

### 3- Phase transition and instabilities

#### 1. Nuclear phase coexistence in the grand-canonical ensemble

In the case of the thermodynamic limit, the system can exist even beyond its flash temperature (see course 2) because it can be viewed as the juxtaposition of a high density (liquid-like) and a low density (gas-like) component, which exert the same pressure on each other.

We now turn to show that the inversed pressure slope indicates the instability of the system with respect to separation into two phases of different densities.

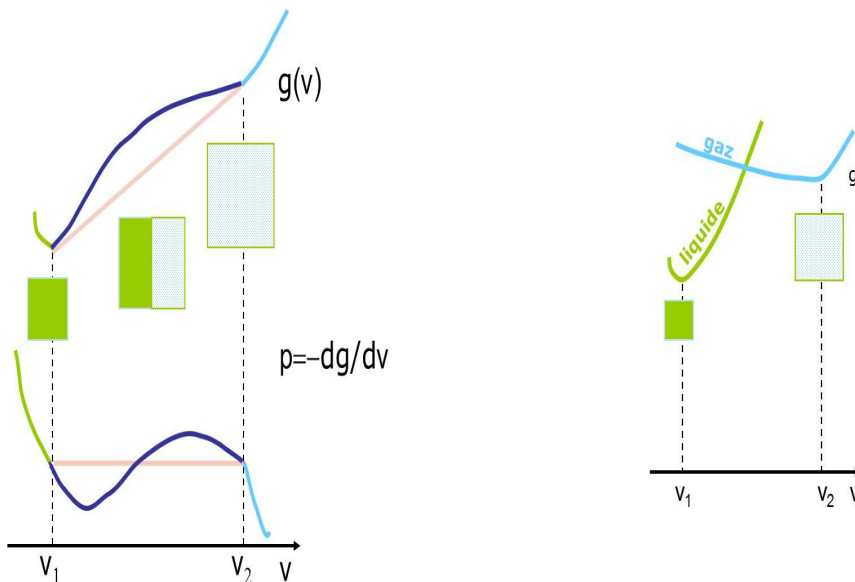
We have worked in the previous lecture in the grand-canonical ensemble. Let us consider for simplicity the case of symmetric matter, characterized by a unique chemical potential. In the grand-canonical ensemble, the thermodynamic potential is given by the Gibbs free energy (or free enthalpy), given by:

$$G = -T \ln Z_{\beta\mu}(V) = E - TS - \mu A \quad . \quad (1.1)$$

At the thermodynamic limit we can write  $G(V) = Ag(V/A) = g(v)$ . The definition of pressure then implies:

$$p = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = - \frac{\partial G}{\partial V} = - \frac{dg}{dv} \quad . \quad (1.2)$$

This relation means that, if the pressure presents a slope inversion, then  $g$  must show a convexity anomaly, as shown in the left part of the following figure.



Schematic representation of the behavior of the thermodynamic potential and of the pressure, in the case of a first order liquid-gas phase transition.

From the physical viewpoint, such a convexity anomaly corresponds to the fact that the system can exist in two different forms (or *phases*) ; in each of them, the enthalpy is minimal for a well defined density value, a value which is different for the two phases, and which depends on temperature. This is schematically shown in the right part of the figure above. For intermediate values between the two equilibrium solutions, the enthalpy is concave and the pressure decreases for increasing density.

The straight lines in the figure correspond to a separation of the system into two parts, L and G, each of them characterized by the equilibrium values  $v_1$  et  $v_2$  of the two phases :  $A=A_L+A_G$ ,  $V=A_L v_1+A_G v_2$ .

Indeed the free enthalpy corresponding to such a phase separation can be written as:

$$G = G_L + G_G = A_L g(v_1) + A_G g(v_2) \quad . \quad (1.3)$$

Dividing this expression by the total particle number we obtain the equation of a straight line :

$$g(v) = \frac{A_L}{A} g(v_1) + \frac{A_G}{A} g(v_2) = \frac{g(v_1) - g(v_2)}{v_1 - v_2} v - \frac{v_1 g(v_2) - v_2 g(v_1)}{v_1 - v_2} \quad , \quad (1.4)$$

where we have used  $v = \frac{V}{A} = \frac{A_L}{A} v_1 + \left(1 - \frac{A_L}{A}\right) v_2$ .

