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Nucleation theory

The dynamics of first-order phase transitions has fascinated scientists at least since the time of Maxwell and Van der Waals. Much work on the classical theory of the nucleation of gases and liquids was carried out in the early part of the 1900s, culminating in the theory of Becker and Döring [1]. There were and still are many important applications, such as cloud and bubble chambers, the freezing of liquids, and precipitation in the atmosphere. The modern theory of nucleation was pioneered by Langer [2]. Langer's theory is based in a more fundamental way on the microscopic interactions of atoms and molecules. It can also be applied close to a critical point. Nucleation theory has been extended to relativistic quantum field theory by Coleman and Callan [3] for zero temperature and by Affleck [4] and Linde [5] for finite temperature. A coarse-grained relativistic field theory description was developed by Csernai and Kapusta [6] for finite temperature and extended to finite density by Venugopalan and Vischer [7]. Langer's results are recovered in the nonrelativistic limit. Applications here are to elementary particle phase transitions in the early universe, heavy ion collisions, and even the nucleation of black holes.

The goal of nucleation theory is to compute the probability that a bubble or droplet of the A-phase appears in a system initially in the B-phase near the critical temperature. Homogeneous nucleation theory applies when the system is pure; inhomogeneous nucleation theory applies when impurities cause the formation of bubbles or droplets. For the applications we have in mind, namely the early universe and very-high-energy nuclear collisions, it seems that homogeneous nucleation theory is appropriate. In the everyday world it is usually the opposite; dust or ions in the atmosphere are much more efficient in producing precipitation. Nucleation theory is applicable for first-order phase transitions when the matter is not dramatically supercooled or superheated. If substantial supercooling or superheating is present, or if the phase transition is second-order, then

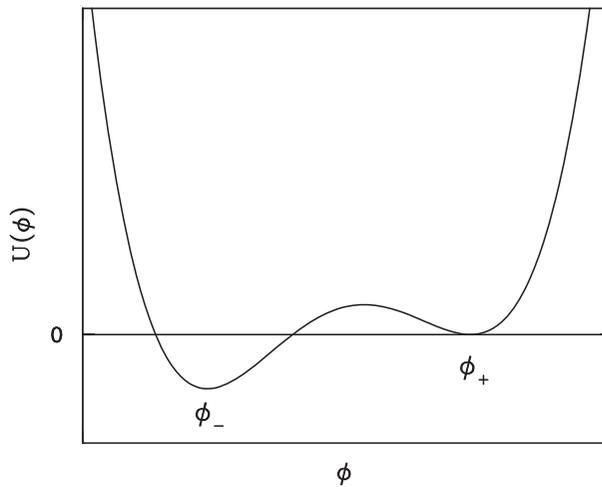


Fig. 13.1. A potential with two nondegenerate minima.

the relevant dynamics is spinodal decomposition. In this chapter we concern ourselves only with homogeneous nucleation theory.

13.1 Quantum nucleation

A relativistic quantum field theory approach has been worked out by Coleman and Callan [3] for nucleation from one vacuum to another. This is essentially a straightforward extension of the semiclassical formula for tunneling through a barrier in quantum mechanics, generalizing from one degree of freedom to many degrees of freedom and then to an infinite number – a field theory. This approach will be illustrated for a single scalar field.

The Lagrangian is

$$\mathcal{L} = \frac{1}{2} \partial_\mu \phi \partial^\mu \phi - U(\phi) \quad (13.1)$$

Suppose that U has a local minimum at ϕ_+ and a global minimum at ϕ_- , with $U(\phi_-) < U(\phi_+)$, as illustrated in Figure 13.1. If the system is at ϕ_+ , the false vacuum, it can tunnel through the barrier to enter the region near the true vacuum, ϕ_- . In nonrelativistic quantum mechanics, the tunneling probability amplitude is dominated by the exponential of minus the action of a trajectory which goes from one side of the barrier to the other. The probability itself is proportional to the exponential of minus the action for a trajectory which begins near ϕ_+ , goes through the barrier, and returns to its starting point (on account of time reversal). In the path integral approach to quantum mechanics, this corresponds to the motion of a point particle in imaginary time, as opposed to real time,

or equivalently to the motion of a particle in the inverted potential. The process of starting near the false vacuum, going through the barrier, and returning to the starting point was called a “bounce” by Coleman.

