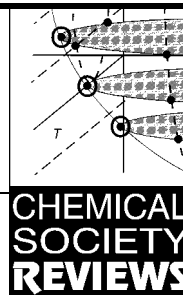# Liquid–liquid equilibria in polymer solutions at negative pressure

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Properties of liquids under tension (*i.e.* at negative pressure) are discussed together with methods of producing negative pressure. That established, the pressure dependence of liquid–liquid demixing in certain polymer–solvent solutions, including demixing at negative pressure is described.

Yes, we know that many physical quantities cannot be negative by their very nature. There is no negative volume, no negative mass, and early on, probably in High School, we learned that temperature, once properly expressed using the Kelvin (absolute) scale, has a natural zero. It is intrinsically positive. (At least this is true for systems in thermodynamic equilibrium; quantum systems forced far from equilibrium— LASERS, MASERS, *etc.*—, show population inversions which can be usefully described using the idea of negative temperature.[1] Ordinarily, however, with feet firmly on classical ground, one thinks of temperature as inherently positive.)

And what about pressure? In beginning science courses pressure is usually introduced during a discussion of introductory level kinetic-molecular theory. In this approach, pressure, which is rigorously and simply defined as applied force per unit area, is derived by calculating the net momentum change (force) per unit area which results when particles hit a wall, then rebound. At that level of analysis pressure is certainly a positive number. As particle density drops so does pressure, and this is satisfying. At zero number density (*i.e.* in a vacuum) one calculates zero pressure, thereby falling into the logical trap of (correctly) correlating pressure with number density for the example under discussion, then later on (incorrectly) generally identifying or implicitly defining pressure as proportional to number density. We know this line of thought is correct for gases in the low density limit (ideal gases), and by implication think it should work for liquids and solids. It is for reasons like this that most of us (even engineers, chemists, and physicists) think of pressure as always positive.

Actually this is wrong. Pressure is not necessarily positive. It is simply and rigorously defined as force per unit area—and force is a vectorial quantity. One can pull as well as push—we push on an object to pressurize it—by pulling we must depressurize. If we pull hard enough, we place the object under tension and it is useful to articulate this result as corresponding to *negative pressure*. One **cannot** do this for gases—they collapse—and that accounts for the logical trap of the last paragraph. One **can** do it for solids, they are strong enough to resist tensile forces tending to distortion, perhaps to very high tensions—at which point they fracture. Even so, although it is easy to pull on a solid (at least in one or another of its dimensions), it is harder to imagine similar experiments on fluids. The problem is how to support the fluid structure and prevent its fracture as tension increases, *i.e.* as pressure falls below zero.

Hard, but not impossible. In 1662, only 19 years after Torricelli's studies and the development of the barometer, Christian Huygens experimented with a long Toricelli-tube which he completely filled with mercury and then inverted. To his surprise, he found that almost 2 m of mercury could be supported in the tube, and this without increasing the outer pressure (provided the mercury was carefully degassed).[2] This is shown in Fig. 1 which compares two Torricelli tubes. Both have been filled with carefully degassed mercury, and then

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Attila Imre

inverted and placed in a dish of mercury. In high school science we learned that the atmosphere at sea level (on a nice day) supports a column of mercury 76 cm high [Fig. 1, left]. The space above the mercury in the lefthand tube, (a) is occupied by mercury vapor (the famous Torricellian vacuum), and $P_a = P_{torr} = P_{external} - \rho_{Hg}gh_{AB} = 0.5$ pa or 5×10^{-6} atm. Here ρ is the density of mercury, h_{AB} is the height of the column (76 cm when $P_{ext} = 1$ atm) and g is the gravitational constant. Huygens, however, carried out a slightly different experiment. He used carefully degassed mercury and most likely scrupulously cleaned and dried the glass tube prior to filling. This time [Fig. 1(b)] a much longer column of mercury was supported, but clearly only 76 cm can be supported by the external pressure. External pressure must be independent of the particular Torricelli tube we use to measure it. One can calculate the pressure at the top of tube (b) just as we did for tube (a). For example, should $h_{AC} = 152$ cm the pressure at the top of tube (b) must be $P_b = P_a - \rho_{Hg}gh_{AC} = -101\,325$ pa $= -1$ atm. The liquid inside the tube is under tension; it is at negative pressure. The liquid column is supported in part by the external pressure, and in part by the adhesive forces which exist between glass and mercury.
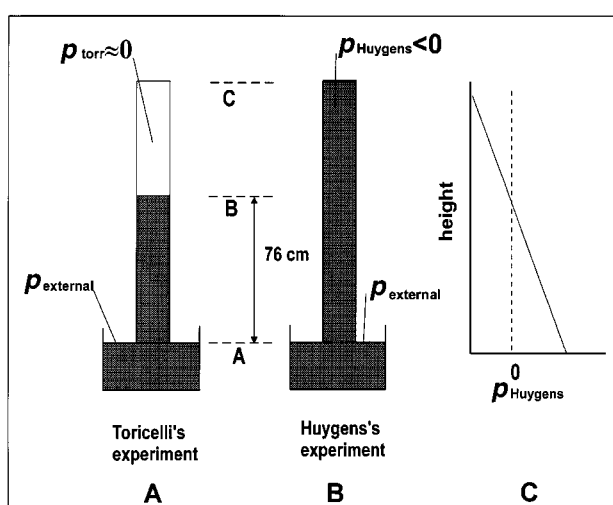

