Conference summary and conclusions

Conference summary and conclusions

B Widom

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853, USA

The organizers of this conference asked me to listen to a dozen plenary lectures, to attend eighty-four symposium talks, including those being given in three different places simultaneously, to absorb the contents of three hundred posters, to summarize all this for you, to give you my assessment of the present state of the physics of liquids, and to predict future developments—for which I have forty minutes. The only solution I was able to find to this problem was to choose three or four of the many important themes represented here, and for each of them to give a little history and background, to mention some related problems of current interest that may not have been discussed here, and to point to some likely future developments.

When I was a student it was accepted as a theorem that, 'There can be no theory of liquids.' At Sunday night's roundtable on 'Teaching Liquids' Professor Anisimov quoted no lesser authorities than Landau and Lifshitz as having made a similar remark: 'Unlike solids and gases, liquids do not allow a general calculation of their thermodynamic quantities or even their temperature dependence' [1].

The reason for that pessimism is contained in the phase diagram in figure 1. There we see the critical point at the terminus of the liquid–gas equilibrium line. It was recognized by Andrews and van der Waals that the existence of such a critical point implies continuity of the liquid and gaseous states: one can go continuously from a liquid to its coexisting vapour (dashed curve). There being then no fundamental distinction between a liquid and a gas, it seemed that one should be able to base a theory of liquids on that of an imperfect gas—from the virial expansion, for example. Heroic, and at first promising, attempts were made [2], but these, while fruitful in other ways, failed as a theory of liquids.

We also see in figure 1 the triple point, where a dense liquid is in equilibrium with a solid (and also with a gas). There, the liquid and solid are very similar: their densities differ usually by less than 10%; the heat of fusion is much less than the heats of vaporization, so the liquid and solid are closer to each other in their energy and entropy than either is to the gas; and x-ray scattering shows the liquid to have local crystallinity (although not the long-range crystallinity that gives the solid its rigidity), and thus, locally, to have a solid-like structure, very different from the nearly random structure of a gas. It might seem, then, that a liquid could be successfully treated as a solid with defects. But as Jean-Pierre Hansen also reminded us at Sunday night's roundtable discussion, a liquid is something different from a defective solid.
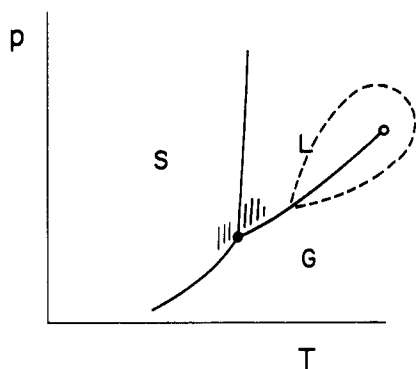
Figure 1. Pressure–temperature phase diagram of a simple substance, showing the liquid–vapour critical point and a continuous path around it connecting coexisting liquid and gas, and the neighbourhood of the solid–liquid–gas triple point.

If all we know about are gases and solids, and if a liquid is neither, then, it would seem, we are in trouble. I refer you now to the brilliant essay Rowlinson wrote as an introduction to his edition of van der Waals's thesis, in which he traces the evolution of van der Waals's original ideas on the different rôles played by the repulsive and attractive components of the intermolecular forces [3]. It ultimately became clear that the structure of a liquid is determined primarily by the strong, short-ranged repulsion between molecules, which can even be successfully modelled as that between hard spheres, and that the attractive forces can then be treated in mean-field approximation. This idea, suitably extended and elaborated, evolved into the modern theories of liquids, such as that of Barker and Henderson [4], and culminating in that of Weeks, Chandler and Andersen [5]. Now, for nearly twenty years, we have indeed had a realistic, quantitatively reliable theory of simple liquids.

