

Lectures on Spinodal Instabilities in Phase Transitions: Solutions

Jørgen Randrup [last modified August 31, 2012]

I-1

Thermodynamic limit: Consider uniform matter in a volume V ; its total energy is E and it contains a total of N “particles”. In the thermodynamics limit, $V \rightarrow \infty$, the physical properties depend only on the intensive quantities $\varepsilon \equiv E/V$ (the energy density) and $\rho \equiv N/V$ (the number density); so the entropy is $S(V, E, N) = V\sigma(\varepsilon, \rho)$ where $\sigma \equiv S/V$ is the entropy density.

1. Show that $1/T = \partial_E S(V, E, N)_{VN}$ is given by $\beta(\varepsilon, \rho) = \partial_\varepsilon \sigma(\varepsilon, \rho)$ and the quantity $-\mu/T = \partial_N S(V, E, N)_{VE}$ is given by $\alpha(\varepsilon, \rho) = \partial_\rho \sigma(\varepsilon, \rho)$.

$$\beta : \partial_E S(V, E, N)_{VN} = \partial_E V \sigma(E/V, N/V) = V \partial_\varepsilon \sigma(\varepsilon, \rho) \partial_E (E/V) = \partial_\varepsilon \sigma(\varepsilon, \rho)$$

$$\alpha : \partial_N S(V, E, N)_{VE} = \partial_N V \sigma(E/V, N/V) = V \partial_\rho \sigma(\varepsilon, \rho) \partial_N (N/V) = \partial_\rho \sigma(\varepsilon, \rho)$$

2. Show that $p/T = \partial_V S(V, E, N)_{EN}$ is given by $\pi(\varepsilon, \rho) = \sigma(\varepsilon, \rho) - \beta(\varepsilon, \rho)\varepsilon - \alpha(\varepsilon, \rho)\rho$.

$$\begin{aligned} \pi : \partial_V S(V, E, N)_{EN} &= \partial_V V \sigma(E/V, N/V) \\ &= \sigma(\varepsilon, \rho) + V \partial_\varepsilon \sigma(\varepsilon, \rho) \partial_V (E/V) + V \partial_\rho \sigma(\varepsilon, \rho) \partial_V (N/V) \\ &= \sigma(\varepsilon, \rho) - V \beta E/V^2 - V \alpha N/V^2 = \sigma(\varepsilon, \rho) - \beta(\varepsilon, \rho)\varepsilon - \alpha(\varepsilon, \rho)\rho \end{aligned}$$

I-2

Canonical scenario: In the canonical scenario the independent variables are ρ and T and the basic function is the free energy density $f = \varepsilon - T\sigma$. Show that the chemical potential and the entropy density can be obtained as $\mu_T(\rho) = \partial_\rho f_T(\rho)$ and $\sigma_T(\rho) = -\partial_T f_T(\rho)$; show furthermore that the pressure is $p_T(\rho) = \rho^2 \partial_\rho (f_T(\rho)/\rho)$.

See how f responds to a variation in ρ and ε , using $\partial_\varepsilon \sigma = \beta = 1/T$ and $\partial_\rho \sigma = \alpha = -\mu/T$:

$$\delta f = \delta \varepsilon - T \delta \sigma - \sigma \delta T = \delta \varepsilon - T[\partial_\varepsilon \sigma \delta \varepsilon + \partial_\rho \sigma \delta \rho] - \sigma \delta T = \mu \delta \rho - \sigma \delta T,$$

so $(\partial f / \delta T)_T \rho = \mu$ and $(\partial f / \delta T)_\rho = -\sigma$. Furthermore, $\rho^2 \partial_\rho (f_T(\rho)/\rho) = \rho^2 [\mu_T(\rho)/\rho - f_T(\rho)/\rho^2] = \mu_T(\rho)\rho - f_T(\rho) = T[\sigma_T(\rho) - \beta \varepsilon_T(\rho) - \alpha_T(\rho)\rho] = T(p_T(\rho)/T) = p_T(\rho)$.

I-3

Phase coexistence: Assume that the free energy density $f_T(\rho)$ is locally concave. Then there must exist two densities, $\rho_1(T)$ and $\rho_2(T)$, at which the tangents to $f_T(\rho)$ coincide.

