Spinodal strength of liquids, solids and glasses

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Abstract

With isotropic tri-axial stretching (negative pressure) and/or with heating, the thermodynamic stability limit (spinodal) of condensed matter—like solids, liquids and glasses—can be reached. In this paper, we analyse and compare the spinodal strength (i.e. the negative pressure necessary to reach the spinodal) of liquids, solids and glasses. Some examples with uni-axial stretches are also presented. Moreover, we discuss the possibility to step over the spinodal and to reach the region where the system can exhibit negative compressibility for a finite, nonzero time.

1. Introduction

From our daily experience, by heating or de-pressurizing liquid water, we know that one can obtain boiling (i.e. liquid–vapour phase transition) at $100\,°C$ for atmospheric pressure or at 0.03 bar for room temperature. These are the limiting points, above (in temperature) or below (in pressure) at which the stable liquid phase does not exist any more and a phase transition is favourable. It is less known, however, that liquid water can exist almost up to $300\,°C$ (for atmospheric pressure) [1] and down to -120 MPa (for room temperature) [2]. In that 100–$300\,°C$ or -1200–0.03 bar range liquid water can exist, but it is metastable, which means that external disturbances or even internal fluctuations can initiate immediate boiling. These disturbances or fluctuations define two limits, namely the heterogeneous and homogeneous nucleation limits [1, 3]. Experimentally, only these limits can be reached, but there is a third limit, the so-called spinodal limit (also called thermodynamic stability limit). This is the limit, where the isothermal compressibility and the isobaric heat capacity switches from positive to negative, i.e. the stability criteria are violated [1]. The spinodal cannot be reached, but it can be approached in condensed matter such as solids and liquids [4]. The usual method for the estimation of the spinodal is by interpolation of the compressibility or the heat capacity, as discussed below.

The 'spinodal strength' in the title of our paper implies that our main interest is in the spinodal limit approached by changing the pressure. This can be realized by stretching an isotropic material along the three major axes, applying the same pressure component in each direction. This may be difficult—although not impossible—in reality [5, 6]. For liquids the difficulty is to 'catch and hold' them during stretching, while for many solids, the isotropy is difficult to realize in practice and the shear elements in the pressure tensor cannot be neglected.

In this paper, the spinodal strength—i.e. the largest negative pressure where the condensed phase still can exist—is discussed for liquids, glasses and solids. In addition, we discuss the possibility of obtaining information about the region below the spinodal.

2. Thermodynamic stability limit

There are two measurable criteria for the thermodynamic stability limit of an isolated macroscopic body [1, 7]:

$$\left(-\frac{\partial p}{\partial V}\right)_T = \frac{1}{V\kappa_T} \geqslant 0 \qquad (1a)$$

$$\left(-\frac{\partial T}{\partial S}\right)_P = \frac{T}{c_P} \geqslant 0 \qquad (1b)$$

where p is the pressure, V is the volume, T is the temperature, κ_T is the isothermal compressibility, S is the entropy and c_P is the isobaric heat capacity. These two equations are equivalent, i.e. they are satisfied or violated simultaneously. Depending on the degrees of freedom the points, lines or surfaces at which the conditions are violated are called spinodal. For solids, and sometimes also for liquids, stability also requires a positive shear modulus. In the main part of this paper, this criterion— and also, the pressure induced zero-shear instability—will be neglected. Furthermore, all materials and external mechanical fields are assumed to be isotropic; except where stated otherwise.

Reaching the stability limit (possible only in theory, in experiments it can be only approached) the formerly homogeneous material *must* split into two phases (the old one and a new one) or turn completely into a new phase. In case of a pure, homogeneous liquid as the initial phase, the new phase is almost certainly a vapour [1, 5], although there are some new theoretical (and a very few indirect experimental results) showing that the liquid–liquid phase transition is also possible [8]. In case of a solid initial phase, the situation is not clear. The results suggest that the new phase can be a vapour or a liquid [9, 10].

The spinodal can be calculated for model systems by calculating the pressure and temperature dependence of the compressibility and specific heat, respectively (equation (1)). Experimentally, the only method is via the extrapolation of the measured values (mostly in the positive pressure range). Since the pressure and temperature dependence of κ_T and c_P may be different close to the spinodal than in the experimentally accessible region, these extrapolated values are sometimes referred as pseudo-spinodal [1].