Fig. 1 The tension manometer described, a manometric device for generating negative pressure. (a) Torricellian barometer. A glass tube is filled with mercury then inverted and held in a dish of mercury as shown. In this manner the external barometric pressure (sea level in fair weather) is shown to be equivalent to a column of mercury 76 cm high. Minor corrections to account for variation in room temperature and capillary effects are required for high precision measurements. (b) The Huygens–Torricelli method for generating negative pressure. A glass tube is filled with mercury, inverted, and held in the dish as shown. At normal atmospheric conditions a column longer than 76 cm is supported, partly by the atmospheric pressure and partly by adhesive forces. This 'extra' column of length BC is a measure of the negative pressure or tension on the liquid. See text for further discussion. (c) Schematic representation of data from the modified Huygens–Torricelli manometer.

Almost two hundred years after Huygens the phenomenon shown in Fig. 1 was rediscovered by Donny (1848),[3] then a little later by Berthelot (1850),[4] although his experiment was a bit different—see below, and finally by Reynolds (1882),[5] all independently. In contrast to Huygens, who did not have a correct explanation for the effect he witnessed, these latter authors recognized the close connection between negative pressure and the adhesive forces between glass and liquid.[2] This was clearly articulated by Donny who wrote in 1846:[3]

'It is well known to manufacturers of barometers that, after the mercury has been boiled in one of these instruments, when the device is slowly turned upright without tapping, sometimes it happens that the mercury stays totally supported and only falls to its level relative to the weight of the atmosphere when the barometer is given a tap. However, no

one has tried to get at the cause of this phenomenon, nor has deduced its consequences. Only in the work of Laplace on capillary action do I find a passage where it seems the author has at least suspected a relation between this hanging of the mercury column and cohesion.'

Although one would think such multiple discoveries, buttressed by the prominence of at least three of the four personalities, would have brought this phenomenon forward to general recognition, such has not been the case. The concept of negative pressure has unfortunately remained obscure. In this paper we join others[2,6–8] in taking another small step in the direction of removing this obscurity. Our method will be to review some of our experimental observations on the pressure dependence of solubility of polymers, including solubility at negative pressure.

1 Introduction

1.1 Polymer phase equilibria and negative pressure

Many polymers dissolve in one or more well known solvents at all accessible temperatures (*i.e.* between the melting and critical points of the solvent) no matter how long the polymer chain. These are the so called "good solvents", and solutions of polymers in good solvents, while viscous and perhaps hard to handle, are nicely homogeneous [*e.g.* polystyrene (PS) in tetrahydrofuran (THF)]. Other solvents (*e.g.* PS–cyclohexane) only dissolve an infinite polymer chain between two well defined temperatures. Above and below those temperatures, depending on the concentration, we find precipitation followed by macroscopic phase separation into two fluid phases (one polymer rich, the other polymer poor—therefore this is a liquid–liquid phase transition). In other cases the precipitating phase may be a solid. Our present interest is in the liquid–liquid case. The solvents in this case are known as θ-solvents and the limiting temperatures (*i.e.* the precipitation temperatures of the infinite chain at its critical concentration which is found at or near the maximum in the solubility curve, *vide infra*) are the so-called θ-temperatures. Finally, there exists a class of poor solvents which are unable to dissolve long polymer chains (and in some cases unable to dissolve even short chains) at appreciable concentrations. A good example is the PS–acetone system. Acetone will dissolve short chain versions of polystyrene, but the limit (192 monomer units at the critical concentration) is low enough to destroy the utility of this solvent in all but special cases.

So far in this section we have not spoken of pressure. The effect of pressure on solubility is well known, especially in gas–liquid systems (Henry's Law), but also in liquid–liquid systems. In polymer solutions pressure markedly affects solubility and the thermodynamic and molecular origins of that observation are now beginning to be understood. For polymers in θ-solvents pressure usually increases solubility, *i.e.* the solution remains homogeneous to lower temperatures than before, and stays homogeneous to higher ones [Fig. 2(a), with the variable X equal or proportional to P]. Also poor solvents usually become better with the application of pressure, so the extent of the homogeneous part of the phase diagram increases with P [Fig. 2(b), X equal or proportional to P], as does the limiting chain length which can be dissolved by that particular solvent.[9]

Let's spend a bit more time discussing solutions in θ-solvents and poor solvents. Fig. (2a) and (b) show phase diagrams for such solutions in (ψ,T,X) space, [ψ = concentration (segment fraction), T = temperature, X a third variable of interest]. For the moment, consider a solution held at constant pressure (nominally 1 atm), and let X scale as a function of molecular mass (M_W). The standard Flory–Huggins theory of polymer thermodynamics suggests $X = M_W^{-1/2}$. In the figures X increases moving out from the page (M_W dropping as X increases), and as expected, the extent of the one phase homogeneous region expands with X. For the θ-solvent [Fig.