The solution corresponding to phase mixing produces a linear variation of the free enthalpy as a function of the volume. This free enthalpy is by definition smaller than the free enthalpy corresponding to the homogeneous system, the coexistence solution is thus preferred at equilibrium. This solution corresponds to a plateau in the pressure, typical sign of a first order phase transition.

It is interesting to observe that this reasoning can be extended to any generic observable  $\Phi = \langle \Phi \rangle / A$ . If the partition sum associated to a constraint applied on this variable  $\ln Z(\Phi)$  changes its convexity, then we can conclude that  $\Phi$  is the *order parameter* of a first order phase transition, consisting in sharing the system into two components characterized by different  $\Phi$  values.

To reproduce the good equilibrium solution, it is therefore necessary to replace the equation of state presenting a slope inversion, with the one obtained after performing the tangent construction of phase equilibrium. From the practical viewpoint, this tangent construction corresponds to join the two points  $v_1, v_2$  characterized by the two conditions :

$$\begin{aligned} p(v_1) &= p(v_2) = p_t \\ g(v_1) - p_t v_1 &= g(v_2) - p_t v_2 \end{aligned} \quad (1.5)$$

The first condition insures that the two phases have the same value for the intensive variables, the second one insures that the straight line  $p=p_t$  corresponding to the phase transition is tangent to the free enthalpy curve. This second condition can also be written as:

$$p_t = \frac{g(v_1) - g(v_2)}{v_2 - v_1} = -\frac{1}{\Delta v} \int_{v_1}^{v_2} dv \frac{dg}{dv} = \frac{1}{\Delta v} \int_{v_1}^{v_2} p dv \quad (1.6)$$

We can recognize the equal area *Maxwell construction*. The coexistence region is indicated by the region delimited by a dotted line in the figure. We can remark that a coexistence region

exists even at zero temperature, where the liquid (that is: the nucleus is at equilibrium with a gas of zero density (that is: it is isolated)). Increasing the temperature, the gas density increases and the liquid one decreases, up to the point where the two are characterized by the same density. This point defines the *critical temperature*, also represented in the figure. The *spinodal curve* is defined by the inversed slope of the pressure.

$$dp/d\rho < 0 . \quad (1.7)$$

The critical point is the terminating point of both the coexistence and the spinodal region, and can therefore be determined by the condition:

$$dp/d\rho = d^2p/d\rho^2 = 0 . \quad (1.8)$$

Above the critical temperature, the system is in a single fluid phase, and the isotherms are monotonic functions.

## 2. Nuclear phase coexistence in the canonical ensemble

We have mentioned in the previous section that the phase coexistence construction can be applied to different observables associated to different thermodynamic potentials, which represent the order parameters of the transition. In the case of the nuclear phase transition, two order parameters exist, namely the volume  $V$  and the particle number  $N$ . This is the same for the liquid-gas phase transition of ordinary fluids, and this is the reason why the nuclear phase transition is called a liquid-gas (LG) phase transition, even if obviously we do not have any liquid nor any gas, but only nuclear matter. To illustrate the existence of different order parameters, we can repeat the tangent construction of the previous section using the observable given by the particle number. At the thermodynamic limit, all extensive observables diverge, and one has to consider observable densities. This means that the particle number has to be replaced by the particle density. The associated thermodynamic potential is the Helmotz free energy, obtained from the Gibbs free energy of the previous section by a Legendre transform with respect to the particle number:

$$F = -T \ln Z_{\beta\mu}(V) + \mu A = E - TS \quad . \quad (2.1)$$

To avoid the thermodynamic divergence, we have to consider the free energy density given by

$$f(\rho) = -T \ln z_{\beta\mu} + \mu\rho = \varepsilon(\rho) - Ts(\rho) \quad . \quad (2.2)$$