We should mention here, that although the phrase 'stability limit' has been used for the spinodal for several decades, this terminology is not correct. The spinodal is the border between the metastable and instable region, while the border between the stable and metastable region (the real border of stability) is the binodal. In the case of liquid–vapour transitions, the binodal is the saturation (or vapour pressure) curve. The correct name for the spinodal would be metastability or instability limit, but in keeping with traditional nomenclature we are going to use the term 'stability limit'.

3. Virtual and temporal violations of the stability criteria

Although equations (1*a*) and (1*b*) must be true in all equilibrium systems where classical thermodynamics can be applied, there are a few examples where the stability criteria are virtually, or temporally, violated.

3.1. Virtual violations

Baughman and his co-workers [11] reported some real materials, where they found negative compressibility '. . . in One or More Dimensions'. One should realize, that in equation (1*a*), the volume (V) has three components; one in each space dimension. V_x, V_y and V_z are the different

lateral sizes (L, lengths), while $V_x^* V_y$, $V_x^* V_z$ and $V_y^* V_z$ are the different surface sizes (A, areas). The isothermal area and length compressibilities can be defined as:

$$-\frac{1}{A}\left(\frac{\partial A}{\partial p}\right)_T = \kappa_{A,T} \tag{2a}$$

$$-\frac{1}{L}\left(\frac{\partial L}{\partial p}\right)_T = \kappa_{L,T}. \tag{2b}$$

A positive isothermal volume compressibility (κ_T) does not require these low-dimensional compressibilities to be positive. Applying a positive hydrostatic pressure to a stable solid (usually with an anisotropic structure) it can expand in one or two directions (with negative $\kappa_{A,T}$ and/or $\kappa_{L,T}$), but cannot do it expand simultaneously in all three dimensions; i.e. the total volume has to decrease ($\kappa_{V,T}$ has to be positive).

Similar 'virtual' violations can happen in materials with a negative Poisson's ratio. These materials are called auxetics. Recent reviews of these materials can be seen in several places, for example in [12–14]. To introduce auxeticity, one has to realize that for condensed matter, the pressure is not necessarily a scalar. In general it is a 3×3 tensor (P), containing three diagonal and six off-diagonal elements. It can be replaced by a scalar pressure, when all off-diagonal elements are zero (no shear components) and all diagonal elements are equal. In that case, $p = p_{xx} = p_{yy} = p_{zz}$. When a positive uni-axial pressure is applied to an auxetic material, one can observe a negative spatial response (contraction) in the other directions. This means that pushing an auxetic body along the x-axis, it will shrink along the y and z axes unlike 'normal' materials, such as rubber, which expand in those directions. Similarly, applying negative pressure, the auxetic material will expand not only along the direction of pulling, but also in the other two directions. Mathematically for auxetic materials one of the following values is negative, while for normal materials they are positive:

$$-\frac{1}{L_i}\left(\frac{\partial L_i}{\partial p_j}\right)_T = \kappa_{ij,T} \tag{3}$$

where i and j ($i \neq j$) are two of the space coordinates (x, y or z) and $\kappa_{ij,T}$ is a new, 'cross' compressibility. For $i = j$, this quantity is negative both for normal and auxetic materials. Although at first sight auxetic systems seem to be unstable, it is easy to show that a negative Poisson's ratio does not violate any stability criteria (see e.g. [15, 16]).

The third example for virtual stability violation was reported by Wojciechowski and his co-workers [17, 18], more than twenty years ago. The system studied was a narrow, rectangular 2D box with periodic boundaries containing hard disks. Denoting the ratio of the length L of the box to the number of disks N by $l = L/N$, and the width by D ($\leqslant 3^{1/2}\sigma$) (where σ is the diameter of the disks), one can find special combinations of D and l for which the compressibility is negative. This is due to the fact that in strongly confined small systems large density fluctuations and hence phase separation are suppressed. Similar instabilities can be found in other small systems (see for example Alder *et al* [19]). It should also be

mentioned that the stability limit can be reached in interfacial systems such as the vapour–liquid interface [20, 21] although these systems are not unstable. There are also some arguments, based on the application of the Onsager equation for liquid–vapour interfaces, where in some parts of the interface even states with negative compressibility can be reached, without losing the stability of the interface [22]. Another approach has been proposed by Lovett and Baus [23] by introducing a locally defined pressure.

