

Nucleation Theory

Joseph Kapusta

University of Minnesota

60'th Karpacz Winter School on Theoretical Physics
Wilhelm and Else Heraeus Physics School

Based on “Finite Temperature Field Theory: Chapter 13” by Kapusta and Gale.

Becker and Döring calculated the nucleation rate of a liquid drop in a supersaturated, dilute gas. It is based on the accretion of molecules by a drop of critical size, meaning that a smaller drop will evaporate while a larger drop will grow.

$$I = \frac{1}{2} n_1 4\pi R_*^2 \exp(-\Delta F_*/T) \sum_j s_j \bar{v}_j n_j \left(\frac{P_j}{n_j \pi T} \right)^{1/2}$$

The sum is over all molecules where $j = 1$ is a monomer, $j = 2$ is a dimer, and so on. The mean speeds are \bar{v}_j , the mean densities are n_j , and the partial pressures are P_j . The s_j are phenomenological sticking factors ranging from 0 to 1. The cost in free energy to form a critical sized droplet is ΔF_* .

The most important factor is the exponential which is a recurring component of all nucleation theories. Note also the factor of the surface area $4\pi R_*^2$. In contrast, when the growth rate is dominated by dissipation, which is the ability to dissipate energy away from the bubble or droplet, the prefactor has only one power of R_* .

The general theory of nucleation developed by Langer. It starts with the introduction of a set of variables $\eta_i, i = 1, \dots, N$, which describe N degrees of freedom of the system of interest. Oftentimes it is convenient to take these to be collective coordinates. The rate

$$I = I_0 \exp(-\Delta F/T)$$

gives the number of critical size droplets created in unit volume in unit time. The activation energy ΔF is given by

$$\Delta F = F\{\bar{\eta}\} - F\{\eta_0\}$$

Here the η_0 represent the initial metastable phase while the $\bar{\eta}$ represent the saddle point. The prefactor I_0 is the product of two terms

$$I_0 = \frac{\kappa}{2\pi} \Omega_0$$

the dynamical prefactor κ (of dimension 1/time) and the statistical prefactor Ω_0 (of dimension 1/length³).

In terms of the eigenvalues $\bar{\lambda}_\alpha$ and $\lambda_\alpha^{(0)}$ of the matrix

$$\frac{\partial^2 F\{\eta\}}{\partial\eta_i\partial\eta_j}$$

evaluated at points $\{\bar{\eta}\}$ and $\{\eta_0\}$, respectively, the statistical prefactor can be written as

$$\Omega_0 = \mathcal{V} \left(\frac{2\pi T}{|\bar{\lambda}_1|} \right)^{1/2} \prod_{\alpha=\alpha_0+2}^N \left(\frac{2\pi T}{\bar{\lambda}_\alpha} \right)^{1/2} \prod_{\alpha=1}^N \left(\frac{\lambda_\alpha^{(0)}}{2\pi T} \right)^{1/2}$$

where \mathcal{V} is the volume of the η -space available for the flux of probability flow. There is just one negative eigenvalue $\bar{\lambda}_1$. There is one zero eigenvalue for each translation invariant degree of freedom.

The dynamical prefactor has been calculated by Langer and Turski and by Kawasaki for a liquid-gas phase transition near the critical point, where the gas is not dilute, to be

$$\kappa = \frac{2\lambda\sigma T}{\ell^2 n_\ell^2 R_*^3}$$

which involves the radius of the critical size droplet R_* , the thermal conductivity λ , the surface free energy σ , the latent heat per molecule ℓ and the density of molecules in the liquid phase n_ℓ .

The interesting physics in this expression is the appearance of the thermal conductivity. In order for the droplet to grow beyond the critical size latent heat must be conducted away from the surface into the gas. For a relativistic system of particles or quantum fields which has no net conserved charge, such as baryon number, the thermal conductivity vanishes. The reason is that there is no rest frame defined by the baryon density to refer to heat transport. Hence this formula obviously cannot be applied to such systems.