The reasoning of the previous chapter can be repeated simply replacing the reduced volume  $v$  with its inverse  $\rho = v^{-1}$ . Specifically, the convexity in the free energy density corresponds to a backbending of its first derivative, the chemical potential. This convexity can be cured if we consider the tangent construction defined by the straight line:

$$f_{\max}(\rho) = \frac{\rho - \rho_2}{\rho_1 - \rho_2} f(\rho_1) + \frac{\rho - \rho_1}{\rho_1 - \rho_2} f(\rho_2) \quad (2.3)$$

This linear combination can be physically obtained by separating the system in two macroscopic inhomogeneous portions  $V=V_L+V_G$  characterized by the two density values  $\rho_1$  and  $\rho_2$ :

$$F = Vf = V_L f(\rho_1) + V_G f(\rho_2) \quad . \quad (2.4)$$

The equations defining the two densities corresponding to the two phases become:

$$\begin{aligned} \mu(\rho_1) &= \mu(\rho_2) = \mu_t \\ f(\rho_1) - \mu_t \rho_1 &= f(\rho_2) - \mu_t \rho_2 \end{aligned} \quad , \quad (2.5)$$

where  $\mu = df / d\rho$ . We can remark that the second condition can be equivalently written as:

$$g(v_1) = g(v_2) = \frac{T \ln Z_{\beta\mu}(V)}{V} = T \frac{\partial \ln Z_{\beta\mu}(V)}{\partial V} = p_t \quad , \quad (2.6)$$

which means again as in the previous section that the two phases have the same pressure. The presence of a convexity implies that there must be density domain where

$$\frac{d^2 f}{d\rho^2} = \frac{d\mu}{d\rho} < 0 \quad . \quad (2.7)$$

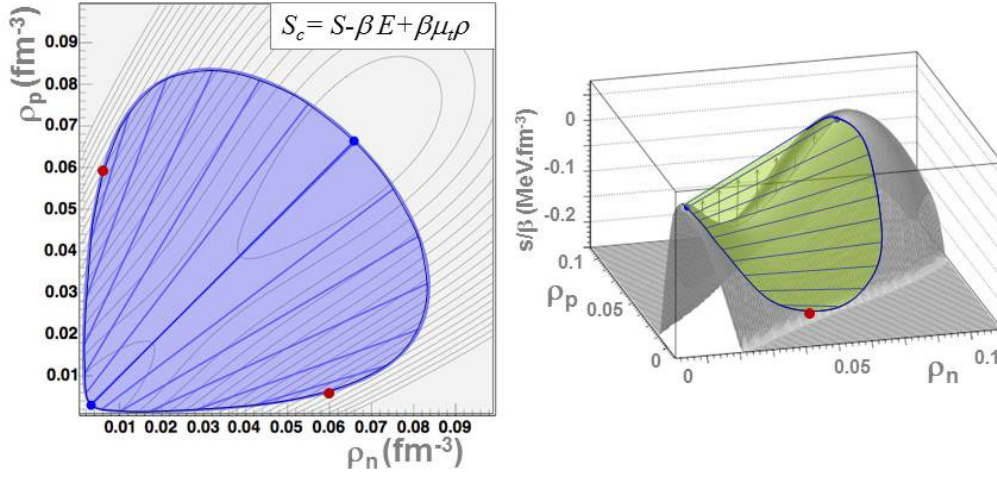
This condition defines the *instability or spinodal* region.

### 3. Extension to a two –fluids system

In the demonstration of the previous sections we have considered for simplicity the case of a single type of particles, leading to a single density  $\rho$ . This can be used for nuclear matter, which is constituted of protons and neutrons, only in the case of symmetric matter, where the proton and neutron density are the same and they can be replaced by a single variable giving the nucleonic number or baryonic density. The generalization to asymmetric matter implies that the thermodynamic potential is a two-variable function and the tangent construction has to be done in a two-dimensional space. As a consequence, the straight line is replaced by a plane surface. As a function of the proton and neutron densities  $\rho_n, \rho_p$  the equations (2.5) are replaced by a system of 4 coupled equations, whose solution gives the lower  $(\rho_{n1}, \rho_{p1})$  and upper  $(\rho_{n2}, \rho_{p2})$  limits of the coexistence zone :