2(a)] the locus of upper and lower consolute temperatures (in first approximation the critical locus) yields upper and lower curves in the $(T,X)_{\psi cr}$ projection with $X = 0$ intercepts (i.e. infinite M_W) which define upper and lower θ-temperatures. In Fig. 2(a), however, the upper and lower curves are connected by a smoothing function (refer to the dotted line) extending into the hypothetical region $X < 0$. In Fig. 2(b), on the other hand, we are in the poor solvent limit and the upper and lower branches join at a hypercritical point where $X > 0$ (i.e. at a real M_W). In such an analysis one soon recognizes that the distinguishing difference between solutions in θ-solvents and poor solvents is a shift in the phase diagrams along the X coordinate [compare Fig. 2(a) and (b)]. In the poor solvent case the $(T,X)_{\psi cr}$

Ψ →

Fig. 2 Schematic cloud point curves of polymer solutions. Liquid–liquid demixing for mixtures showing upper and lower consolute branches. The two phase regions are shaded. (a) For θ-solvents with upper and lower θ-temperatures. Temperature, T, is plotted against segment fraction polymer, Ψ, in the plane of the paper. The third variable might be either the molecular mass parameter, $X = M_W^{-1/2}$, at some chosen pressure, or the pressure, P, at some chosen molecular mass. The curve drawn through the critical points and marked with heavy dots is further illustrated in Fig. 3. For the case $X = M_W^{-1/2}$ θ_U and θ_L correspond to the $(T, X = 0)$ intercept of the line of 'dots' and the large open circle represents the hypercritical molecular mass parameter, which has no physical meaning in this case, but is quite useful in the mathematical description of the phase diagram. See text for further discussion. (b) For poor solvent systems showing upper and lower consolute curves joining at a hypercritical point (marked with the large solid circle). Axes labeled as in Fig. 2(a). The curve drawn through the critical points (heavy dots) is plotted in the (T,X) and (T,P) projections in Fig. 3. See text for further discussion.

projection of the critical loci displays its extremum (hypercritical point) at real X, i.e. $X > 0$. Below that point, i.e. in the range ($0 < X < X_{hypercr}$), the system is collapsed into the hour glass configuration [see the darkest shading in Fig. 2(b)]. Solutions in θ-solvents, on the other hand, have their extrema at $X < 0$, i.e. at negative pressure in the $(T,\psi,X = P)_{M_W>0}$ projection (perhaps experimentally inaccessible), or negative $M_W^{-1/2}$ in the $(T,\psi,X = M_W^{-1/2})_{P>0}$ projection (definitely inaccessible).

So much for projections at constant pressure. Now consider solutions at constant M_W and set X equal to pressure. As $P = X$ increases moving out from the plane of the paper (Fig. 2) the solvent improves. In this state of affairs it should be possible to select solvent quality, pressure, temperature, and M_W such that the system of choice lies in the homogeneous region but not too far from either temperature or pressure induced phase transitions. From such a beginning one might induce precipitation by either raising or lowering the temperature, or by lowering the pressure. Of course in a poor solvent one could also induce precipitation by increasing M_W or by changing solvent quality, but these are variables we earlier agreed to hold steady. At any rate, one could argue that an even more judicious choice of solvent quality, T, and M_W could place a solution in the homogeneous region at $P \sim 0$, but such that further lowering the pressure (to negative values, placing the solution under tension) might induce precipitation. Of course this assumes that the equation of state describing the solution is well behaved and continuous across the boundary $P = 0$, and smoothly extends into the tensile region where $P < 0$. This is the kind of solution which we are going to focus on in the balance of this review.

The points made in the last few paragraphs are further illustrated in Fig. 3. Fig 3(a) is a $(P,T,X = M_W^{-1/2})_\psi$ constant concentration representation of the UCST/LCST demixing diagram. For $\psi = \psi_{crit}$ the diagram includes $(T,P)_{M_W,\psi crit}$ sections at two M_W values and $(T,X = M_W^{-1/2})_{P,\psi crit}$ sections at four pressures, including sections at both positive and negative pressures. The leftmost $(T,P)_{M_W,\psi crit}$ projection is at $X = M_W^{-1/2} = 0$ and therefore maps the pressure dependences of the upper and lower θ-temperatures. Fig. 3(b) shows two $(P,T)_{\psi crit,M_W}$ sections, one (marked B) in a better solvent where the hypercritical demixing point is found at negative pressure, the other (marked A) in a poorer solvent where it is found at $P > 0$. Later in this paper we will show an example of this type. The hypercritical points in Fig. 3(b) lie at the minima of the two curves and correspond to the points marked with encircled dots in Fig. 3(a).