Even so, for ten years or more, 'liquid' in liquid-state physics meant liquid argon. Yet now, as was already mentioned by Professors Bratos and Thoulouze in our opening session, and as has been abundantly demonstrated throughout this conference, we fearlessly study liquids of complex molecules (amphiphiles, polymers, colloids), forming complex structures (liquid crystals, micellar and bicontinuous microemulsions, and the wonderful structures Tom Witten showed us [PL1]), often leading to spatial or temporal instabilities and to pattern formation (Newell [PL2]), and to structures on intermediate ('mesoscopic') length scales, say 100–10 000 Å. (Here I am a little less generous than Lekkerkerker [PL4] and Charvolin [PL11], who had this range starting at about 10 Å.)

These are not new problems; colloids, for example, have been a subject of classical physical chemistry since the nineteenth century. What has happened to make such complexities now amenable to quantitative study and thus respectable parts of physics? Clearly, it was the invention of new tools and techniques, both theoretical and experimental. Prominent among these developments was the advent of high-speed digital computing, which, on the theoretical side, made previously impossibly difficult calculations easy; and also led to a major new industry, that of computer simulation, occupying a place intermediate, in a sense, between theory and experiment, and of which we saw much at this conference. Among the earliest applications of computer simulation to liquids was the pioneering work of Alder and Wainwright [6] and of Wood

and Jacobson [7], determining the equation of state of the fluid of hard spheres and discovering the hard-sphere fluid–solid phase transition. That was the key that unlocked the door that had for so long remained closed after van der Waals, in the developments I described earlier. Breakthroughs on the experimental side are exemplified by Israelachvili's surface forces apparatus [PL12], allowing measurement of intermolecular forces and structure with a directness and precision that were earlier unimaginable.

Now I shall say a little about each of a selected few of the major themes of this conference, as I promised; and I shall do so at a level that will not require you to think very hard, which you will find to be a welcome relief from the intellectual rigours of the past five days.

Polymers

Here I shall point to two further problems that I believe will receive increasing attention in the near future.

Kremer [SY 7-1] and others have recalled for us the reptation mechanism that de Gennes proposed for polymer diffusion, which is postulated to occur by the diffusion of stored length along the chain contour, and they reminded us that a consequence of such a mechanism is that the diffusion coefficient D would be inversely proportional to the square of the degree of polymerization N,

$$D \sim 1/N^2. \tag{1}$$

I wish here to point out an important application of the reptation idea to the drift and diffusion of a charged polymer chain (for example, DNA, with its negatively charged, ionized phosphate groups) in a gel [8], under the influence of an applied electric field E.

One finds that the drift velocity V scales with $x = \sqrt{N}E$; i.e., that V is a power of $\sqrt{N}$ or of E, times some scaling function of x alone. Specifically,

$$V = E^3 H(x^2) \tag{2}$$

where the scaling function H has the properties

$$H(x^2) \sim 1/x^2 \qquad (x \to 0) \tag{3}$$

$$\infty > H(\infty) > 0. \tag{4}$$

From (2) and (3) we see that as E vanishes at fixed N we have $V \sim E/N$. But the total force exerted by the field E on the chain is proportional to NE, so by the Nernst–Einstein relation the diffusion coefficient varies with N as $V/NE \sim D/kT \sim 1/N^2$, so that (1) is recovered. But now from (2) and (4) we find the opposite limit, that in which $N \to \infty$ at fixed E, where we see

$$V_{N=\infty} \sim E^3 \tag{5}$$

which is independent of N. This independence of N at large N means that we have lost molecular-weight discrimination. That is a serious problem in the gel electrophoresis of DNA, and is what motivated the invention of the alternating-field methods [9].

Another problem of current interest is that of the coupling of the orientation of a polymer chain, or that of links in the chain, to a composition gradient. I refer to recent work of Carton and Leibler [10] in Paris and of Szleifer [11] at Cornell. Imagine, as in figure 2, the profile of a spatially varying composition ϕ, with z the spatial co-ordinate, and imagine orientable objects interacting with ϕ. These objects may have dipolar
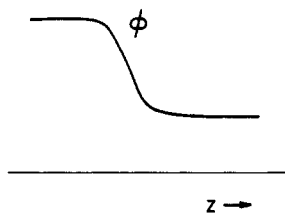
Figure 2. Composition ϕ varying with spatial coordinate z.
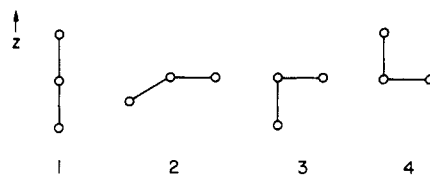
Figure 3. Four different configurations of two successive links of a connected polymer chain.