$$\begin{aligned} \mu_n(\rho_{n1}, \rho_{p1}) &= \mu_n(\rho_{n2}, \rho_{p2}) = \mu_{nt} \\ \mu_p(\rho_{n1}, \rho_{p1}) &= \mu_p(\rho_{n2}, \rho_{p2}) = \mu_{pt} \\ p(\rho_{n1}, \rho_{p1}) &= p(\rho_{n2}, \rho_{p2}) = p_t \\ f(\rho_{n1}, \rho_{p1}) - \mu_{nt} \rho_{n1} - \mu_{pt} \rho_{p1} &= f(\rho_{n2}, \rho_{p2}) - \mu_{nt} \rho_{n2} - \mu_{pt} \rho_{p2} \end{aligned} \quad (3.1)$$

As an example the following figure shows the coexistence zone of asymmetric nuclear matter calculated at a representative temperature of 10 MeV, in the framework of the self-consistent mean-field theory.



*Inverse of the free energy density  $-f$  (right), and the same quantity divided by the temperature  $-\beta f$  (left) as a function of the proton and neutron density, for a temperature  $T=10$  MeV. In the two figures a straight line  $\beta \mu_i \rho$  was subtracted to better evidence the convexity. The tangent construction (Gibbs construction) is indicated, as well as the direction of phase separation, defined by a constant value for the intensive variables. The red points represent critical points. The calculation is done in the self-consistent mean-field theory using the Sly230a effective interaction.*

We can see that for symmetric matter the tangent construction follows the diagonal in the density plane: both the high and low density phase are symmetric in isospin. Conversely, for neutron rich system, the direction of phase separation has a higher slope with respect to the line of constant isotopic composition  $\rho_n = a \rho_p$ : this means that the low density phase is more neutron rich than the high density phase. The opposite is true for proton rich matter, meaning that the low density phase is systematically more isospin asymmetric than the high density phase: it is the *isospin fractionation* phenomenon.

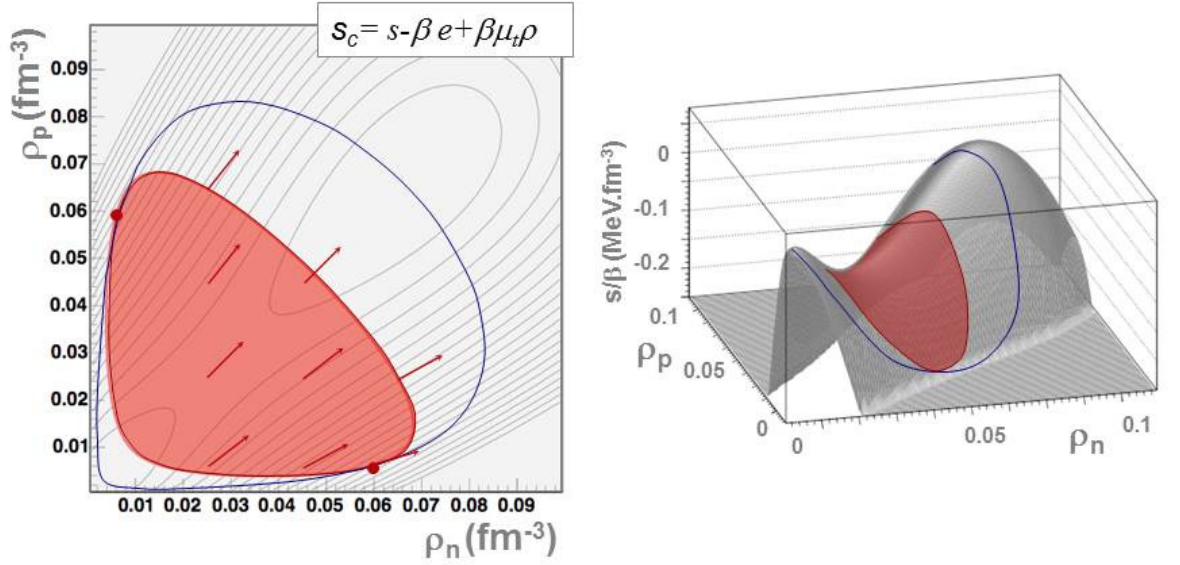
In two dimensions, the curvature function is replaced by a curvature matrix:

$$C = \begin{pmatrix} \frac{\partial \mu_n}{\partial \rho_n} & \frac{\partial \mu_n}{\partial \rho_p} \\ \frac{\partial \mu_p}{\partial \rho_n} & \frac{\partial \mu_p}{\partial \rho_p} \end{pmatrix} \quad (3.2)$$

and the instability condition (2.7) is replaced by the condition

$$\det C < 0 \quad (3.3)$$

which defines the two-dimensional spinodal zone. The spinodal region, in the same conditions as for the coexistence region above, is represented in the figure below.



*Inverse of the free energy density  $-f$  (right), and the same quantity divided by the temperature  $-\beta f$  (left) as a function of the proton and neutron density, for a temperature  $T=10$  MeV. In the two figures a straight line  $\beta \mu_t \rho$  was subtracted to better evidence the convexity. The tangent construction (Gibbs construction) is indicated by a blue curve. The spinodal region is indicated by the red region, as well as the direction of instability, corresponding to the direction of inverse convexity of the thermodynamic potential. The red points represent critical points. The calculation is done in the self-consistent mean-field theory using the Sly230a effective interaction.*

#### 4. Finite size fluctuations

Inside the spinodal region, an homogeneous system will be unstable with respect to phase separation. Since the two different phases correspond to different densities, we can expect that this instability corresponds to the spontaneous amplification of density fluctuations. In a finite system as an excited atomic nucleus a phase separation is not possible, but we can expect that a similar instability with respect to density fluctuations may survive on a smaller spatial scale. For this reason, in this section we turn to examine how homogeneous matter reacts to a density inhomogeneity.

The local free energy density can in principle depend on local densities as well as on density gradients

$$f(\vec{r}) = f_0(\rho_n, \rho_p) + \sum_{q,q'} C_{qq'} \nabla \rho_q \nabla \rho_{q'} + \frac{e^2}{4\pi\epsilon_0} \int d\vec{r}' \frac{\rho_p(\vec{r}')}{|\vec{r} - \vec{r}'|} + O(\nabla \rho_q)^3 \quad (4.1)$$

We consider an arbitrary fluctuation  $\rho_q(\vec{r}) = \rho_q^0 + \delta\rho_q(\vec{r})$ . Using the completeness of the plane wave basis we can write:

$$\delta\rho_q(\vec{r}) = \int d^3k a_q(\vec{k}) e^{i\vec{k} \cdot \vec{r}} + c.c. \quad (4.2)$$

with the condition  $a_q(\vec{k}) = a_q^*(-\vec{k})$  which insures that the density is a real function. The fluctuation is subject to the condition of particle number conservation

$$\int d^3r \delta\rho_q(\vec{r}) = 0 \quad (4.3)$$

The density fluctuation leads to a free energy variation:

$$f(\vec{\rho}) = f(\vec{\rho}_0) + \sum_q \frac{\partial f}{\partial \rho_q} \delta\rho_q + \frac{1}{2} \sum_{qq'} \frac{\partial^2 f}{\partial \rho_q \partial \rho_{q'}} \delta\rho_q \delta\rho_{q'} \quad (4.4)$$

where we have used the notation  $\vec{\rho} = (\rho_n, \rho_p)$ . We compute the total free energy variation  $\delta F = \int d\vec{r} \delta f(\vec{\rho}(\vec{r}))$ ,  $\delta f(\vec{r}) = f(\vec{r}) - f(\vec{\rho}_0)$ . After some algebra we get:

$$\frac{\delta F}{V} = \delta f = \sum_{qq'} \frac{a_q a_{q'}^* + a_q^* a_{q'}}{2} \left[ \frac{\partial \mu_q}{\partial \rho_{q'}}(\vec{\rho}_0) + 2C_{qq'} k^2 + \frac{4\pi e_q e_{q'}}{k^2} \right] = \vec{a}^T C \vec{a} \quad (4.5)$$