Csernai and I generalized the result of Langer, Turski, and Kawasaki to a relativistic system with zero net charge of all types. In this case temperature is the controlling variable. However, extrapolation in energy density ϵ away from the equilibrium states is necessary to describe the metastable states and find the parameters of the critical sized bubble. Before going into details here is the answer for nucleation of a hadronic bubble in the quark–gluon plasma.

$$I = \frac{4}{\pi} \left(\frac{\sigma}{3T} \right)^{3/2} \frac{\sigma(\zeta_H + 4\eta_H/3)R_*}{\xi_H^4(\Delta w)^2} \exp(-\Delta F/T)$$

The η_H and ζ_H are the shear and bulk viscosities which are to be evaluated in the hadronic phase. The correlation length in the hadronic phase is ξ_H . The discontinuity in the enthalpy density (latent heat) between the two phases is Δw .

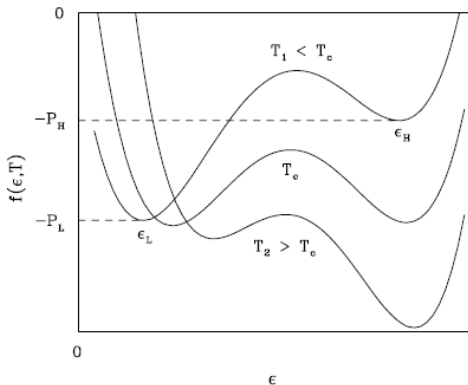
We choose as our basic variables the local energy density and momentum density fields $\epsilon(\mathbf{x}, t)$ and $\mathbf{M}(\mathbf{x}, t)$. For relativistic matter the pressure P is not assumed small compared to energy density ϵ . However, it is assumed that the flow of matter v is much smaller than c (using units where $c = 1$). The free energy F consists of a kinetic energy F_K and an interaction term F_I . The kinetic term is

$$F_K(\epsilon, \mathbf{M}) = \frac{1}{2} \int d^3x w \mathbf{v}^2 = \int d^3x \frac{\mathbf{M}^2}{2w}$$

We shall assume that F_I is a functional of ϵ only, and that it can be written in the form

$$F_I\{\epsilon(\mathbf{x})\} = \int d^3x \left[\frac{1}{2} K (\nabla\epsilon)^2 + f(\epsilon) \right]$$

where $f(\epsilon)$ is the Helmholtz free energy density and $\frac{1}{2} K (\nabla\epsilon)^2$ is the usual gradient energy. The K is a constant to be determined. In this discussion we assume that the temperature T is constant.



Parametrize $f(\epsilon)$ by a fourth order polynomial in ϵ .

$$f(\epsilon) = f_0 + \frac{f_0''(\epsilon - \epsilon_0)^2}{2} - \frac{(\epsilon_L + \epsilon_H - 2\epsilon_0)f_0''}{3(\epsilon_L - \epsilon_0)(\epsilon_H - \epsilon_0)}(\epsilon - \epsilon_0)^3 + \frac{f_0''}{4(\epsilon_L - \epsilon_0)(\epsilon_H - \epsilon_0)}(\epsilon - \epsilon_0)^4$$

where $\epsilon_L(T)$, $\epsilon_H(T)$, $P_L(T)$ and $P_H(T)$ are specified functions of T , and f_0'' is the curvature of f at the top of the barrier located at ϵ_0 ($f_0'' < 0$).

Define $\Delta\epsilon \equiv \epsilon_H - \epsilon_L > 0$ and $\Delta P \equiv P_L - P_H$. In terms of these variables

$$\epsilon_0 = \frac{\epsilon_L + \epsilon_H}{2} + \frac{f_0''(\Delta\epsilon)^3}{12\Delta P} \pm \left[\left(\frac{f_0''(\Delta\epsilon)^3}{12\Delta P} \right)^2 + \frac{(\Delta\epsilon)^2}{4} \right]^{1/2}$$

where the + (-) is chosen when $\Delta P > 0$ ($\Delta P < 0$) and

$$f_0 = -P_H + \frac{f_0''(\epsilon_H - \epsilon_0)^2(\epsilon_H - 2\epsilon_L + \epsilon_0)}{12(\epsilon_L - \epsilon_0)}$$