symmetry, ↑ , or may have what we may call nematic symmetry, ↕ , which can distinguish north–south from east–west but cannot distinguish north from south or east from west. The orientation of objects of the first type couples to $d\phi/dz$, that of objects of the second type to $(d\phi/dz)^2$ and $d^2\phi/dz^2$.

We are interested in the case in which the objects are two or more successive links in a connected polymer chain. In figure 3, for example, we see four possible orientations of two successive links: both vertical (the z direction), both horizontal, one link vertically downward and one horizontal, and one link vertically upward and one horizontal; numbered 1–4, respectively. The first two have nematic symmetry with respect to the z direction (the direction of the gradient of ϕ), the last two dipolar symmetry.

In figure 4 we see the resulting profiles of concentration of the four different configurations. We see that 3 and 4 are positively and negatively adsorbed, respectively, in the high-gradient region, that 1 is negatively adsorbed on the high-ϕ side of the gradient and positively on the low-ϕ side, and vice versa for configuration 2. The latter two imply that vertical orientation is favoured on the low-ϕ side of the gradient and horizontal orientation on the high-ϕ side. The effects are subtle: the amplitudes of the variations in the profiles 1 and 2 are less than those in 3 and 4 by the factor $1/\sqrt{N}$. The qualitative results appear to be universal, and will no doubt be seen in diverse physical contexts in future studies.

Chemical reactions in liquids

Let me remind you of two of the nice stories Chandler told us [PL3].

We see in figure 5 the chair ↔ boat interconversion of cyclohexane and in figure 6 a qualitative representation of the experimental measurements of Jonas, according to which the rate of that chemical reaction increases with increasing pressure. Chandler showed us that the increase is not due to a lowering of the energy barrier between the two conformations—that, on the contrary, that barrier may even increase slightly with increasing pressure. Instead, the result is interpreted as that reaction's being in the inertial régime of the Kramers theory, where the pre-exponential factor or transmission coefficient κ is increasing with increasing strength of the coupling of the reacting molecule to its environment ('viscosity'), η, which itself increases with increasing pressure.

Chandler also showed us the intersecting-parabola picture of the Marcus theory of electron-transfer reactions, figure 7, with particular reference to the ferrous–ferric couple, in which an electron is transferred between two equivalent Fe^{+++} centres. The two parabolas represent the energy as a function of the reaction co-ordinate, with the
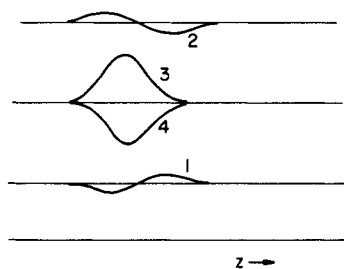
Figure 4. Profiles of concentration of the four different configurations in figure 3.
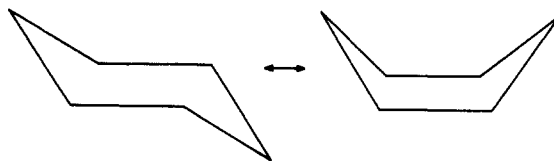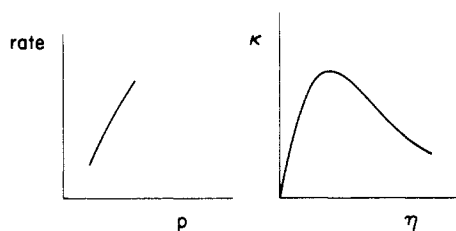

**Figure 5.** Chair–boat interconversion of cyclohexane.

solvent rearranging as the electron transfer proceeds and with the electronic state adjusting adiabatically to the solvent structure. Each parabola corresponds to the electron's being associated with one of the two Fe^{+++} centres as a Fe^{++} ion. The ground state is the lower of the two solid curves that results from the splitting that occurs where the parabolas intersect. We see that it is a double-minimum potential with a barrier. This picture has, on the whole, been the basis of a very successful theory of electron-transfer reactions. Although Chandler did not mention this, his own work [12] has provided a deep theoretical underpinning for the intersecting-parabola picture of Marcus.