Although we are interested in the vacuum tunneling rate we can still use the formalism of finite-temperature field theory, taking the zero temperature, or $\beta \rightarrow \infty$, limit in the end. In Euclidean space the classical equation of motion is

$$\frac{\partial^2 \phi}{\partial \tau^2} + \nabla^2 \phi = U'(\phi) \quad (13.2)$$

The boundary conditions we impose are

$$\phi(\mathbf{x}, 0) = \phi(\mathbf{x}, \beta) = \phi_+ \quad (13.3)$$

$$\lim_{|\mathbf{x}| \rightarrow \infty} \phi(\mathbf{x}, \tau) = \phi_+ \quad (13.4)$$

$$\frac{\partial \phi}{\partial \tau}(\mathbf{x}, \tau_0) = 0 \quad (13.5)$$

The first of these means that the bounce begins and ends at the false vacuum. The second means that the bounce is localized, being surrounded by false vacuum. The third means that the field has zero velocity at the time τ_0 , the time at which the field penetrates the barrier: $U(\phi(\mathbf{x}, \tau_0)) = U(\phi_+)$. Solutions to the classical field equation will be dominant in the classical ($\hbar \rightarrow 0$) limit since they have minimal values of the action.

One should expect that the vacuum tunneling solution with the smallest action has $O(4)$ invariance, from the symmetry of the problem. The bounce solution, referred to as $\bar{\phi}$, depends only on the variable $\rho = \sqrt{\tau^2 + \mathbf{x}^2}$. Rather than taking $0 < \tau < \beta$ one may just as well take $-\beta/2 < \tau < \beta/2$. Then the equation of motion simplifies to

$$\frac{d^2 \bar{\phi}}{d^2 \rho} + \frac{3}{\rho} \frac{d\bar{\phi}}{d\rho} = U'(\bar{\phi}) \quad (13.6)$$

The boundary conditions are

$$\lim_{\rho \rightarrow \infty} \bar{\phi}(\rho) = \phi_+ \quad (13.7)$$

$$\frac{\partial \bar{\phi}}{\partial \rho}(0) = 0 \quad (13.8)$$

The last of these is needed to avoid a singularity at the origin. The action is then computed from

$$S = 2\pi^2 \int_0^\infty d\rho \rho^2 \left[\frac{1}{2} \left(\frac{d\bar{\phi}}{d\rho} \right)^2 + U(\bar{\phi}) \right] \quad (13.9)$$

Let us refer to S evaluated with the bounce solution $\bar{\phi}$ as S_B . Since the bounce is a solution to the equation of motion and is localized, it will have finite action.

At zero temperature the system would sit at ϕ_- , where the potential energy is a minimum. Of course there will be quantum corrections to the energy density. The most important of these will arise from fluctuations about ϕ_- . From Chapter 2 we know that we can express the quadratic fluctuations to the partition function around this minimum as

$$N \{ \det[-\partial_\tau^2 - \nabla^2 + U''(\phi_-)] \}^{-1/2} \quad (13.10)$$

where N is a normalization constant. The bounce solution, together with the quadratic fluctuations about it, will contribute

$$N\beta V \exp(-S_B) \{ \det[-\partial_\tau^2 - \nabla^2 + U''(\bar{\phi})] \}^{-1/2} \quad (13.11)$$

where N is the same normalization. This expression neglects complications due to any zero eigenvalues when performing the functional integral. The factor of spacetime volume βV arises from integration over the position of the center of the bounce: it may be centered anywhere, not necessarily at $\tau = 0$, $\mathbf{x} = \mathbf{0}$ as assumed above. The vacuum energy density is computed in the limit $\beta \rightarrow \infty$ from the formula $E_0 = -\partial \ln Z_0 / \partial \beta$. In this semiclassical approximation,

$$\begin{aligned} \ln Z_0 = \ln \left\{ N [-\partial_\tau^2 - \nabla^2 + U''(\phi_-)]^{-1/2} \right\} \\ + \ln \left\{ 1 + \frac{\det[-\partial_\tau^2 - \nabla^2 + U''(\bar{\phi})]^{-1/2}}{\det[-\partial_\tau^2 - \nabla^2 + U''(\phi_-)]^{-1/2}} \exp(-S_B) \right\} \end{aligned} \quad (13.12)$$

Notice that the normalization N drops out from the second logarithm.