## 5. Applications

### a. Dynamics of the phase transition.

In the following we consider different applications of the free energy variation equation (4.5). The simplest case consists in considering an uncharged infinite system with a single density (symmetric nuclear matter). Eq.(4.5) reads:

$$\delta f = a^2 \left( \frac{d\mu}{d\rho} + 2Ck^2 \right) \quad (5.1)$$

If we put  $k=0$  we recover the result of Eq.(2.7): a macroscopic (that is: of infinite wavelength  $\lambda=2\pi/k$ ) fluctuation leads to an increase of the free energy density if the susceptibility  $d\mu/d\rho > 0$ ; this is not thermodynamically favorable and the fluctuation will be suppressed. If on the contrary  $d\mu/d\rho < 0$ , that is inside the spinodal region, such a fluctuation is preferred in terms of free energy, and will be spontaneously increased in amplitude. This phenomenon represents the mechanism of phase separation (*spinodal decomposition*) in a simple fluid. If the system is inside the spinodal region, a finite  $k$  fluctuation will also lead to a free energy decrease if

$$\lambda^2 \geq -4\pi^2 C \left( \frac{d\mu}{d\rho} \right)^{-1} \quad (5.2)$$

This result is easy to understand: if the energy functional contains a (repulsive) gradient term, as it is the case for the nuclear functional, a density fluctuation of a too short wavelength is too expensive in terms of surface energy and will not be spontaneously amplified. Long wavelengths are still unstable, but the highest free energy gain is obtained with the macroscopic  $k=0$  fluctuation: phase separation leads to a more favorable free energy balance than smaller fluctuations as cluster formation.

### b. Two-dimensional spinodal

In the case of asymmetric nuclear matter composed of protons and neutrons, but still uncharged, the Coulomb term is zero and the curvature matrix defined by Eq.(4.5) reads:

$$C = \begin{pmatrix} \frac{\partial \mu_n}{\partial \rho_n} & \frac{\partial \mu_n}{\partial \rho_p} \\ \frac{\partial \mu_p}{\partial \rho_n} & \frac{\partial \mu_p}{\partial \rho_p} \end{pmatrix} + 2k^2 \begin{pmatrix} C_{nn} & C_{np} \\ C_{pn} & C_{pp} \end{pmatrix} \quad (5.3)$$

We can recognize the same curvature matrix that we had in the space of densities (recall here we are in the space of density fluctuations) Eq.(3.2) if  $k=0$ , the same reasoning as in the case of symmetric matter can be done, with the only difference that now the instability is in a two-dimensional space, that is it connects a low density region with a given isospin asymmetry with a high density region with a different isospin asymmetry.

### c. Instabilities in finite nuclei

If we extend the instability study to finite charged nuclei we have to include the electromagnetic contribution to the curvature matrix:

$$C = \begin{pmatrix} \frac{\partial \mu_n}{\partial \rho_n} & \frac{\partial \mu_n}{\partial \rho_p} \\ \frac{\partial \mu_p}{\partial \rho_n} & \frac{\partial \mu_p}{\partial \rho_p} \end{pmatrix} + 2k^2 \begin{pmatrix} C_{nn} & C_{np} \\ C_{pn} & C_{pp} \end{pmatrix} + \frac{4\pi e^2}{k^2} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \quad (5.4)$$

We can see that  $k=0$  is not an unstable mode any more, because of the long-range Coulomb energy which disfavors long range proton density fluctuations. Still a wave number domain

$k_{\min} \leq k \leq k_{\max}$  exists, which corresponds to the instability condition  $\det C < 0$ : a phase transition cannot occur, but fluctuations of finite size can still be energetically favorable in the density domain that corresponds to the phase transition in the bulk limit. This finite size instability is at the origin of the multi-fragmentation phenomenon .