These examples illustrate a noteworthy development in the theoretical study of chemical reaction kinetics, as seen in the reports of Chandler [PL3], Ciccotti [SY 3–6], and others at this conference: the combining of the statistical mechanics of irreversible processes with modern liquid-state theory to account for or predict the rates of chemical reactions in liquids.

Important advances on the experimental side were also reported at this conference, mostly new spectroscopic methods capable of resolving ultra-short times. Nelson's methods for studying liquid dynamics on femtosecond time scales [SY 1–3], for example, are adaptable to the study of solvent involvement in chemical reactions, and McPhail [SY 3–4] has shown how Raman spectroscopy may be used to follow reaction dynamics in liquids.


Figure 6. Experimentally measured pressure-dependence of rate of chair–boat interconversion of cyclohexane (Jonas) and the pre-exponential factor or transmission coefficient κ versus strength of coupling to the environment ('viscosity') η in Kramers theory.
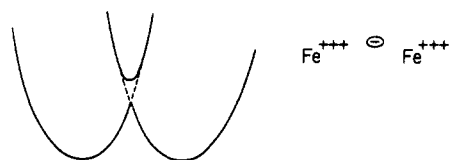
Figure 7. Intersecting-parabola picture of Marcus, and the ferrous–ferric electron-transfer reaction.
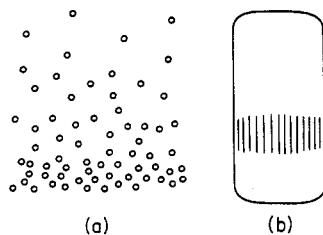
Figure 8. (a) Colloidal dispersion in a gravitational field, (b) maximum turbidity at an intermediate height.
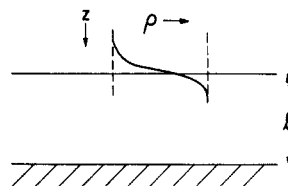
Figure 9. Film of thickness l on a substrate, and the density or composition profile, $\rho(z)$, of its upper surface.

The Brussels school of Prigogine, Nicolis *et al* pioneered in the study of the coupling of chemical reaction to diffusion and to hydrodynamics. In his report to this conference [PL7], Nicolis showed how the coupling of reaction to diffusion, in particular, can produce spatial and temporal self-organization and chaotic behaviour.

These are still early days in what is destined to be a rich new field at the interface between chemistry and liquid-state physics.

Colloids

Lekkerkerker [PL4] has introduced us to some of the fascinating properties of colloidal dispersions. He explained how the mesoscopic length scale is manifested in them, and how, with the appropriate change of scale, they may be studied by the traditional theoretical and experimental techniques of liquid-state physics.

He showed us (figure 8) a colloidal dispersion in a gravitational field, with the density increasing monotonically from top to bottom, but with maximum turbidity at an intermediate height. As an impressive example of how fundamental ideas from the physics of liquids may be carried over to the colloidal scale, he pointed out that the turbidity maximum could be understood from the maximum in the (osmotic) compressibility as a function of density that follows from the equation of state of the simple hard-sphere model even in Percus-Yevick approximation.

Lekkerkerker also showed us the Bragg diffraction of visible light by colloidal crystals, as the analog, on this mesoscopic length scale, of the familiar diffraction of x-rays by ordinary crystals: a beautiful example of a single principle's manifesting itself on two vastly different scales.