More than 20 years ago Wolf measured UCS and LCS loci for PS– diethyl ether solutions as a function of pressure.[10] He observed that the UCS and LCS branches approached each other at low pressure, and went on to speculate that they might join at even lower pressures (negative pressures), as in curve B, Fig. 3(b), but did not experimentally demonstrate that to be the case. In fact only recently has it been demonstrated in experiments from our laboratory that one can employ pressure and negative pressure to demonstrate continuity of state for these polymer solutions. These experiments have shown that certain systems with separate UCS and LCS branches join smoothly to yield a hypercritical point at negative pressure,[11,12] and certain solutions in poor solvents which display a hypercritical point at $P \sim 0$ or $P > 0$, can literally be pushed into the θ configuration by raising the pressure.[12,13] To further illustrate, we return to Fig. 2. This time consider the two parts of the figure as $(T,\psi,X = M_W^{-1/2})_P$ projections taken at two pressures, P[Fig. 2(a)] > P[Fig. 2(b)]. It is the choice of solvent quality which dictates whether the hypercritical point lies at $P > 0$, $P \sim 0$, or $P < 0$ and in the material below we review experiments showing this to be the case. It must be understood in designing these kinds of experiments that one is strictly limited to negative pressures of magnitude smaller than the breaking strength (cavitation limit) of the liquid itself, or the adhesive forces joining the liquid to the wall.[6]
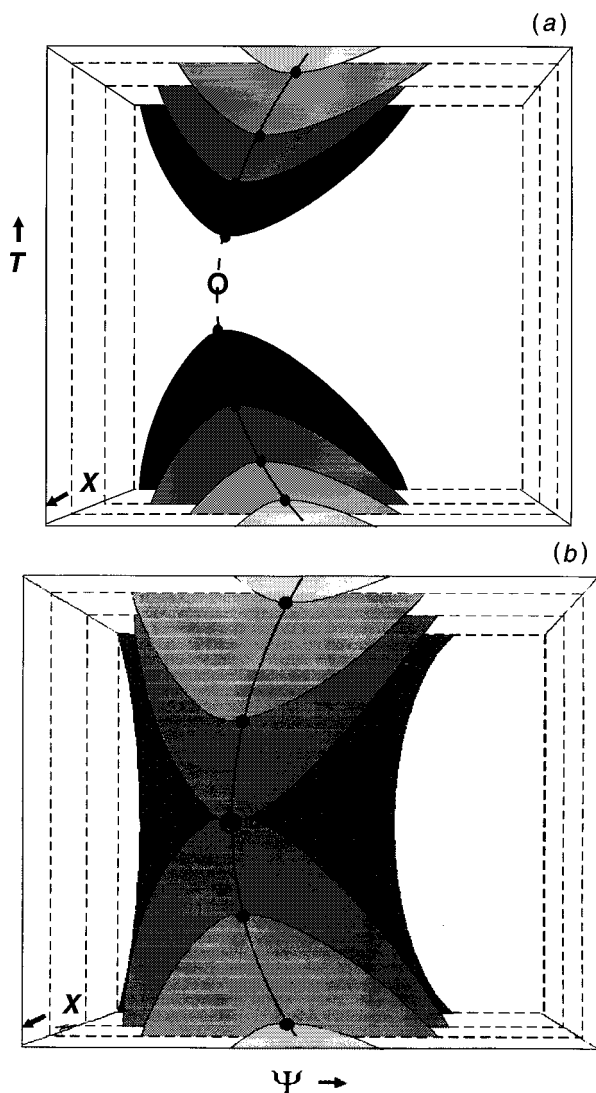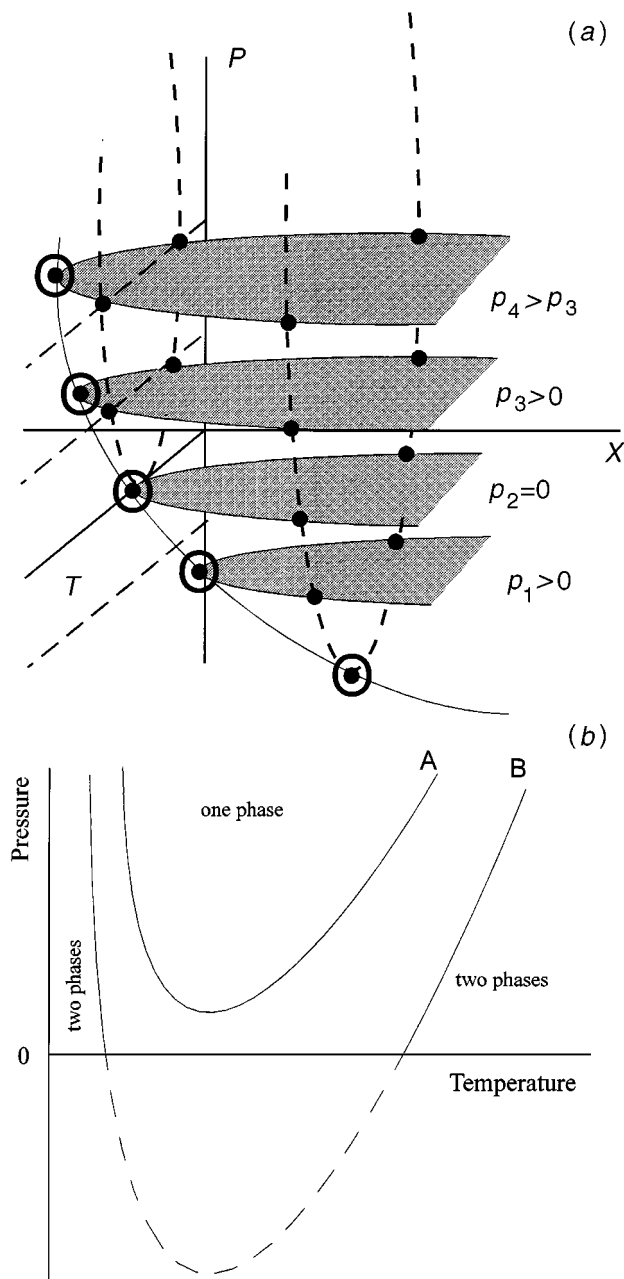
Fig. 3 (*a*) Schematics for UCST–LCST demixing in (*T, P, X* = $M_W^{-1/2}$) space. Depending on the precise strength of the polymer–solvent interaction (*i.e.* on solvent quality) the system can make a transition from a θ to a non-θ (poor) solvent at positive pressure, at a reachable negative pressure (tension) as shown, or at a negative pressure too low to be experimentally observed (because obscured by cavitation). The dashed lines drawn through the dots show isopleths, (*T,P*) projections, at finite M_W and Fig. 3(*b*) shows several such projections. The shaded areas are (*T, X* = $M_W^{-1/2}$) projections at several pressures, both negative and positive. (*b*) (*P,T*)$_{\psi,X}$ projections of demixing isopleths for two solvent qualities. A = poor solvent, B = θ-solvent.