The operator $-\partial_\tau^2 - \nabla^2 + U''(\bar{\phi})$ has four zero eigenvalues owing to the invariance of the bounce solution under translation of its center. Thus, if $\bar{\phi}$ is a solution to the classical equation of motion then so are the $\phi_\mu = b\partial_\mu\bar{\phi}$, where b is a constant. The normalization b can be determined as follows. First, since $\bar{\phi}$ is a solution to the classical equation of motion, the action is stationary under general variations, in particular under the infinitesimal scale transformation

$$\delta\bar{\phi} = x_\nu\partial_\nu\bar{\phi} \quad (13.13)$$

Evaluating the action with $\bar{\phi} + \delta\bar{\phi}$ and setting the first-order variation of it to zero, we get

$$\int d^4x (\partial_\mu\bar{\phi})(\partial_\mu\bar{\phi}) = 4 \int d^4x \mathcal{L}(\bar{\phi}) = 4S_B \quad (13.14)$$

Requiring that each ϕ_μ be normalized to unity determines the factor $b = S_B^{-1/2}$.

The functions $\partial_\mu \bar{\phi}$ all have one node, hence none of them represents the lowest state. There must be at least one mode with a negative eigenvalue. Owing to the power 1/2 in (13.12), the bounce solution contributes an imaginary part to the vacuum energy density. This means that the bounce solution is actually a saddle point of the action, not a local minimum.

If we somehow prepare the system in a state at or near ϕ_+ then it will decay by quantum tunneling, and this is reflected in the imaginary part of the energy. If the bounce solution is left out of the sum over states in the partition function then the energy density is real, as it must be if we explicitly sum over the energy eigenstates of the Hamiltonian. If the bounce solution is kept, its contribution should be isolated and identified as an instability of a state that does not belong to the spectrum of the Hamiltonian.

Putting Planck's constant back into our formulae for the moment, we realize that in the semiclassical limit the bounce solution is exponentially suppressed via the factor $\exp(-S_B/\hbar)$. To lowest order in this small quantity, the imaginary part of the energy density is

$$I = \left(\frac{S_B}{2\pi}\right)^2 \left| \frac{\det'[-\partial_\tau^2 - \nabla^2 + U''(\bar{\phi})]}{\det[-\partial_\tau^2 - \nabla^2 + U''(\phi_-)]} \right|^{-1/2} \exp(-S_B) \quad (13.15)$$

where the prime means that the four zero eigenvalues are omitted from the determinant. The first factor arises from the integration over the four zero modes. The factor involving the ratio of determinants has the dimension $1/\text{length}^4$ since four eigenvalues are deleted from one of the operators, yielding an I with the proper dimensions of the number of tunnelings per unit time per unit volume. The exponential is the dominant factor in the tunneling, and is analogous to the Boltzmann factor in producing a critical-sized droplet in the classical nucleation rate.

Generally the classical equation of motion must be solved numerically to obtain the bounce solution, which is then used to compute the bounce action and the tower of eigenvalues of the fluctuation operator. However, in some circumstances one can make a thin-wall approximation to obtain the bounce solution, the action, and the negative eigenvalue. For example, consider the potential

$$U(\phi) = \lambda (\phi^2 - a^2)^2 + \frac{\epsilon}{2a}(\phi - a) \quad (13.16)$$

where ϵ is a small quantity that represents the breaking of the reflection symmetry of the potential. To lowest order in this quantity, $\phi_\pm = \pm a$. The bounce solution has the behavior that it equals $-a$ for $\rho \ll R$ and a

for $\rho \gg R$, and crosses zero at $\rho = R$. This defines the four-dimensional radius of the bounce R . The approximate solution is

$$\bar{\phi}(\rho) = \begin{cases} -a & \rho \ll R \\ a \tanh\left(\frac{\rho - R}{2\xi}\right) & \rho \approx R \\ a & \rho \gg R \end{cases} \quad (13.17)$$