The Utrecht group of Vrij, Lekkerkerker, and their co-workers has pioneered in such studies, and has thought of extending them to the study of the interface between coexisting colloidal phases, a high-density ('liquid') phase and a low-density ('gas') phase. This would open up the possibility of determining the interfacial profile, and thus testing the capillary-wave and van der Waalsian intrinsic-structure pictures, on a more nearly macroscopic scale—the mesoscopic analogue of Als-Nielsen's x-ray studies of liquid surfaces [SY 10–1], or, if one could approach the critical point of that colloidal phase separation, the analogue of Webb's pioneering reflectivity measurements [13]. The report by Murray [SY 9–3] has shown us that one can already study the structure of colloidal fluid/crystal interfaces in this way. I believe we may look forward to important developments on these lines in the near future.

Intermediate length scales from van der Waals forces

We have seen that length scales intermediate between the molecular and the macroscopic characterize many of the structures that have been of interest in our conference. Such structures in the 100–10 000 Å range are often at least partly produced or stabilized by van der Waals forces. I wish here to point to an important unsolved problem in this connection, that of the structure of a three-phase line.

I refer first to an older problem, which will provide the background and a little history. In figure 9 we see a film of thickness l on a liquid or solid substrate, and we see the density or composition profile $\rho(z)$ of its upper surface. If we wish to determine the equilibrium l and $\rho(z)$—or, more generally, the variation of ρ through the whole film, including its upper and lower surfaces—we may find it in mean-field approximation as the solution of

$$\mu[\rho(r)] = \mu_0 + \int \phi(r, r') \left[\rho(r) - \rho(r')\right] d\tau \tag{6}$$

where $\mu[\rho(r)]$ is the analytic mean-field chemical potential $\mu(\rho)$ evaluated with the local $\rho(r)$ at a point r in the film or in the bounding phases near the film, μ_0 is the uniform chemical potential in the system, $d\tau$ is an element of volume at a variable point r' in the film and in the two phases that bound it, and $\phi(r, r')$ is the energy of interaction between molecules at r and r'.

Tarazona *et al* [14] have made the important observation that when (6) is solved by iteration, starting with a trial $\rho(z)$ on the right-hand side and then inverting the known function $\mu(\rho)$ to find the new $\rho(z)$, which is then the new trial function, etc., the solution converges quickly to the final equilibrium $\rho(z)$ at the two bounding surfaces of the film but only very slowly to the equilibrium thickness l. It is as though the solution by iteration were imitating the dynamics of film formation, in which the film's surface structures, determined mostly by short-range interactions, form quickly, but then, only very slowly, and impelled by longer ranged interactions, does the film thicken (or thin) to its equilibrium thickness.

The explanation of that behaviour is the great difference in the two length scales: the film surfaces are sharp—only a few molecular diameters in thickness—while the film itself may be hundreds or even thousands of times thicker. It is that great discrepancy of lengths that justifies de Gennes' calculation [15] of the equilibrium l: it is sufficient to take $\rho(z)$ equal to the bulk densities of the film and its two bounding phases, with discontinuities at the two film surfaces, take explicit account of the van der Waals interactions and of external forces such as gravity, and minimize the resulting free energy, which has become a function of l alone. The shorter length scales, including the microscopic structures of the interfaces, have disappeared from the problem.

With that background, I shall now state the question about the structure of a three-phase line. In figure 10(a) we see a substrate and two other phases meeting at it with contact angle θ. The line in which the three phases meet is perpendicular to the plane of the figure. Viewed on a macroscopic scale, the surfaces are sharp and the angle θ is well defined. On a molecular scale there are no interfaces and no θ; there is nothing there but molecules (as indicated schematically by the dots near the three-phase line in figure 10(a)), distributed with some density that may have more or less sharp gradients in it but is nevertheless diffuse, with no discontinuities. A question that has often arisen, and that has been elegantly treated by Joanny and de Gennes [16], is what, under the influence of van der Waals forces, and viewed on an intermediate length scale, is the
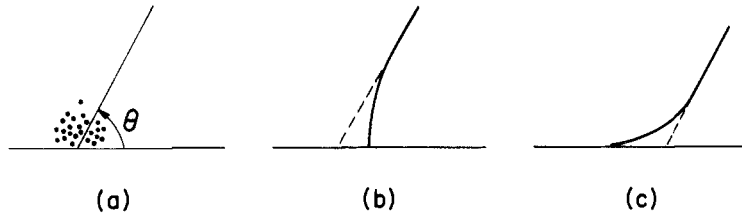
Figure 10. (a) Contact angle θ at a three-phase junction, and (b), (c) possible shapes of the interface viewed on an intermediate length scale.

shape of the boundary where the three phases meet? In their treatment, Joanny and de Gennes find a shape such as that in figure 10(b), while with more general assumptions, as L Léger has explained to me at this conference, Brochard [17] finds that of figure 10(c) to be also possible.