We conclude this section by commenting that the 'solubility-worsening' effect of negative pressure has significant implications: to begin with, it demonstrates that the UCS and LCS precipitation branches are separate manifestations of the same phenomena. In other words the poor-solvent/θ-solvent dichotomy is not rigid, it can be shifted in either direction by pressure (and possibly by other variables). More practically this phenomenon gives us the opportunity to precipitate polymer from θ-solvents simply by varying pressure, without adding a third component (cosolvent). One could take advantage of this

in designing pressure fractionation processes for the purification of polymers. This might be useful, for example, in sharpening M_W distributions.

1.2 Further remarks. Negative pressure in liquids and solutions

Above, we saw that the existence of negative pressure (tension) in liquids was experimentally confirmed more than three hundred years ago (see the historical descriptions given by Kell[2] and Trevenna[6]). Stress is induced in a solid when it is pulled, in the same sense negative pressures are generated in liquids when they are pulled. Of course one expects that negative pressure in liquids cannot be too deep, or exist too long, because liquids cannot hold stress for a long time, but sometimes negative pressures (even tens of megapascals!) have been maintained for days,[14] and theoretically (maybe) there is no time limit on moderate negative pressures.[15] Certainly negative pressures of large enough magnitude may tear liquids, just like big stresses fracture solids, this maximum tension is the so-called homogeneous nucleation limit for cavitation.

During the 'three hundred year' history of negative pressure research[16] most effort lay in the attempt to reach the homogeneous nucleation limit.[6] This limit is important in defining the equation of state for liquids. In addition there have been a few measurements on other physico-chemical properties.[17–19] Some researchers examined the effect of the negative pressure on the properties of various liquids including water, and especially on the freezing point curves.[20] However, except for the liquid–liquid demixing experiments on PS solutions described by us,[11,12] there has been very little work at negative pressure on the phase behavior of two component solutions. We are convinced that systematic measurements of physico-chemical properties of liquids and solutions at negative pressure yield valuable information, and that usefulness extends far beyond the mere mapping of the homogeneous nucleation limit.

2 Methods

It is a well established maxim in hydraulics that pressurized fluids at rest are isotropically strained. Thus, to make effective comparisons of fluid properties at positive and negative pressure it is important to ensure that the applied negative pressures are also isotropic. Anisotropic effects are common in polymer solutions under flow. For example, the effects of shear on polymer solubility, and on light scattering and neutron scattering from polymer solutions are well known[21] and are of considerable theoretical and commercial interest. Nonetheless in the present context they are effects to be avoided. For the experiments described below we need a method to produce and maintain a large enough negative pressure, preferably in a transparent cell (to permit direct observation of precipitation), for times which are long compared to the characteristic time of the phase transition. Additionally, it will be convenient to provide mixing and it will be necessary to incorporate some method to measure or calculate the tension.

Trevena[6] describes several techniques to generate negative pressures in liquids. To begin with, it is important to keep in mind that negative pressure is not a thermodynamically stable state, *i.e.* any untoward disturbance or any contamination (especially suspended colloidal particles or traces of gases) can serve as nucleation centers to break the stressed liquid, generating vapor bubbles (cavities) and initiating the process eqn. (1) whence the liquid pressure once more becomes

(metastable fluid)$_{P < 0} \rightarrow$ (thermodynamically stable

$$[\text{fluid} + \text{vapor}])_{P = \text{P(vap)} > 0} \quad (1)$$

positive. Therefore any method used to produce negative pressures must either exclude or reduce these problems if one desires deep tensions.

Methods in common use to place liquids under tension can be divided into two groups: static and dynamic (see Table 1). By static we infer methods which produce and hold tensions for long times, minutes to hours or even longer, while dynamic methods only produce transient tensions which last but fractions of a second (typically a few milliseconds or less).

Table 1 Some methods to generate negative pressures

Dynamic methods	Comments
Sudden pulling of a piston	Mechanical generation of short tension pulse of continuously changing value, delocalized, characterized by anisotropic pressure tensor
Backside of positive pressure wave	Very short tensile pulse of continuously changing value, delocalized, anisotropic pressure tensor
Sound waves (acoustic method)	Short, cyclic tensile pulses of periodically changing value, anisotropic, localized when cell geometry permits standing waves.