Here $\xi \equiv 1/\sqrt{8\lambda a}$ is the correlation length. This ought to be a good approximation when the wall thickness, characterized by ξ , is much less than the radius R . Substitution into the action yields

$$S_B = -\frac{\pi^2 \epsilon}{2} R^4 + \frac{\pi^2}{12\lambda \xi^3} R^3 \quad (13.18)$$

which displays the competition between the four-dimensional volume energy and the three-dimensional surface energy. The radius is determined by minimization:

$$R_B = \frac{1}{8\lambda \epsilon \xi^3} \quad (13.19)$$

For self-consistency, we must therefore require $\epsilon \ll 1/(8\lambda \xi^4)$. The resulting action is

$$S_B = \frac{\pi^2}{6} \epsilon R_B^4 \quad (13.20)$$

The semiclassical calculation ought to be valid when $S_B \gg 1$. A detailed calculation proves that there is one and only one negative eigenvalue, which is $-3/(2R_B^2)$.

13.2 Classical nucleation

The classical theory of nucleation culminated in the work of Becker and Döring [1]; it was nicely reviewed by McDonald [8]. This theory was developed to describe the nucleation of a liquid droplet in a dilute yet super-saturated vapor.

The classical expression for the nucleation of a droplet of dense liquid in a dilute gas is

$$I = a(i_*) \left(\frac{|\Delta E''(i_*)|}{2\pi T} \right)^{1/2} n_1 \exp\left(\frac{-\Delta E(i_*)}{T} \right) \quad (13.21)$$

where $\Delta E(i_*)$ is the formation energy of a critical sized droplet consisting of i_* molecules, a prime denotes differentiation with respect to the number of molecules i , T is the temperature, n_1 is the density of single molecules,

and $a(i_*)$ is the accretion rate of single molecules on a critical droplet. Usually the accretion rate is taken to be

$$a(i_*) = \frac{1}{2}n_1\bar{v}4\pi R_*^2s \quad (13.22)$$

which is the flux of particles (\bar{v} is the mean speed of gas molecules) striking the surface of the critical droplet times a “sticking fraction” s less than unity. The first term in the nucleation rate is a dynamical factor influencing the growth rate, the second term characterizes fluctuations about the critical droplet, and the product of the third and fourth terms gives the quasi-equilibrium number density of critical-sized droplets. The energy is measured with respect to the gas molecules, so that $\Delta E(1) = 0$.

To extend the classical expression to the nucleation of a droplet in a somewhat denser gas, the first thing to do is to multiply the Boltzmann factor by the number of states available to the hot droplet:

$$e^{-\Delta E/T} \rightarrow e^{-\Delta E/T} e^{\Delta S} \quad (13.23)$$

Owing to the thermodynamic identities $S = -dF/dT$ and $F = E - TS$, this modifies the Boltzmann factor to $e^{-\Delta F/T}$.

The size of the droplet can be characterized not by the number of molecules it contains but by its radius. Then integration over quadratic fluctuations about the mean size will give the prefactor

$$\left(\frac{|\Delta F''(R_*)|}{2\pi T}\right)^{1/2} \quad (13.24)$$

The accretion rate must be multiplied by the increase in radius per particle absorbed to compensate for this change of variable. Upon absorption of one more particle, the droplet free energy changes by

$$\delta\Delta F = \Delta F'(R_*)\delta R + \frac{1}{2}\Delta F''(R_*)(\delta R)^2 \quad (13.25)$$

The derivatives are evaluated at R_* , where the first derivative vanishes. The (Gibbs) free energy added by one gas molecule is just minus the pressure of the gas molecules divided by their number density. Therefore the accretion rate is multiplied by the factor

$$\delta R = \left(-\frac{P_1}{n_1\Delta F''(R_*)}\right)^{1/2} \quad (13.26)$$

Putting everything together we arrive at

$$I = 2\pi s\bar{v}R_*^2n_1^2\left(\frac{P_1}{n_1\pi T}\right)^{1/2}\exp\left(\frac{-\Delta F_*}{T}\right) \quad (13.27)$$