The question that I now raise is, can one give to pictures such as those in figures 10(b) and (c) the same kind of theoretical foundation as to that in figure 9, starting, for example, from (6)? Will the mechanism of Tarazona *et al* again operate to yield a sharp interface with a shape determined by a small number of geometrical parameters, the values of which are then found by minimizing an effective free energy? Far from the three-phase line the answer is surely yes; a problem arises only near the three-phase line, where the fluid–fluid interface comes close to the substrate. Do the intermediate-length-scale pictures of figures 10(b) and (c) remain meaningful in that neighbourhood? This is an outstanding unsolved problem.

Wetting transitions/microemulsions

Evans [PL5] and Telo da Gama [SY 10–4] have told us about that interesting interfacial phase transition, the transition between complete and incomplete wetting, and Langevin [SY 8–2] and Telo da Gama described an important manifestation of it in microemulsions.

Before we consider the wetting problem let us look at figure 11(a), which shows a middle microemulsion phase in equilibrium with excess oil and water phases, and figure 11(b), which shows the intensity of small-angle x-ray or neutron scattering from the microemulsion as a function of the wave vector. Kotlarchyk *et al* [18], for example, have
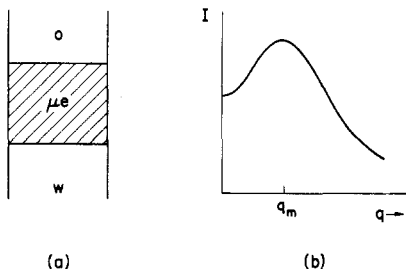
Figure 11. (a) A middle-phase microemulsion (μe) in equilibrium with excess oil (o) and water (w) phases; (b) intensity I of small-angle x-ray or neutron scattering from the microemulsion phase as a function of the wave vector q, with a characteristic maximum at some q_m.

obtained curves like that of figure 11(b) from small-angle neutron scattering, as has Charvolin, as he reported at this conference [PL11].

Teubner and Strey [19] have shown that such curves are fit by

$$I(q) = I(0)/(1 + aq^2 + bq^4) \tag{7}$$

with $a < 0$, $b > 0$, and they remark (with reference to Debye) that (7) implies by Fourier transformation a pair-correlation function of the form

$$G(r) = (1/r)\, e^{-r/\xi} \sin(2\pi r/d) \tag{8}$$

i.e., a sinusoid damped by an Ornstein–Zernike exponential. The wavelength d of the incipient periodicity, the exponential decay length ξ, and the length q_m^{-1} associated with the maximum in $I(q)$ at q_m, are different combinations of the two lengths $(-a)^{1/2}$ and $b^{1/4}$. While the term *microemulsion* is usually applied only to an isotropic phase, liquid-crystalline phases are prominent in microemulsion phase diagrams, often in close proximity to the microemulsion regions. That near crystallinity is prefigured in the wavelength d. We note also that the presence of a distinct maximum at $q = q_m > 0$ in figure 11(b) is connected with the sign $a < 0$; when $a > 0$ the maximum is at $q = 0$.

It is observed (for example, by Lang *et al* [20] and by Seeto *et al* [21]) that in solutions of oil and water that have been solubilized by small amphiphiles the amphiphile-rich middle phase (figure 11(a)) wets completely the interface between the oil and water phases, but, as both Langevin and Telo da Gama have told us here, that is not true when the amphiphile is a long surfactant and the middle phase a true microemulsion. Langevin has remarked further that in the former case the maximum in the scattering from the amphiphile-rich middle phase occurs at $q = 0$, while in the latter case, as we see in figure 11(b), it is at $q = q_m > 0$.