Static methods	Comments
Thermal pressure method. Tendency to contraction induced by cooling, but prevented by liquid–wall adhesion. (Berthelot's method, or Vincent's viscosity tonometer.[27])	Constant value of tension can be even for days (but not easily), isotropic pressure tensor, requires very good temperature control.
Hydrostatic forces (Huygen's method)	Tension changes continuously along the tube but is locally isotropic. High tensions require very long tubes and this is experimentally inconvenient.
Centrifugal force (Briggs' method[28])	Used to generate very high tensions in the middle of a spinning capillary, but the tension is anisotropic and changes continuously along the tube.
Flow through Venturi constriction (based on Bernoulli's law).	Although static as viewed from an outer coordinate system this method is locally dynamic from the point of view of the liquid. Also the pressure tensor is anisotropic.

All dynamic methods basically employ a pressure pulse technique to generate tension.[6] A pulse moving through a fluid generates a compressive (positive pressure) disturbance to its front and is followed by a decompression (negative pressure) to its rear. Pulses can be generated mechanically, chemically (by explosions), or acoustically, but in any of these cases the characteristic lifetime of the disturbance is determined by the mechanical relaxation time of the fluid which in turn is closely related to the speed of sound in that fluid. Thus the timescale during which the fluid at any point is under tension is of the order of milliseconds or less, and the magnitude of that tension is rapidly changing even on the millisecond timescale. A second difficulty is that dynamically or acoustically generated tensile pulses are directional in character. This is very much a disadvantage since it is our goal to compare fluid properties of (isotropically) pressurized solutions with those same solutions under tension.

Most of the static methods used to produce longer lasting (> 1 s) tensions are based on the adhesion which exists between a solid wall and the fluid. Further information is found in Table 1. Trevena gives excellent and detailed discussions of the more common methods.[6] Although the manometer method (Fig. 1),

first used by Huygens and briefly described early in this paper is conceptually simple, its use to generate deep negative pressures in ordinary fluids (say $0.8 < \rho/(g\ cm^{-3}) < 1.2$) would require capillaries many metres long. This is much too clumsy and the Huygens method is inconvenient for general use. The technique in most common use for generation of static fluid tensions, and luckily the best for our purposes, is the so called Berthelot-tube method[4,6,14] (Fig.4). In the Berthelot method one almost fills a capillary with clean and degassed liquid or solution, cools the sample now held under modest vacuum (thus eliminating residual air or other low boiling contaminants), then flame-seals the tube still under vacuum. At this point, after the sample melts, the capillary contains mostly fluid plus a small vapor bubble at the top [leftmost tube (tube 1, Fig. 4)]. On heating the fluid expands so the vapor bubble disappears at a well-defined temperature which depends on the initial fluid/vapor ratio and the thermal expansivity of the liquid [T_{fill}, the filling temperature, tube 2, Fig. 4]. Normally one continues to warm a few degrees above T_{fill} to dissolve all vapor bubbles and incipient nuclei, and to ensure that liquid thoroughly permeates whatever pores exist at the wall (tube 3, Fig. 4). It is well established that pre-pressurizing almost always significantly increases the maximum tension in a given apparatus. That limit is usually determined by one or another of the mechanisms of heterogeneous nucleation of the vapor phase. In any event after heating (pre-pressurizing), the sample is cooled. As the temperature drops the fluid would contract were it not held to the wall by surface adhesive forces (tube 4, Fig. 4). The resulting tension accounts for the negative pressure. Obviously at T_{fill}, $p = p_v$, where p_v is the equilibrium vapor pressure of the fluid system. For $T < T_{fill}$ the negative pressure can be calculated from the thermal properties of the liquid or solution using the thermal pressure coefficient, Γ eqn. (2).

$$\Gamma = (\partial P/\partial T)_V = -(\partial V/\partial T)_P/(\partial V/\partial P)_T = \alpha/\kappa \qquad (2)$$

Here α is the isobaric expansivity, $\alpha = (1/V)(\partial V/\partial T)_P = (\partial \ln V/\partial T)_P$ and κ is the isothermal compressibility, $\kappa = -(1/V)(\partial V/\partial P)_T = -(\partial \ln V/\partial P)_T$. Both α and κ are weakly dependent functions of T and P so $\Gamma = \Gamma(T,P)$. To first approximation we write eqn. (3)

$$\alpha = \alpha_0 + \alpha_{1,T}(T - T_{fill}) + \alpha_{1,P}(P - P_{fill}) + ...\ higher\ order\ terms\ (H.O.T.) \qquad (3)$$

and eqn. (4)

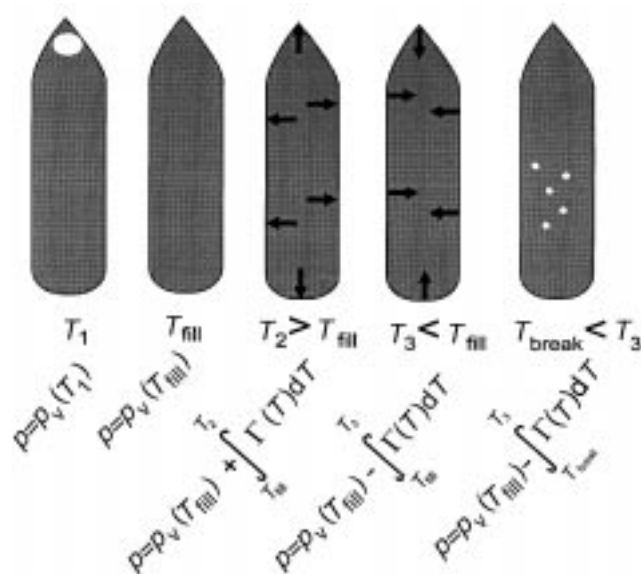**Fig. 4** The Berthelot method schematically illustrated. See text for detailed discussion.