Generalizing to different species of molecules we write

$$I = 2\pi R_*^2 n_1 \exp\left(\frac{-\Delta F_*}{T}\right) \sum_j s_j \bar{v}_j n_j \left(\frac{P_j}{n_j \pi T}\right)^{1/2} \quad (13.28)$$

where P_j is the partial pressure of the j th species, n_j is their density, etc. The quasi-equilibrium density of critical droplets is normalized to the density of the lightest species of particles, n_1 . Note especially the appearance of R_*^2 in the prefactor. This arises from the fact that the absorption rate is proportional to the surface area. In contrast, when the growth rate is dominated by dissipation, as will be the case in Sections 13.3 and 13.4, the prefactor has only one power of R_* .

13.3 Nonrelativistic thermal nucleation

The theory of nucleation developed by Langer [2] starts with the introduction of a set of variables η_i , $i = 1, \dots, N$, that describe N collective degrees of freedom of the system. We introduce a distribution function $\rho(\{\eta\}, t)$ that is a probability density for the configurations $\{\eta\}$ as a function of time t . We assume that $\rho(\{\eta\}, t)$ satisfies a continuity equation of the form

$$\frac{\partial \rho}{\partial t} = \partial_t \rho = - \sum_{i=1}^N \frac{\partial J_i}{\partial \eta_i} \quad (13.29)$$

where the probability current is given by

$$J_i = - \sum_{j=1}^N \mathcal{M}_{ij} \left(\frac{\partial F}{\partial \eta_j} \rho + T \frac{\partial \rho}{\partial \eta_j} \right) \quad (13.30)$$

Here \mathcal{M} is a generalized mobility matrix and $F\{\eta\}$ is a coarse-grained free energy. Both of these quantities will be discussed in more detail below. Note that (13.29)–(13.30) can be derived via standard statistical techniques by adding a suitable Langevin force to the Hamiltonian equations of motion

$$\partial_t \eta_i = - \sum_{j=1}^N A_{ij} \frac{\partial F}{\partial \eta_j} \quad (13.31)$$

where A is an antisymmetric matrix with entries 0 or 1.

The choice of variables η_i will depend on the problem. Generally one chooses the smallest set that describes the system to sufficient accuracy yet allows for a tractable analysis. The equilibrium configurations, for

which $\partial_t \rho = 0$, have a probability distribution of the form

$$\rho_{\text{eq}}\{\eta\} \propto \exp\left(\frac{-F\{\eta\}}{T}\right) \quad (13.32)$$

Such configurations represent either the initial metastable point in the η -space denoted by $\{\eta_0\}$, or the final state. The phase transition starts from a metastable point $\{\eta_0\}$ and moves to the vicinity of a stable point, a point where F has its minimum. In this process the system is likely to pass a saddle point. The configuration at the saddle point, $\{\bar{\eta}\}$, is close to $\{\eta_0\}$ except for the presence of one critical-sized droplet of the new phase. At the saddle point we assume stationary flow, $\partial_t \rho = 0$, and calculate the current across this saddle. The rate of probability flow, $\{\bar{\eta}\}$, determines the droplet-formation rate in the system. This rate is

$$I = I_0 \exp\left(\frac{-\Delta F}{T}\right) \quad (13.33)$$

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

$$\Delta F = F\{\bar{\eta}\} - F\{\eta_0\} \quad (13.34)$$

The prefactor I_0 in (13.33) is the product of two terms:

$$I_0 = \frac{\kappa}{2\pi} \Omega_0 \quad (13.35)$$

Here the dynamical prefactor is κ (with dimension inverse time) and the statistical prefactor is Ω_0 (with dimension inverse volume). Langer showed that the statistical prefactor can be written as

$$\Omega_0 = \mathcal{V} \left(\frac{2\pi T}{|\bar{\lambda}_1|}\right)^{1/2} \prod_{\alpha=\alpha_0+2}^N \left(\frac{2\pi T}{\bar{\lambda}_\alpha}\right)^{1/2} \prod_{\alpha=1}^N \left(\frac{\lambda_\alpha^{(0)}}{2\pi T}\right)^{1/2} \quad (13.36)$$