This has led to the question, are the incompleteness of the wetting by the microemulsion and the presence of a maximum at $q_m > 0$ in the scattering always associated with each other? If that were so, then these two criteria together could be taken to define a microemulsion and to distinguish it sharply from other homogeneous, isotropic oil–water–amphiphile phases. Interestingly, as Langevin and Telo da Gama remark, that association between incomplete wetting and $q_m > 0$ is indeed found by Gompper and Schick in their microemulsion model [22], where, in effect, a wetting transition occurs at $a = 0$.

It is thus of great interest that Langevin has now tested this proposition by experiment, and that she finds a wetting transition to occur while $q_m > 0$ ($a < 0$). That means that there is a range of thermodynamic states in which the surfactant-rich middle phase completely wets the interface between the oil and water phases and yet has a maximum at $q = q_m > 0$ in its scattering function. Thus, the two microemulsion criteria are not equivalent; an oil–water–amphiphile solution may be a microemulsion by one criterion and not the other. The lesson is that 'microemulsion' is probably best thought of as being roughly rather than sharply defined.

Critical phenomena

On the theoretical side of critical phenomena we have heard reports of advances such as that by Reatto on his hierarchical-reference-system theory, which essentially reproduces the results of the renormalization-group theory near the critical point while remaining accurate in the dense liquid far from the critical point [SY 1–5]. I wish here, though,

Critical Phenomena

Debye (posthumous)
      and Jacobsen (1968) – critical
      fluctuations by phase–
      contrast microscopy

M. Green

D. Beysens ξ = 1 μm   (IBA/H_2O
                                    $\Delta T = 10^{-3} K$)

F. Hensel – liquid metals –
      failure of corresponding states –
      state – dependence of forces
            width of coexistence curve
            slope of diameter
            amplitude of singularity
                  (Goldstein, Pitzer)

The future of liquid–state physics:

Figure 12. The last transparency.

mainly to recall two of the advances that have been reported on the experimental side. But first, a little history.

Peter Debye died in November 1966. His last preoccupation was with critical phenomena. A posthumous paper by him and his co-worker R T Jacobsen, entitled 'Direct Visual Observation of Concentration Fluctuations in a Critical Mixture', was submitted for publication in the *Journal of Chemical Physics* in August 1967 and appeared in that journal's first issue of 1968 [23]. That is the paper Beysens referred to in his talk [SY 1–6]. In it, Debye and Jacobsen suggested that one might actually see—with one's eye, so to speak—fluctuations of concentration near a critical point by phase-contrast microscopy, and they made the first attempts to do so.

The late statistical-mechanical theorist Melville Green once told me how important he believed that experiment to be and he argued eloquently that it be pursued. From the report by Beysens at this conference we now see that it has been, successfully. He showed us a picture of the fluctuations in isobutyric acid–water mixtures at 0.001 K from the critical point (near room temperature), where the coherence length of the composition fluctuations is about 1 μm. That was a magnificent technical achievement.

Hensel [PL6] has described his beautiful results on the properties of liquid metals near their critical points. He emphasized that, as a group, they fail to satisfy the principle of corresponding states, and he argued convincingly that that was a consequence of the strong thermodynamic-state dependence of the effective interatomic forces in a metal. He showed us that failure of the corresponding-states principle in the width of the coexistence curve, in the slope of the coexistence-curve diameter, and in the amplitude of the singularity in the diameter at the critical point.

In this connection I may mention the important theoretical work of Goldstein *et al*, both on the liquid metals [24] and on insulating fluids [25], accounting for such deviations from corresponding states as due to three-body forces in the insulating fluids and to their effective equivalents in the metals. An alternative and perhaps parallel explanation for the deviations in insulating fluids, based on Pitzer's early ideas about an acentric factor as a measure of the deviation of the pair potential from spherical symmetry, has been given by Singh and Pitzer [26].

You have all heard the story of Fermat's last theorem—how Fermat said he had a wonderful proof but that the margin of the book in which he was writing was too small to hold it. Similarly, I was going to predict for you, with great certainty, the future of liquid-state physics, but (figure 12), ...