The stationary point $\{\bar{\eta}\}$ is given by $\mathbf{v}(\mathbf{x}) = 0$ and $\epsilon(\mathbf{x}) = \bar{\epsilon}(\mathbf{x})$, where $\bar{\epsilon}$ satisfies

$$\frac{\delta F_I}{\delta \bar{\epsilon}(r)} = -K\nabla^2 \bar{\epsilon} + \frac{\partial f}{\partial \bar{\epsilon}} = 0$$

For a spherical bubble of L phase surrounded by H phase at $T < T_c$ the energy density $\bar{\epsilon}$ depends only on the distance r from the center of the bubble. Deep inside the bubble the energy density should be ϵ_L ; far away from the bubble the energy density should be ϵ_H . The energy density profile $\bar{\epsilon}(r)$ then describes a smooth transition from one phase to the other. We assume that the surface is located at a distance R from the center which is much greater than the surface thickness.

Introduce a correlation length defined at the top of the barrier by $\xi_0^2 \equiv -K/f_0''$. Then

$$\frac{d^2 \bar{\epsilon}}{dr^2} + \frac{2}{r} \frac{d\bar{\epsilon}}{dr} + \frac{(\bar{\epsilon} - \epsilon_0)(\bar{\epsilon} - \epsilon_L)(\bar{\epsilon} - \epsilon_H)}{\xi_0^2(\epsilon_L - \epsilon_0)(\epsilon_H - \epsilon_0)} = 0$$

Let us find the behavior of the solution in each of three regions.

In the interior

$$\bar{\epsilon}(r) = A_0 + \frac{A_1}{r} \sinh\left(\frac{r}{\xi_L}\right) \approx \epsilon_L \quad \xi_L^2 = \frac{\epsilon_H - \epsilon_0}{\epsilon_H - \epsilon_L} \xi_0^2$$

In the vicinity of the surface

$$\bar{\epsilon}(r) = \epsilon_0 + \frac{A_2}{r} \sin\left(\frac{r - R}{\xi_0}\right)$$

In the exterior

$$\bar{\epsilon}(r) = \epsilon_H - \frac{A_3}{r} \exp(-r/\xi_H) \quad \xi_H^2 = \frac{\epsilon_0 - \epsilon_L}{\epsilon_H - \epsilon_L} \xi_0^2$$

At the critical temperature $f(\epsilon_L) = f(\epsilon_H)$. Then the free energy becomes symmetric, $\epsilon_0 = (\epsilon_L + \epsilon_H)/2$ and $\xi_H^2 = \xi_L^2 = \xi_0^2/2$. In this case the interfacial profile has a nice analytical solution in the planar ($R \rightarrow \infty$) limit:

$$\bar{\epsilon}(z) = \frac{1}{2} \left[\epsilon_L + \epsilon_H + \Delta\epsilon \tanh \left(\frac{z}{2\xi_H} \right) \right]$$

Here the surface is located at $z = 0$ with L phase on the left and H phase on the right.

Suppose that an L phase bubble has formed in the H phase at $T < T_c$ because of statistical fluctuations. The change in free energy of the system is

$$\Delta F = \frac{4\pi}{3} (f_L - f_H) R^3 + 4\pi R^2 \sigma$$

where σ is the surface free energy. For baryon free matter

$$\Delta F = \frac{4\pi}{3} [P_H(T) - P_L(T)] R^3 + 4\pi R^2 \sigma$$

The hadronic droplet is stationary if $\partial_R \Delta F = 0$, which leads to Laplace's formula

$$P_L(T) - P_H(T) = \frac{2\sigma}{R(T)}$$

Thus the activation energy, in our approximation, is

$$\Delta F = \frac{4}{3}\pi\sigma R^2$$

The surface free energy can be calculated from our parametrization of F_I . For a planar interface or for a sphere whose radius is much greater than its surface thickness the formula was given by Cahn and Hilliard.

$$\sigma = K \int_{-\infty}^{\infty} dx \left(\frac{d\bar{\epsilon}}{dx} \right)^2$$