3.2. Temporal violation

When a system moves out of the stable region, in the case of metastability it *should*, while in case of instability it *has to* undergo a phase transition. The change of temperature or pressure can be slow or fast. In the case of fast changes, pressure is more favourable (see for example [24]). Performing a pressure jump, one can reach the metastable region, where the system might stay in the initial phase, because of insufficient energy to overcome the activation energy required to form a new phase by nucleation. When the pressure jump is larger, the system might approach the unstable region. Here the phase transition and separation (by spinodal decomposition, rather than by nucleation) do not have an activation barrier and hence occur spontaneously. But as with any physical process, it still requires some time to occur. Being on the timescale of molecular relaxation processes (on the picosecond scale), 'quasi-stable' instable states can be obtained, for example by MD simulations, by applying a shorter time step [21]. In experiments, one can rapidly de-pressurize an over-pressurized liquid very close to its liquid–vapour critical point. In this case an explosive spinodal-type phase transition can be observed [3, 25], but because the transition is very fast, this mechanism has not been very well studied.

Although here we discuss one-component systems, we should mention that with binary or multicomponent liquid systems having a limited miscibility, the diffusion spinodal is the relevant stability limit [26]. This spinodal can be jumped over by very fast pressure change. After the jump, the initially homogeneous system separates into two phases (like oil–water emulsion). It is a widely used method in polymeric systems [24] and the morphology of the phase-separated material can be affected by the magnitude of the jump. With smaller jumps (a phase transition in the metastable region) the result will be a continuous first and separated second phase, or small nano-domains of the new phase within the old phase in case of rapid solidification. In the case of a larger jump (a phase transition below the spinodal) the new system will have bi-continuous first and second phases. The phase transition is slower when a liquid–liquid transition is involved, especially with very long-chain polymers. This is the reason why bicontinuous structures—caused by spinodal decomposition—can be observed more often after liquid–liquid phase transitions than after their liquid–vapour counterpart.

Although such short-living states in slow separating systems are not real equilibrium states, one can still obtain some information about them when the characteristic time of the measurement (or the measured effect) is short enough compared to the finite speed of the phase transition. As an analogy, one might refer to fractals; it is known that real materials are not really fractals, but they may appear as such in a limited size range. Processes where only a certain size range is important, such as light scattering (50 nm–1 μm) or diffusion-limited electrochemical processes (1 μm–1 mm) [27, 28], could be studied on real samples which are fractal-like in that size range. Then the result could be applied for real fractals too. Similarly, a process which has characteristic time of 100 fs can be studied while jumping through the liquid–vapour spinodal, because the system will almost be in temporal equilibrium.

4. Spinodal strength of various systems

4.1. Liquid

The spinodal strength of liquids has been discussed in various places, including several books [1, 3, 5, 29, 30]. By stretching a stable ($p < p_{\text{vap}}$) liquid, one first intersects the binodal (vapour pressure or saturation curve). Starting from that point, the liquid is metastable. It could boil in response to an impact from outside (mechanical impact, cosmic ray, etc). The boiling occurs by nucleation, i.e. first several tiny vapour nuclei (nano-bubbles) will form, which then grow and merge, forming a macroscopic vapour phase. Nucleation can happen by heterogeneous nucleation (due to contamination) or by homogeneous nucleation (due to density fluctuations). Homogeneous nucleation is the ultimate limit for overheating/stretching. For water, the limit of overheating (on atmospheric pressure) is approx. 300 °C, while for stretching, it is approx. −120 MPa [1, 2]. Spinodals can be calculated from the equation of states (EoS) or extrapolated by compressibility or thermal expansion measurements. In the negative pressure region, these measurements are almost impossible, while the EoS are accurate only in the stable liquid range, therefore not only the actual values, but even the shape of the spinodal curve is still debated [31–35]. Some authors say that the spinodal goes down monotonically from the liquid–vapour critical point, while others expect that in some systems, such as water, the spinodal might have a minimum. Recently there have been increasing theoretical objections against the second model, which is called the re-entrant spinodal, but one cannot fully exclude it. For water, at room temperature the spinodal pressure is expected to be below −200 MPa for the re-entrant model or below −400 MPa otherwise. Water is a very 'strong' liquid in the sense that large negative pressures can be realized. Other liquids may be weaker: for example helium-3 can withstand only −0.3 MPa [3]. For simple van der Waals liquids, one can calculate that the spinodal, starting from the vapour–liquid critical point, will intersect $p = 0$ at a temperature of $27T_{\text{c}}/32$, giving its limit of overheating [5] and reach $T = 0$ at $-27p_{\text{c}}$ (giving the largest spinodal pressure) [36]. Applying this method to water gives $p_{\text{sp}}(T = 0) = -586$ MPa, whilst for liquid potassium using the estimated, but not yet established, value of Skripov and Faizullin [30] it gives $p_{\text{sp}}(T = 0) = -59.3$ GPa.

