtures (for which the theoretical predictions are essentially the same), finds no such definite results. For several types of fluids, the λ^{-4}-law and the angular symmetry (forward and backward) are preserved up to the critical point. In other cases, the exponent n decreases to a value of about 3 and, at the same time, an asymmetry between forward and backward scattering appears.

Summing up, it seems safe to say that there are experimental indications that the correlation effects are real and observable, although not in all cases.

APPENDIX

We wish to evaluate

$$\langle z_k z_l\rangle_{\text{Av}} = \frac{\int z_k z_l \exp\left[-\frac{1}{2}\sum_{k,l} a_{kl}z_k z_l\right]d\tau'}{\int \exp\left[-\frac{1}{2}\sum_{k,l} a_{kl}z_k z_l\right]d\tau'}. \tag{A1}$$

Let us introduce the (real) eigenvectors of $\|a_{kl}\|$:

$$\eta_{kl} = \left(\frac{2}{M^3}\right)^{\frac{1}{2}} \cos\left(\frac{2\pi}{M}k\cdot l + \frac{\pi}{2}\frac{l_1+l_2+l_3}{3M}\right); \quad l \neq 0. \tag{A2}$$

$$\eta_{k0} = \left(\frac{1}{M^3}\right)^{\frac{1}{2}}.$$

The eigenvalues are given in Eq. (24). We use real eigenvectors to avoid complex integration.

Let

$$z_k = \sum_l \eta_{kl} y_l; \quad y_l = \sum_k \eta_{lk}^{-1} z_k = \sum_k \eta_{kl} z_k; \tag{A3}$$

(since $\|\eta_{kl}\|$ is orthogonal).

The restriction of Eq. (22) is now simple:

$$\sum_k z_k = \sum_{k,l} \eta_{kl} y_l = \sum_l y_l \sum_k \eta_{kl} = M^{3/2} y_0 = 0. \tag{A4}$$

Hence, all we need to do to observe the restriction is to set $y_0=0$ and drop this variable.

$$\sum_{k,l} a_{kl} z_k z_l = \sum_k \lambda_k y_k^2. \tag{A5}$$

$$\langle z_k z_l\rangle_{\text{Av}} = \frac{\sum_{m,n} \eta_{km}\eta_{ln} \int y_m y_n \exp\left[-\frac{1}{2}\sum_k{}' \lambda_k y_k^2\right]d\tau'}{\int \exp\left[-\frac{1}{2}\sum_k{}' \lambda_k y_k^2\right]d\tau'}, \tag{A6}$$

$$\langle z_k z_l\rangle_{\text{Av}} = \frac{\sum_m \eta_{km}\eta_{lm} \int y_m^2 \exp\left[-\frac{1}{2}\sum_k{}' \lambda_k y_k^2\right]d\tau'}{\int \exp\left[-\frac{1}{2}\sum_k{}' \lambda_k y_k^2\right]d\tau'}. \tag{A7}$$

The integrals are now simple and we obtain:[7]

$$\langle z_k z_l\rangle = \sum_m{}' \frac{\eta_{km}\eta_{lm}}{\lambda_m}, \tag{A8}$$

Let us put this expression into a simple explicit form by introducing the values of the η_{km} from Eq. (A2).

$$\langle z_k z_l\rangle_{\text{Av}} = \frac{2}{M^3}\sum_m{}' \frac{\cos[(2\pi/M)k\cdot m + (\pi/2)(m_1+m_2+m_3/3M)]}{\lambda_m}$$
$$\times \cos[(2\pi/M)l\cdot m + (\pi/2)(m_1+m_2+m_3/3M)]. \tag{A9}$$

Expanding the cosines and making use of the fact that $\lambda_m = \lambda_{M(j_1+j_2+j_3)-m}$, we obtain

$$\langle z_k z_l\rangle_{\text{Av}} = \frac{1}{M^3}\sum_m{}' \frac{\cos(2\pi/M)(k-l)\cdot m}{\lambda_m}, \tag{A10}$$

which is the result given in the text, Eq. (31).

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[12] G. Placzek, Physik Zeits. 31, 1052 (1930).

[13] A. Andant, J. de phys. et rad. 5, 193 (1924).

[14] D. K. Battacharya, Proc. Ind. Assoc. Cultiv. Sci. 8, 277 (1923).

[15] A. Rousset, Ann. de physique 5, 5 (1936).