Inserting the solution for the planar interface at T_c , this integral takes the form

$$\sigma = K \left(\frac{\Delta\epsilon}{2} \right)^2 \frac{1}{2\xi_H} \int_{-\infty}^{\infty} dz \frac{1}{\cosh^4(z)} = \frac{K(\Delta\epsilon)^2}{6\xi_H}$$

Now let's find the statistical prefactor. The $\lambda_\alpha^{(0)}$ are eigenvalues of the operator

$$\left. \frac{\delta^2 F_I}{\delta\epsilon(\mathbf{x})\delta\epsilon(\mathbf{x}')} \right|_{e=\epsilon_H} = \left(-K\nabla^2 + \frac{\partial^2 f}{\partial\epsilon_H^2} \right) \delta(\mathbf{x} - \mathbf{x}')$$

By $\partial^2 f/\partial\epsilon_H^2$ we mean the second derivative of f with respect to ϵ at fixed temperature evaluated in the equilibrium H phase. This is a measure of fluctuations in the system. The eigenfunctions are plane waves, with wave vectors \mathbf{q} and eigenvalues

$$\lambda_{\mathbf{q}}^{(0)} = K\mathbf{q}^2 + \frac{\partial^2 f}{\partial\epsilon_H^2}$$

At the saddle point, $\epsilon(\mathbf{x}) = \bar{\epsilon}(r)$, the operator

$$\left. \frac{\delta^2 F_I}{\delta\epsilon(\mathbf{x})\delta\epsilon(\mathbf{x}')} \right|_{e=\bar{\epsilon}(r)} = \left(-K\nabla^2 + \frac{\partial^2 f}{\partial\bar{\epsilon}^2} \right) \delta(\mathbf{x} - \mathbf{x}')$$

is no longer translationally invariant because of the r dependence of $\bar{\epsilon}$. As has been discussed by Langer, the resulting spherically symmetric Schrödinger-like eigenvalue equation has an s -wave ground state with a radial eigenfunction proportional to $d\bar{\epsilon}/dr$ and a negative eigenvalue

$$\bar{\lambda}_1 \approx -2K/R^2 \tag{1}$$

This eigenstate is associated with the instability of the critical bubble against uniform expansions or contractions.

The next states are the three p -waves, with eigenvalues $\bar{\lambda} = 0$, which occur because of the broken translational symmetry. Then there are higher-order partial waves with positive $\bar{\lambda}$ corresponding to volume-conserving deformations of the shape of the droplet. Finally, there is a continuum of nonlocalized eigenfunctions of starting at $\bar{\lambda} = \partial^2 f / \partial \epsilon_H^2$. These eigenfunctions are similar to the states associated with the $\lambda^{(0)}$ in that they describe fluctuations in the bulk plasma, but here these fluctuations are perturbed by the presence of the bubble. This leaves four unpaired $\lambda^{(0)}$'s at the bottom of the spectrum which are not accounted for by the matching. Specifically, we have

$$\lim_{V \rightarrow \infty} \prod_{\beta=1}^4 \left(\frac{\lambda_{\beta}^{(0)}}{2\pi T} \right)^{1/2} = \left(\frac{1}{2\pi T} \frac{\partial^2 f}{\partial \epsilon_H^2} \right)^2$$

remaining as the sole explicit contribution from the complicated products over the α .

The formula for \mathcal{V} , the volume of η space available for the flux of probability flow, has been given by Langer.

$$\mathcal{V} = V \left[\frac{1}{3} \int dr (\nabla \bar{\epsilon})^2 \right]^{3/2} = V \left[\frac{4\pi R^2 \sigma}{3 K} \right]^{3/2}$$

The resulting expression for Ω_0 is

$$\Omega_0 = V \left(\frac{4\pi R^2 \sigma}{3 K} \right)^{3/2} \left(\frac{\pi T R^2}{K} \right)^{1/2} \left(\frac{1}{2\pi T} \frac{\partial^2 f}{\partial \epsilon_H^2} \right)^2$$

Identifying the correlation length ξ_H in the H phase by

$$\frac{1}{K} \frac{\partial^2 f}{\partial \epsilon_H^2} = \frac{1}{\xi_H^2}$$

we can write

$$\Omega_0 = \frac{2}{3\sqrt{3}} \left(\frac{\sigma}{T} \right)^{3/2} \left(\frac{R}{\xi_H} \right)^4 V$$

If one considers the nucleation rate to be per unit volume then the volume V should be divided out of the above expression. Usually we mean the rate per unit volume and so Ω_0 will not include the factor V in subsequent discussion.