### d. Instabilities in neutron star matter

The existence of a thermodynamic limit imposes that the bulk system is uncharged, because the energy density of a charged system is a diverging quantity. From the physical point of view, if macroscopic charges are present in the bulk of matter, they give rise to macroscopic electric fields which lead to the displacement of these charges to the macroscopic surface leading to a neutral system. This macroscopic neutrality, which is a simple theoretical assumption in the modelization of nuclear matter, in nature is realized by the presence of negative charges which neutralize the proton charges. Specifically, in the case of the dense matter formed by core collapse supernova explosions and which composes neutron stars, the electroneutrality is guaranteed by the presence of a uniform background of completely delocalized electrons which exactly compensate the proton charge :

$$\int d^3r \rho_p(\vec{r}) = \int d^3r \rho_e(\vec{r}) \quad (5.5)$$

If matter is uniform, this condition implies  $\rho_e = \rho_p$ . The free energy density has to account for the extra contribution of the electrons. In the mean-field approximation, this contribution is additive and we can write

$$f = f_N(\rho_n, \rho_p) + f_e(\rho_e = \rho_p) \quad (5.5)$$

This extra contribution modifies the curvature matrix as

$$C = \begin{pmatrix} \frac{\partial \mu_n}{\partial \rho_n} & \frac{\partial \mu_n}{\partial \rho_p} \\ \frac{\partial \mu_p}{\partial \rho_n} & \frac{\partial \mu_p}{\partial \rho_p} + \frac{\partial \mu_e}{\partial \rho_e} \end{pmatrix} . \quad (5.6)$$

Electrons being a degenerate ultrarelativistic gas, this extra term is positive and typically bigger than the other matrix elements: this means that the condition  $\det C < 0$  is more

difficult to achieve, and the instability is quenched. In realistic numerical applications, the inclusion of the electrons in the calculation makes the phase transition completely disappear. This result is easy to understand: a macroscopic density fluctuation leads to a macroscopic proton density fluctuation. Such a fluctuation leads to a macroscopic charge, that is a diverging contribution of the coulomb energy, unless it is compensated by an identical electron fluctuation. Electrons being strongly incompressible, this latter has a free energy cost that overcomes the free energy gain given by the phase transition.

This reasoning does not exclude that finite size fluctuations can take place in stellar matter: indeed the condition (5.5) is not a local condition, and does not exclude the presence of charged microscopic regions.

If the fluctuation has a finite wavelength, the three densities are independent variables and the curvature matrix is a three dimensional matrix associated to the independent variations of neutrons, protons, and electrons. It reads:

$$C = \begin{pmatrix} \frac{\partial \mu_n}{\partial \rho_n} & \frac{\partial \mu_n}{\partial \rho_p} & 0 \\ \frac{\partial \mu_p}{\partial \rho_n} & \frac{\partial \mu_p}{\partial \rho_p} & 0 \\ 0 & 0 & \frac{\partial \mu_e}{\partial \rho_e} \end{pmatrix} + 2k^2 \begin{pmatrix} C_{nn} & C_{np} & 0 \\ C_{pn} & C_{pp} & 0 \\ 0 & 0 & 0 \end{pmatrix} + \frac{4\pi e^2}{k^2} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & -1 \\ 0 & -1 & 1 \end{pmatrix} \quad (5.7)$$

The condition  $\det C < 0$  admits again an ensemble of solutions  $k_{\min} \leq k \leq k_{\max}$ . Because of the high value of the electron compressibility, the numerical solution of this equation leads to wave numbers values very close to the solutions of Eq.(5.4). This means that we can expect in stellar matter nuclear clusters of sizes comparable to the ones of laboratory nuclei.

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## Exercices

1. Consider the simplified nuclear equation of state :  $p = \rho T - A\rho^2 + 2C\rho^3$ 
  - a. Evaluate A and C in order to reproduce the empirical energy per particle of symmetric nuclear matter  $e=-16$  MeV at the saturation density  $\rho = \rho_0$ .
  - b. Calculate the value of the state variables at the critical point  $\rho_c, T_c, p_c$ .
  - c. Express the equation of state in terms of the reduced state variables  $\pi = p/p_c, \tau = T/T_c, \nu = \rho/\rho_c$ .
  - d. The Van der Waals equation of state is written as :  $p = \frac{\rho T}{1 - b\rho} - a\rho^2$ . Compare the functional form of the two equations of state expressed in terms of reduced variables.
  - e. Determine the equation of the spinodal curve.
  - f. Determine the equation of the liquid-gas coexistence curve.