$$\kappa = \kappa_0 + \kappa_{1,T}(T - T_{fill}) + \kappa_{1,P}(P - P_{fill}) + ... \text{ H.O.T. (4)}$$

so eqn. (5)

$$\Gamma = (\alpha_0/\kappa_0)[1 + (\alpha_{1,T}/\alpha_0 - \kappa_{1,T}/\kappa_0)(T - T_{fill}) +$$
$$(\alpha_{1,P}/\alpha_0 - \kappa_{1,P}/\kappa_0)(P - P_{fill}) + ... \text{ H.O.T.}] \quad (5)$$

Here α_0 and κ_0 are the expansivity and compressibility at the fill temperature and pressure. For most fluids of interest the first order correction terms are small (*i.e.* $\alpha_{1,T}/\alpha_0$, $\kappa_{1,T}/\kappa_0$, $\alpha_{1,P}/\alpha_0$, and $\kappa_{1,P}/\kappa_0$ are all $\ll 0$). To sufficient precision one can thus write $\Gamma = (\partial P/\partial T)_V \sim \Gamma_0 \sim (\alpha_0/\kappa_0)$. The negative pressure which results from cooling to a temperature some few degrees below T_{fill} is then eqn. (6)

$$\int dP \sim P - P_{fill} \sim P \sim \int \Gamma_0 dT \sim \Gamma_0(T - T_{fill}) \quad (6)$$

because $|P_{fill}/P| << 1$. Typically fluids of interest have expansivities of the order of 10^{-3} K^{-1} and isothermal compressibilities of the order 10^{-9} Pa^{-1}, so $\Gamma_0 \sim 10^6$ Pa$\cdot$ K$^{-1} \sim 1$ MPa K^{-1}. Also $T < T_{fill}$ so P is negative and of the order of -1 MPa (10 bars) per degree of cooling. This simple calculation nicely demonstrates that the Berthelot technique is a simple and effective method to conveniently generate negative pressures of appreciable magnitude. Ordinarily $\Gamma(T,P)$ is determined for $P > 0$, then extended to the fluid under tension. In an actual Berthelot experiment the pressure which is developed can be measured by determining the deformation of the container[22] [which some, Henderson and Speedy for example,[20] construct in the form of a delicate spiral (an *in situ* Bourbon gauge)], or can be calculated from the temperature as outlined above. Alternatively, it may be possible to incorporate a strain guage or other type pressure guage into the sample cell, but this will be only at the risk of introducing new sites for heterogeneous nucleation.

As one continues to cool the Berthelot cell below T_{fill} the pressure rapidly falls; before long the liquid breaks and tiny bubbles appear to witness the end of the negative pressure session (tube 5, Fig. 4). At this point the system jumps back to its equilibrium vapor pressure. Usually cavitation occurs at the wall–liquid interface and at a few MPa tension but Henderson and Speedy have succeeded in generating and maintaining measured negative pressures as high as ~ 20 MPa for highly purified water held in fine spiral capillaries,[14,20] while Green *et al.* reached 80 MPa negative pressure (calculated from the thermal pressure coefficient) in water trapped in a quartz fissure.[23] The homogeneous nucleation limit (*i.e.* that tension at which cavitation occurs because the cohesive forces between fluid molecules are exceeded by the applied tension) is usually unreachable in a practical sense. Below the heterogeneous limit usually seen at several MPa, or more, the tension can be held for minutes, sometimes for days.