We now want to determine the equations of motion of dissipative fluid dynamics for small deviations about the stationary configuration $\epsilon(\mathbf{x}, t) = \bar{\epsilon}(r)$, $\mathbf{v}(\mathbf{x}, t) = 0$. To that end we write $\epsilon = \bar{\epsilon}(r) + \nu(\mathbf{x}, t)$ and $\mathbf{v} = \mathbf{v}(\mathbf{x}, t)$ and linearize the full equations of motion, including the gradient term F_K , in terms of ν and \mathbf{v} .

$$\partial_t \nu = -\nabla \cdot \mathbf{M} = -\nabla \cdot (\bar{w} \mathbf{v})$$

$$\partial_t (\bar{w} \mathbf{v}) = \nabla \bar{\epsilon} [-K \nabla^2 \nu + f'' \nu] + \nabla [(\zeta + 4\eta/3) \nabla \cdot \mathbf{v}]$$

Here and after when we write f , f' or f'' we intend that they be evaluated at the stationary configuration, so that they are complicated functions of r . To determine κ we look for radial perturbations of the form

$$\nu(\mathbf{x}, t) = \nu(r) e^{\kappa t}$$

$$\mathbf{v}(\mathbf{x}, t) = v(r) \hat{r} e^{\kappa t}$$

These radial deviations are governed by the equations of motion

$$\kappa \nu(r) = -\frac{1}{r^2} \frac{d}{dr} [r^2 \bar{w} v(r)]$$

$$\kappa \bar{w} v(r) = -\frac{d\bar{\epsilon}}{dr} \left[-K \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + f'' \right] \nu(r) + \frac{d}{dr} \left[(\zeta + 4\eta/3) \frac{1}{r^2} \frac{d}{dr} (r^2 v(r)) \right]$$

Eliminating $\nu(r)$ using the first equation we obtain a linear, third-order differential equation for the velocity profile

$$\begin{aligned} \kappa^2 \bar{w}v(r) = & -\frac{d\bar{\epsilon}}{dr} \left[K \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) - f'' \right] \left[\frac{1}{r^2} \frac{d}{dr} (r^2 \bar{w}v(r)) \right] \\ & + \frac{d}{dr} \left[\kappa(\zeta + 4\eta/3) \frac{1}{r^2} \frac{d}{dr} (r^2 v(r)) \right] \end{aligned}$$

Note a constraint which follows from the first equation together with the conditions that $v(r)$ vanish at the origin and at infinity

$$\int_0^\infty dr 4\pi r^2 \nu(r) = 0$$

In the interior region, from the origin to within a few correlation lengths of the surface, recall that $\bar{\epsilon}$ is approximately constant. We must require that v and v' vanish at $r = 0$. Consequently, the velocity vanishes in the interior of the bubble.

In the exterior region the energy and enthalpy densities approach their equilibrium values in the bulk H phase. Then the solution with the proper large r behavior is

$$v(r) = C \left(\frac{a_H}{r} + \frac{1}{r^2} \right) e^{-a_H r}$$

where C is a constant and $a_H^2 = \kappa w_H / (\zeta_H + 4\eta_H/3)$.