1. Show that then the chemical potentials at ρ_1 and ρ_2 are equal.

The chemical potential is given by $\mu_T(\rho) = \partial_\rho f_T(\rho)$, *i.e.* it is the slope of the curve $f_T(\rho)$, so it is obviously the same at the two tangent points, $\mu_T(\rho_1) = \mu_T(\rho_2) = \mu_0(T)$.

2. Show that the corresponding two pressures are also equal.

The general relation $\pi \equiv p/T = \sigma - \beta\varepsilon - \alpha\rho$ together with the definition $f \equiv \varepsilon - T\sigma$ imply that the pressure is given by $p_T(\rho) = \mu\rho - f_T(\rho)$. Therefore the pressure difference is given by $p_T(\rho_2) - p_T(\rho_1) = f_T(\rho_1) + (\rho_2 - \rho_1)\mu_0 - f_T(\rho_2)$ which vanishes because f at one of the touching densities can be obtained by extrapolating from the other touching density along the common tangent having the slope μ_0 .

Thus a common tangent guarantees that both μ and p match, hence that the corresponding two phases are therefore in mutual thermodynamic equilibrium: $T_1 = T_2$, $\mu_1 = \mu_2$, $p_1 = p_2$.

I-4

Interface profile: Consider two coexisting phases of bulk matter having a common interface. The interface profile $\rho(x)$ is determined by the equation $C\partial_x^2\rho(x) = \mu_T(\rho(x)) - \mu_0$. This equation is mathematically equivalent to that governing the motion $\xi(t)$ of a particle in a potential, $M\partial_t^2\xi = \partial_\xi U(\xi)$, identifying x with the ‘time’ t and ρ with the ‘position’ ξ ; C is then the ‘mass’ M , while $-\Delta f_T(\rho) = f_T^M(\rho) - f_T(\rho)$ is the ‘potential’ $U(\xi)$. Show that the limiting behavior is $\xi \rightarrow \rho_1$ and $\partial_t\xi \rightarrow 0$ for $t \rightarrow -\infty$ and $\xi \rightarrow \rho_2$ and $\partial_t\xi \rightarrow 0$ for $t \rightarrow +\infty$. Furthermore, show that energy conservation yields the relation $\frac{1}{2}C(\partial_x\rho)^2 = \Delta f_T(\rho(x))$.

The potential vanishes at both end points, $U(\xi_i) = 0$, because $\Delta f_T(\rho_i) = 0$. Furthermore, $\rho(x)$ must approach the bulk values far away from the interface, so $\partial_x\rho(x)$ must approach zero, equivalent to $\xi(t) \rightarrow 0$ for $t \rightarrow \pm\infty$. The sum of kinetic and potential energy is constant in time; the constant is zero because both quantities vanish for $t \rightarrow \pm\infty$. Thus there is neither potential nor kinetic energy in these limits, so the total energy is zero. Consequently, the kinetic energy equals minus the potential energy, $\frac{1}{2}(\partial_t\xi)^2 = -U(\xi)$, *i.e.* $\frac{1}{2}C(\partial_x\rho)^2 = \Delta f_T(\rho(x))$.

II-1

Isotropic flow in N dimensions: If the spatial variation of the viscosity coefficients η (shear) and ζ (bulk) may be ignored, the Euler equation becomes $\nabla \cdot \mathbf{T} = \nabla p - \eta\Delta\mathbf{v} - [\frac{1}{3}\eta + \zeta]\nabla(\nabla \cdot \mathbf{v})$, where $\mathbf{T}(\mathbf{r}, t)$ is the spatial part of the stress tensor $T^{\mu\nu}$ and $\mathbf{v}(\mathbf{r}, t)$ is the local flow velocity.

1. Show that for an isotropic expansion [$\rho(\mathbf{r}) = \rho(r)$ and $\mathbf{v}(\mathbf{r}) = v(r)\hat{\mathbf{r}}$] the dissipative term in the Euler equation contains η and ζ only in the combination $\xi = \frac{4}{3}\eta + \zeta$, in any spatial dimension N .