Here \mathcal{V} is the volume of η -space available for the flux of probability flow and $\{\bar{\eta}\}$ and $\{\eta_0\}$ are the eigenvalues of the matrix

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

evaluated at the points $\{\bar{\eta}\}$ and $\{\eta_0\}$. We will evaluate Ω_0 in the next section.

Since $\{\eta_0\}$ is a minimum of F , all the $\lambda_\alpha^{(0)}$ must be positive. Because $\{\bar{\eta}\}$ resides at the highest point along the path of lowest energy leading away from $\{\eta_0\}$, there is only one eigenvalue $\bar{\lambda}_\alpha$ that is negative. This is the eigenvalue denoted by $\bar{\lambda}_1$ in (13.36). If $F\{\eta\}$ has translational symmetry in three-space then there will be at least three other eigenvalues $\bar{\lambda}_\alpha$, which are zero. These correspond to the three independent translations

of the position of the symmetry-breaking fluctuation (bubble or droplet) described by $\{\bar{\eta}\}$. The product of $\bar{\lambda}$'s appearing in (13.36) starts with $\alpha = \alpha_0 + 2$, where α_0 is the total number of symmetries of F which are broken by $\{\bar{\eta}\}$. The integration over these α_0 degrees of freedom defines the factor \mathcal{V} in (13.36).

The dynamical factor κ is the exponential growth rate of the unstable mode $\{\bar{\eta}\}$. To compute κ , we linearize (13.31) about $\eta_i = \bar{\eta}_i$:

$$\partial_t \nu_i = - \sum_{j,l=1}^N A_{ij} \frac{\partial^2 F}{\partial \bar{\eta}_j \partial \bar{\eta}_l} \nu_l \quad (13.37)$$

where $\nu_i = \eta_i - \bar{\eta}_i$. Then, setting $\nu \propto e^{\kappa t}$, we identify κ as the positive eigenvalue of the matrix

$$- \sum_{j=1}^N A_{ij} \frac{\partial^2 F}{\partial \bar{\eta}_j \partial \bar{\eta}_l} \quad (13.38)$$

In the nucleation problem the instability described by κ is the initial growth rate of a bubble or droplet that has just exceeded the critical size.

The dynamical prefactor has been calculated by Langer and Turski [9, 10] and by Kawasaki [11] for a liquid–gas phase transition near the critical point, where the gas is not dilute, to be

$$\kappa = \frac{2\lambda\sigma T}{\ell^2 n_\ell^2 R_*^3} \quad (13.39)$$

This involves 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 that 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.

13.4 Relativistic thermal nucleation

The relativistic quantum field theory approach for nucleation from one vacuum to another as worked out in Section 13.1 was extended by Affleck [4] and Linde [5] to finite temperature. In the limit where thermal

fluctuations dominate quantum fluctuations the rate is

$$I = \frac{\omega_-}{\pi} \left(\frac{S_3}{2\pi T} \right)^{3/2} \left\{ \frac{\det'[-\nabla^2 + U''(\bar{\phi}, T)]}{\det[-\nabla^2 + U''(0, T)]} \right\}^{-1/2} \exp\left(\frac{-S_3}{T}\right) \quad (13.40)$$

where S_3 is the three-dimensional action associated with the formation of a critical-sized bubble or droplet. This follows from the assumption that the radius of the bubble is much larger than the inverse temperature β . It is assumed that the bounce solution depends on three-dimensional r instead of four-dimensional ρ , namely, $\bar{\phi}(\rho) \rightarrow \bar{\phi}(r)$. Integration over τ in the action just produces an overall factor $\beta = 1/T$. The factor ω_- is the frequency of the unstable mode. The ratio of determinants is almost never evaluated because it would have to be done numerically. Usually dimensional analysis is invoked to approximate this pre-exponential factor by T^4 or by T_c^4 , so that

$$I \approx T^4 e^{-S_3/T} \quad \text{or} \quad I = T_c^4 e^{-S_3/T} \quad (13.41)$$

The expression (13.40) is very similar to the nucleation rate given by Langer for nonrelativistic systems, which itself is a generalization from the classical nucleation rate. It is our goal here to derive an expression that is fully relativistic, has Langer's rate formula as a nonrelativistic limit, and is expressed in terms of physically measurable observables such as surface energy, latent heat, transport coefficients, and so on. This involves the use of collective coordinates and coarse-graining.