In the region of the surface, $r \approx R$, the stationary configuration $\bar{\epsilon}(r)$ is varying rapidly and $d\bar{\epsilon}/dr$ is nonzero. To good approximation, in the surface region $v(r)$ satisfies

$$[-K\nabla^2 + f''] v(r) = 0$$

Corrections to this would be second order in the viscosities and it would be inconsistent to keep them. Given the constraint, and that $v(r)$ must go to zero at the origin and at infinity, means the solution to the above equation is

$$v(r) \sim \frac{d\bar{\epsilon}}{dr}$$

This implies that in the surface region

$$v(r) = \frac{D}{r^2 \bar{w}(r)} \int_0^r dr' r'^2 \frac{d\bar{\epsilon}}{dr'}$$

where D is a constant. For distances r exceeding the bubble radius R by more than a few correlation lengths, but less than $2R$, this can be integrated to give

$$v(r) \approx \frac{D \Delta\epsilon R^2}{w_H r^2}$$

The energy flux density which must be transported outwards is $\Delta w dR/dt$. Here we do not distinguish between the difference of energy densities and the difference in enthalpy densities of the two bulk phases because the pressure difference is small compared to the energy density differences. This energy flux must be balanced by that due to dissipation, which is $-(\zeta + 4\eta/3)v dv/dr$. We evaluate the flow velocity just outside the surface of the bubble. Accordingly the derivative is $dv/dr \approx -2v/R$. Therefore energy balance gives us the relation

$$\Delta w \frac{dR}{dt} = 2(\zeta_H + 4\eta_H/3) \frac{v^2}{R}$$

The momentum flux density must be equated to the force per unit area which comes from the Laplace formula

$$\Delta w v^2 = 2\sigma \left(\frac{1}{R_*} - \frac{1}{R} \right) \quad (2)$$

Again, the velocity is to be evaluated just outside the surface.

Using both energy and momentum conservation we can eliminate the velocity and solve for dR/dt ,

$$\frac{dR}{dt} = \frac{4(\zeta_H + 4\eta_H/3)\sigma(R - R_*)}{(\Delta w)^2 R^2 R_*}$$

This is a differential equation for $R(t)$ from which we can read off the value of κ via $R - R_* \propto e^{\kappa t}$. It is

$$\kappa = \frac{4\sigma(\zeta_H + 4\eta_H/3)}{(\Delta w)^2 R_*^3}$$

Venugopalan and Vischer subsequently generalized this result by including nonzero baryon number and diffusion is a rather different approach using the Kotchine conditions, which are a generalization of the Rankine-Hugoniot conditions for shock waves. They found

$$\kappa = \frac{2\sigma[\lambda_H T + 2(\zeta_H + 4\eta_H/3)]}{(\Delta w)^2 R_*^3}$$

This is proportional to a linear combination of the three dissipation coefficients. It reduces to the expression derived here when thermal conduction can be neglected, and it reduces to the expression of Langer and Turski in the nonrelativistic limit and when shear and bulk viscosities are small. The physics limiting the growth of a bubble is the ability to transport energy away from the surface.

The fully relativistic rate for producing a bubble in the lower density L phase within the higher density H phase is

$$I = \frac{2\sigma}{\pi} \left(\frac{\sigma}{3T} \right)^{3/2} \frac{\lambda_H T + 2(\zeta_H + 4\eta_H/3)}{\xi_H^4 (\Delta w)^2} R_* \exp(-\Delta F/T)$$

The formula for the rate for producing a droplet in the higher density H phase within the lower density L phase is clear.

A long time ago, not in a galaxy far far away but right here on Earth, it was thought that the transition between hadron and quarks and gluons was first order. Therefore Csernai and I worked out what should happen dynamically in a high energy heavy ion collisions with zero net baryon number using nucleation theory. Although now out of date, it serves as an example for future calculations. The modelling goes as follows.

The boost invariant hydrodynamic model of Bjorken says that the energy density evolves as

$$\frac{d\epsilon}{dt} = -\frac{w}{t}$$

The energy density in the transition region is

$$\epsilon(T) = h(t)\epsilon_h(T) + [1 - h(t)]\epsilon_q(T)$$

where $h(t)$ is the volume fraction of the hadronic phase at time t with T the temperature at that time.

$$h(t) = \int_{t_c}^t dt' I(T(t')) [1 - h(t')] V(t', t)$$

The $V(t', t)$ is the volume of a hadronic bubble which was nucleated at t' and since grown to that volume at t .