Nevertheless, there is one very obvious and safe prediction that I may make: as we come to be more confident in our mastery of the new experimental and theoretical techniques, the study of biological structures and processes will become an ever more prominent part of our subject. Pioneering work such as that of Helfrich at the mesoscopic level of the cell membrane [Sy 8–1] has already shown that that will be so; and we heard from Newell [PL2] that we may even dare to try to understand the morphology of the saguaro cactus of Arizona.

It now remains for me only to thank the organizers of this conference, Professor Bratos, Professor Hansen, and Dr Leicknam, on my own behalf and that of the other speakers, and indeed on behalf of all six hundred participants, for having organized this memorable scientific event and given us the privilege of participating in it.

Acknowledgment

References

[1] Landau L D and Lifshitz E M 1958 *Statistical Physics (Course of Theoretical Physics 5)* (Transl. by E. Peierls and R F Peierls) (Oxford: Pergamon) ch VI, §66, p 198
[2] Mayer J E and Mayer M G 1940 *Statistical Mechanics* (New York: Wiley) ch14, pp 295 *et seq*
[3] Rowlinson J S 1988 Van der Waals and the physics of liquids (introductory essay) *J. D. van der Waals: On the Continuity of the Gaseous and Liquid States (Studies in Statistical Mechanics XIV)* ed J S Rowlinson (Amsterdam: North-Holland)
[4] Barker J A and Henderson D 1967 *J. Chem. Phys.* **47** 2856, 4714
[5] Weeks J D, Chandler D and Andersen H C 1971 *J. Chem. Phys.* **54** 5237
[6] Alder B J and Wainwright T E 1957 *J. Chem. Phys.* **27** 1208
[7] Wood W W and Jacobson J D 1957 *J. Chem. Phys.* **27** 1207
[8] Viovy J L 1988 *Europhys. Lett.* **7** 657
[9] Schwartz D C and Cantor C R 1984 *Cell* **37** 67
[10] Carton J-P and Leibler L 1990 *J. Physique* **51** 1683
[11] Szleifer I and Widom B 1989 *J. Chem. Phys.* **90** 7524
    Szleifer I 1990 *J. Chem. Phys.* **92** 6940
[12] Kuharski R A, Bader J S, Chandler D, Sprik M, Klein M L and Impey R W 1988 *J. Chem. Phys.* **89** 3248
[13] Gilmer G H, Gilmore W, Huang J and Webb W W 1965 *Phys. Rev. Lett.* **14** 491
[14] Tarazona P and Evans R 1983 *Mol. Phys.* **48** 799
    Tarazona P, Telo da Gama M M and Evans R 1983 *Mol. Phys.* **49** 283, 301
[15] de Gennes P G 1981 *J. Physique Lett.* **42** L377
[16] Joanny J F and de Gennes P G 1984 *C R Acad. Sci., Paris (II)* **299** 279
[17] Brochard F 1990 as reported in a seminar at the Collège de France (29 March)
[18] Kotlarchyk M, Chen H S, Huang J S and Kim M W 1984 *Phys. Rev. Lett.* **53** 941
[19] Teubner M and Strey R 1987 *J. Chem. Phys.* **87** 3195
[20] Lang J C, Lim P K and Widom B 1976 *J. Phys. Chem.* **80** 1719
[21] Seeto Y, Puig J E, Scriven L E and Davis H T 1983 *J. Colloid Interface Sci.* **96** 360

[22] Gompper G and Schick M 1990 *Phys. Rev. Lett.* **65** 1116
[23] Debye P and Jacobsen R T 1968 *J. Chem. Phys.* **48** 203
[24] Goldstein R E, Parola A and Smith A P 1989 *J. Chem. Phys.* **91** 1843
[25] Pestak M W, Goldstein R E, Chan M H W, de Bruyn J R, Balzarini D A and Ashcroft N W 1987 *Phys. Rev.* B **36** 599
[26] Singh R R and Pitzer K S 1990 *J. Chem. Phys.* **92** 3096