The model of nucleation adopted here will be defined by the choice of the statistical variables, η_i , and the corresponding coarse-grained free energy $F\{\eta\}$. The conventional formulation of classical many-body statistical mechanics in terms of particle positions and momenta is not very convenient for the present purpose. Nucleation is characterized by semi-macroscopic fluctuations involving large numbers of particles. Therefore hydrodynamic-type collective variables are more appropriate to describe the formation of bubbles or droplets.

Hydrodynamics can be derived from microscopic kinetic theory by a coarse-graining or cellular method. That is, one divides up the macroscopic system into semimacroscopic cells of a given volume and assigns specific densities and flows to each of these cells. The free energy computed by performing a partition sum subject to the cellular constraints is the coarse-grained F that we are talking about. There is no problem, in principle, in summing over the cellular densities and flows to obtain the true equilibrium free energy. Moreover, as long as each cell comes to local thermal equilibrium rapidly compared with the times required for the hydrodynamic processes that one wants to consider, then one can

use the coarse-grained F for computing nonequilibrium properties of the system.

The question that arises at this point is, what is a suitable size for the coarse-graining cells? In order for the hydrodynamic description to make sense, the cell volume must be much larger than the average volume per molecule. However, the cells cannot have linear dimensions appreciably larger than a correlation length. If the cells are chosen to be too large, phase separation will occur within single cells and the interesting details of the condensation mechanism will be lost in the process of taking cellular averages. To put this another way, we expect F as a function of the average energy density ϵ to be a nonconvex function with distinct minima corresponding to the two phases. But, if the cell size is large enough for well-defined phase separation to occur within a cell then F must approach its convex envelope and cannot possibly have the above property. We conclude that the cell size can be neither much larger nor much smaller than a correlation length.

13.4.1 Relativistic fluid dynamics

The equations of motion of relativistic fluid dynamics, $\partial_\mu T^{\nu\mu} = 0$, can be given in terms of $E \equiv T^{00}$ and $M^i = T^{0i}$, that is, $E = (\epsilon + Pv^2)\gamma^2$ and $\mathbf{M} = (\epsilon + P)\gamma^2\mathbf{v}$, where ϵ is the energy density and P is the pressure; see Section 6.9. The low-speed limit of relativistic fluid dynamics ($\gamma^2 \approx 1$ and $Pv^2 \ll \epsilon$, but P not assumed small compared to ϵ) is given by

$$\partial_t \epsilon = -\nabla \cdot \mathbf{M} \quad (13.42)$$

and

$$\partial_t \mathbf{M} = -\nabla \cdot \left(\frac{1}{w} \mathbf{M} \otimes \mathbf{M} \right) - \nabla P \quad (13.43)$$

Here $w = \epsilon + P$ is the enthalpy density, and we have assumed that the relativistic energy density is $E = (\epsilon + Pv^2)\gamma^2 \approx \epsilon$ and that the relativistic momentum density is $\mathbf{M} = w\gamma^2\mathbf{v} \approx w\mathbf{v}$. The low-speed limit of relativistic fluid dynamics finds applications not only in cosmology and astrophysics but also in terrestrial environments dominated by radiation processes, such as nuclear detonations, high-energy shock waves, and rocket engines.