Based on numerical hydrodynamical calculations by Miller and Pantano the velocity of a bubble which slightly exceeds critical size is

$$v(T) \approx 3(1 - T/T_c)^{3/2}$$

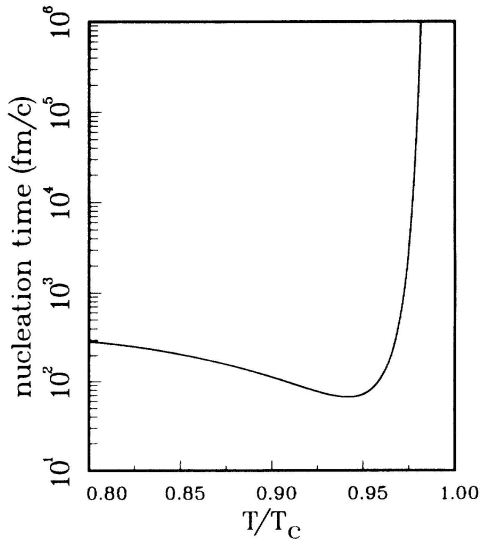
A simple model for bubble growth is

$$V(t', t) = \frac{4\pi}{3} \left[R_*(T(t')) + \int_{t'}^t dt'' v(T(t'')) \right]^3$$

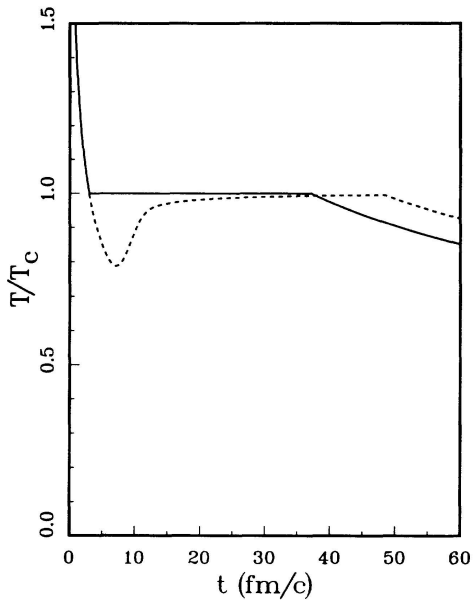
The equation of state was a gas of up and down quarks with a bag constant above T_c and a gas of pions below T_c . The choice of parameters were $B^{1/4} = 235$ MeV, $\sigma = 50$ MeV/fm², $\eta = 14.4T^3$, and $\xi = 0.7$ fm. This gives $T_c = 169$ MeV and a large latent heat.

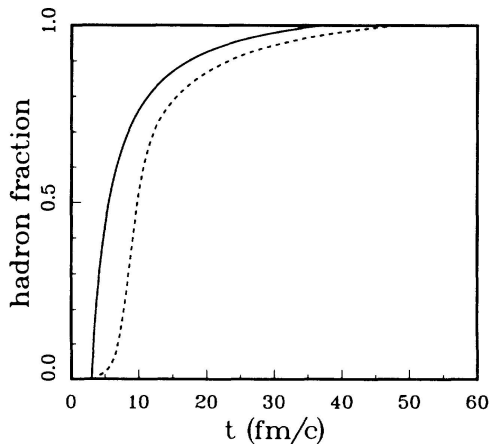
$$P_q = aT^4 - B$$

$$P_h = \frac{3\pi^2}{90} T^4$$



$$\tau_{\text{nucleate}}^{-1} = \frac{4\pi}{3} R_*^3 I$$





Conclusion

- Nucleation of critical sized bubbles or droplets in metastable phases has as the most important factor $\exp(-\Delta F/T)$.
- Classical nucleation theory should be applicable to the formation of droplets in a supersaturated gas when the gas is dilute. The prefactor is quadratic in the radius of the critical sized droplet.
- Nucleation theory based on Langer's approach should be applicable when the gaseous phase is not dilute. In that case energy is carried away from the surface due to viscosity and dissipation to allow the bubble or droplet to grow. The prefactor is linear in the radius of the critical sized droplet.
- These ideas can be used to calculate the nucleation of black holes at finite temperature.
- Quantum nucleation of metastable states can be calculated.