The course of a phase transition induced by negative pressure in a polymer–solvent mixture can be seen in Fig. 5. Point A represents the initial pressure and temperature—here the capillary contains liquid with small vapour bubbles and $P = P_{vapor}$. The filling temperature is at B. As the temperature is increased beyond B and towards C pressure increases rapidly. At the pre-pressurization limit, C, the sample is cooled, the system passes through B again and thence into tension. With sufficient cooling the (T,P) path crosses the cloud point locus and the solution goes turbid (point D). Knowing the temperature difference between B and D, $(T_D - T_{fill})$ the tension can be calculated and recorded. One can stop the session by rewarming the system. Alternatively, further cooling can cause cavitation (point E); in that case the pressure jumps discontinuously and rapidly, clearing at point F, and ending at G where $P = P_{fill} = P_{vapor}$. Each sample in its sealed capillary gives one point on the (T,P) isopleth for the cloud point. (The positive side of the cloud point curve can also be observed with this method,[11] in that case adjusting the fill conditions to ensure the cp curve is located between points B and C.)
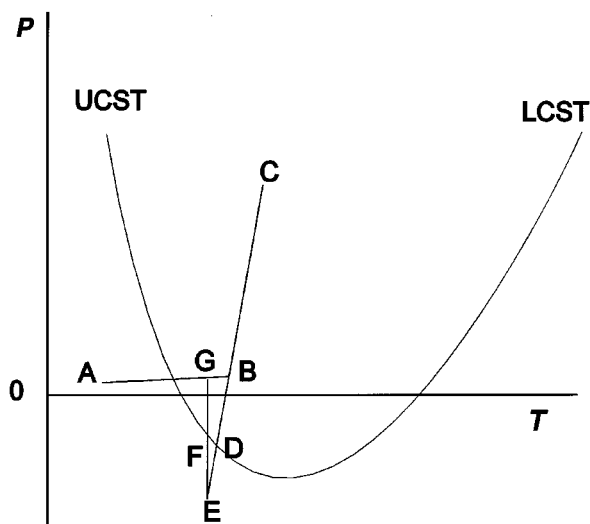
Fig. 5 The course of a Berthelot induced precipitation at negative pressure. The smooth curve is a (T,P) isopleth of the type illustrated in Fig. 3(*b*). The hypercritical point is located at negative pressure. The set of line segments AB–BC–CBDE–EFG describe the course of the Berthelot experiment to induce precipitation at negative pressure. See text for further and more detailed discussion.

3. Results, two examples

We have used the Berthelot negative pressure technique to study phase transitions in two separate polymer–solvent systems.[24] In the first, polystyrene–propionitrile, PS–PPN, where PPN is a poor solvent, we demonstrated[11] the continuity of the phase diagram in the region below $P = 0$. In Fig. 6 we show cloud point data taken for a 0.20 mass fraction PS solution ($M_W = 22\,000$) using the Berthelot technique ($2 > P/$MPa > -0.6), comparing those results with a set of cloud point measurements at higher pressure ($5 > P/$MPa > 0.1) taken by another technique.[26] The two data sets agree for both the upper and the lower consolute branches, agreement is nicely within the combined experimental error. The results confirm the idea that the equation of state describing this solution passes smoothly and continuously across the zero pressure isobar and into the region of negative pressure. Thus it is physically reasonable to compare properties of solutions in regions of positive and negative pressure using continuous smoothly varying functions. For example it may be convenient to represent an isopleth (including the critical isopleth) using an expansion about the hypercritical origin, even if that origin is found at negative pressure. We have found such expansions a
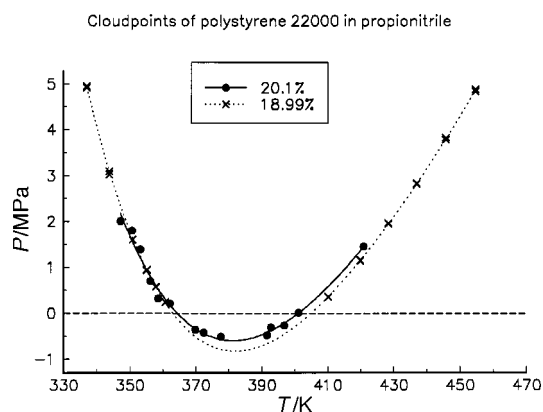

Fig. 6 Polymer–solvent demixing at negative and positive pressures. Cloud points for propionitrile–polystyrene solutions. The solid circles show results obtained by the Berthelot technique for $M_W = 22,000$, $M_w/M_n = 1.03$, mass. Fraction PS $= 0.20$. The x values show results obtained at positive pressure using another technique.[26]

convenient way to represent solution properties even when the hypercritical origin lies so deep as to be experimentally inaccessible, or is below the cavitation tension.[25]

In the second case,[12] PS–methyl acetate (PS–MA), we examined the θ-solvent–poor solvent transition which is expected to occur at negative pressure (refer to the discussion around Fig 2 and 3). MA is a θ-solvent at ordinary pressure and the transition corresponds to a merging of the UCST and LCST at negative pressure. For a solution PS $M_W = 2 \times 10^6$ the point of hypercritical juncture of the upper and lower branches is estimated to lie below −5 MPa and we were unable to reach low enough negative pressures to directly observe the joining point of the two branches (either for this sample or one of $M_W = 2 \times 10^7$, where $P_{hypercr}$ should be somewhat smaller in magnitude). However we were able to demonstrate continuity of the cloud point curve well into the region of negative pressure thus establishing continuity of state, and the likely merging of the UCST and LCST branches.

4 Summary

The important idea presented by these negative pressure experiments is that continuity of state extends across the $P = 0$ boundary into the negative pressure region where solutions are under tension. In this line of thinking the upper and lower UCST and LCST demixing branches share a common cause. The approach therefore forces a certain broadening in the outlook to be employed in describing polymer solution thermodynamics and this has been very useful. One immediate and practical extension was the development of a scaling description of polymer demixing in the $(T,X = M_W^{-1/2})_{\psi crit, P}$ plane which employs an expansion about the hypercritical origin, $X_{hypercr}$, even for $X_{hypercr} < 0$. The approach is in exact analogy of the expansion about $P_{hypercr}$ discussed in this paper in the $(T,P)_{\psi crit, X>0}$ plane, even for $P_{hypercr} < 0$. The considerable advantages of this scaling description are discussed at length in a recent review from this laboratory.[25]

5 Acknowledgement

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