It is advantageous to use spherical coordinates, so $\nabla = \hat{\mathbf{r}}\partial_r + \dots$, where only the radial part is relevant due to the rotational symmetry. So $\nabla \cdot \mathbf{r} = N$, $\nabla r = \hat{\mathbf{r}}$, $\nabla \cdot \hat{\mathbf{r}} = (N-1)/r$. Thus, if $\mathbf{F}(\mathbf{r}) \equiv f(r)\hat{\mathbf{r}}$ then $\nabla \cdot \mathbf{F}(\mathbf{r}) = [\partial_r + (N-1)/r]f(r) = r^{1-N}\partial_r r^{N-1}f(r)$ and $\Delta f(r) = \partial_r r^{1-N}\partial_r r^{N-1}f(r)$, so $\Delta\mathbf{v}(\mathbf{r})$ and $\nabla(\nabla \cdot \mathbf{v}(\mathbf{r}))$ are both equal to $\hat{\mathbf{r}}\partial_r r^{1-N}\partial_r r^{N-1}v(r)$ and consequently $\eta\Delta\mathbf{v}(\mathbf{r}) + [\frac{1}{3}\eta + \zeta]\nabla(\nabla \cdot \mathbf{v}(\mathbf{r})) = [\frac{4}{3}\eta + \zeta]\hat{\mathbf{r}}\partial_r r^{1-N}\partial_r r^{N-1}v(r)$.

2. For such isotropic flows in N dimensions, determine the limiting velocity profile $v(r)$ for which the dissipative term in the Euler equation vanishes.

The viscous term vanishes if $\partial_r r^{1-N}\partial_r r^{N-1}v(r) \doteq 0$ which occurs if $\partial_r r^{N-1}v(r) \sim r^{N-1}$. Consequently, we must have $v(r) \sim r$, *i.e.* a Hubble scaling expansion (or contraction).

Thus, because the evolving fluid will adjust its motion so as to reduce (and eventually eliminate) the (entropy producing) viscous term, it will generally approach a Hubble expansion in time.

II-2

Sound speeds: Verify these expressions for the isentropic and isothermal sound speeds:

1. $v_s^2 \equiv (\rho/h)(\partial p/\partial\rho)_s = -(T/h)[h^2\sigma_{\varepsilon\varepsilon} + 2h\rho\sigma_{\varepsilon\rho} + \rho^2\sigma_{\rho\rho}]$, where $s = \sigma/\rho$: Use $\beta\delta p + p\delta\beta = \delta\beta - \beta\delta\varepsilon - \varepsilon\delta\beta - \alpha\delta\rho - \rho\delta\alpha$ to get $\delta p = -T[h\delta\beta + \rho\delta\alpha]$ together with $\delta\beta = \sigma_{\varepsilon\varepsilon}\delta\varepsilon + \sigma_{\varepsilon\rho}\delta\rho$ and $\delta\alpha = \sigma_{\rho\varepsilon}\delta\varepsilon + \sigma_{\rho\rho}\delta\rho$, and then that $\delta s \doteq 0$ requires $\rho\delta\varepsilon = h\delta\rho$.
2. $v_T^2 \equiv (\rho/h)(\partial p/\partial\rho)_T = -(\rho/h)\rho T[\sigma_{\varepsilon\varepsilon}\sigma_{\rho\rho} - \sigma_{\varepsilon\rho}^2]/\sigma_{\varepsilon\varepsilon}$, with $\sigma_\varepsilon \equiv \partial_\varepsilon\sigma$, *et cetera*: When $\delta T = 0$ then $\delta p = -\rho T\delta\alpha$ and $0 \doteq \delta\beta = \sigma_{\varepsilon\varepsilon}\delta\varepsilon + \sigma_{\varepsilon\rho}\delta\rho$ yields $\sigma_{\varepsilon\varepsilon}\delta\varepsilon = -\sigma_{\varepsilon\rho}\delta\rho$ hence also $\delta\alpha = \sigma_{\rho\varepsilon}\delta\varepsilon + \sigma_{\rho\rho}\delta\rho = [\sigma_{\rho\rho} - \sigma_{\varepsilon\rho}^2/\sigma_{\varepsilon\varepsilon}]\delta\rho$ for $\delta T = 0$.