However, one should keep in mind that neither water nor liquid potassium are typical vdW liquids. Additionally, if the density dependence in the repulsive term of an equation of state for spinodal conditions (i.e. the set of temperature and density values for which $\partial p/\partial \rho$ holds) diverges faster than T approaches zero, the limiting ($T = 0$) liquid spinodal pressure may be above $-27 p_c$. This might lead to a re-entrant spinodal.

4.2. Glasses

Glasses are liquids in the thermodynamic and structural sense, but with respect to the dynamic and mechanical behaviour they are much more like to solids. The so-called ideal glass transition curve might also be a kind of stability limit for liquids (for undercooling) [35], but here our main interest is in the liquid–vapour spinodal, therefore ideal glass transition will not be discussed here. The spinodal or the pseudo-spinodal can be determined, as for liquids, by calculating or extrapolating the compressibility or the heat capacity (equations (1*a*) and (1*b*)). As an alternative method, the pseudo-spinodal can be estimated from the extrapolation of the isothermal relaxation time [37]. For example for glycerol, the extrapolated value for the spinodal is -380 ± 50 MPa, which is a reasonable value, in comparison with the spinodals for other liquids and solids.

4.3. Solids

Some results concerning the spinodal strength and other kinds of stability limit for solids have been presented previously [10, 16]. In this paper, solid means a perfect monocrystalline solid, without any defect or vacancy, even though such perfect materials do not exist at finite temperature. Therefore one should keep in mind that for real solids the spinodal strength is smaller (meaning less negative). Also it should be noted, that—just as for liquids—the spinodal cannot be reached, because various other processes (partial or full melting, break, spallation, etc) will interfere long before reaching the spinodal limit [10].

For perfect monocrystalline solids, the so-called crystal spinodal can be defined by equations (1*a*) and (1*b*). This has been done by several authors [9, 34, 38–40] although the crystal spinodal has been much less investigated than the liquid–vapour spinodal. The reason for this lack of interest might lie in the fact that for solids, the double isotropy (isotropic pressure and isotropic material) are far less realizable experimentally, especially whilst avoiding stress; but theoretical or numerical calculations are still possible as an idealized reference system.

There are two basic questions which should be answered before any study of solid-spinodals. The first one is about the physical meaning of the crystal spinodal; the second one is about the nature of the new (second) phase. These two points are discussed in detail elsewhere [10]; here we give only a brief overview.

While for an overheated or stretched liquid the most trivial way for relaxation back into stable state is the liquid–vapour transition, for solids it might be a solid–vapour, solid–liquid or even a solid–solid one. The last one is highly improbable for any process which requires fast relaxation, while for the first two, several arguments can be found for and against [10]. We would like to note here, that according to some researchers, breaking or fragmentation (which would be the physical manifestation of a sudden solid–vapour transition) is not really a phase transition, but rather a phase break [41]. Counter-examples to this opinion are given elsewhere [10].

Based mainly on the lack of an ordered–disordered (solid–liquid or solid–vapour) critical point, which is a terminating point for the spinodal [30, 42], some researchers have objections to giving any physical meaning to the crystal spinodal. They argue that the extrapolation of the compressibility or heat capacity might give only an artificial pseudo-spinodal [10]. However other calculations, for example in some molecular dynamic calculations [40], support the existence of a solid–vapour crystal spinodal.

Accepting the existence of the crystal spinodal and neglecting the problem about the nature of the second phase, which is irrelevant for the location of the spinodal, the calculated crystal spinodal limit is given as -3 GPa at around 1600 K for silicon [39] and in the range -100 to -400 MPa for noble-gas solids at 5 K [38]. These values are at least one order of magnitude deeper than for most liquids. The exceptions are molten metals, but those values are not well established.

5. Conclusions

The stability limits or spinodals of isotropic liquids, glasses and solids upon a tri-axial isotropic stretch (negative pressure) have been discussed and compared. For various liquids, the known liquid–vapour spinodal is in the -0.3 MPa to -400 MPa range, with the exception of molten metals for which lower values might be obtained. For solids it is in range from -100 MPa to -3 GPa. For glasses, no reliable calculation exists, but the spinodal pressures are probably in between the liquid and solid values. Some possibilities of virtually violating the stability criteria (equations (1*a*) and (1*b*)) have also been discussed.

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Note added.   After the submission of this manuscript, a related review was published dealing with the effect of shock-waves (including parts with *transient* negative pressure) on condensed matter [43].

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