With the above-mentioned restrictions in mind we will try to find a suitable form for the coarse-grained free energy F . This is not a trivial problem. We choose as our basic variables the local energy density and momentum density fields, $\epsilon(\mathbf{x}, t)$ and $\mathbf{M}(\mathbf{x}, t)$. The free energy F must consist of a kinetic energy F_K and an interaction term F_I . The kinetic

term is simply

$$F_K(\epsilon, \mathbf{M}) = \frac{1}{2} \int d^3x w \mathbf{v}^2 = \int d^3x \frac{\mathbf{M}^2}{2w} \tag{13.44}$$

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

$$F_I[\epsilon(\mathbf{x})] = \int d^3x \left(\frac{1}{2} K (\nabla \epsilon)^2 + f(\epsilon) \right) \tag{13.45}$$

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

Using the above F with the mobility matrix

$$\begin{aligned} \mathcal{M}_{ij} &= \partial_j(M_i) + (M_i)\partial_j - \frac{M_j}{2w}(\partial_i w) \\ \mathcal{M}_{i0} &= -\partial_i \epsilon \\ \mathcal{M}_{00} &= 0 \\ \mathcal{M}_{0i} &= (\partial_i w) + w\partial_i \end{aligned} \tag{13.46}$$

the equations of motion for ϵ and \mathbf{M} are obtained as the low-speed limit of relativistic fluid dynamics. The equation for energy conservation is

$$\partial_t \epsilon = -(\nabla w) \cdot \frac{\delta F_K}{\delta \mathbf{M}(\mathbf{x})} - w \nabla \cdot \frac{\delta F_K}{\delta \mathbf{M}(\mathbf{x})} = -\nabla \cdot \mathbf{M}(\mathbf{x}) \tag{13.47}$$

and the equation for momentum conservation, the Euler equation, is

$$\begin{aligned} \partial_t \mathbf{M} &= - \left[\nabla \mathbf{M} + \mathbf{M} \nabla - \frac{\mathbf{M}}{2w} \nabla w \right] \cdot \frac{\delta F_K}{\delta \mathbf{M}(\mathbf{x})} + \frac{\delta F}{\delta \epsilon(\mathbf{x})} \nabla \epsilon \\ &= -\nabla \cdot \left(\frac{1}{w} \mathbf{M} \otimes \mathbf{M} \right) - K (\nabla^2 \epsilon) \nabla \epsilon + \frac{\partial f}{\partial \epsilon} \nabla \epsilon \end{aligned} \tag{13.48}$$

In the limit where we have a uniform system in equilibrium it is clear, from (13.43) and (13.48), that we must identify the last term on the right-hand side with the gradient of the pressure,

$$\frac{\partial f}{\partial \epsilon} \nabla \epsilon = \nabla f \longrightarrow -\nabla P \tag{13.49}$$

Note that when $\epsilon(\mathbf{x})$ is varying so slowly that the gradient energy can be neglected, (13.45) is consistent with

$$f(\epsilon) = \epsilon - Ts = -P \tag{13.50}$$

13.4.2 Parametrization of the free energy

Imagine having two phases in equilibrium with each other at temperature T and, furthermore, that there is an interface separating them. This interface cannot be perfectly sharp. It must have a finite thickness of the order of a correlation length. In a local-density picture the energy density ϵ should vary smoothly from one phase to the other. Since first-order phase transitions have a latent heat, this means that we need to know the free energy density $f(\epsilon)$ for values of the energy density ranging between one phase and the other. To be specific, in what follows the low-temperature low-energy-density phase will be denoted by the subscript L, and the high-temperature high-energy-density phase will be denoted by the subscript H. In addition to the need to know $f(\epsilon)$ for $\epsilon_L < \epsilon < \epsilon_H$ we will also encounter situations where we need to know $f(\epsilon)$ for a range of values about ϵ_L and ϵ_H . Statistical fluctuations about local thermal equilibrium would require such knowledge, for example.

For a range of temperatures about T_c , $f(\epsilon)$ should have minima located at $\epsilon_L(T)$ and $\epsilon_H(T)$. There should also be a barrier between these two minima located at some $\epsilon_0(T)$. We require that

$$\begin{aligned} f(\epsilon_L(T)) &= -P_L(T) \\ f(\epsilon_H(T)) &= -P_H(T) \end{aligned} \quad (13.51)$$

Therefore, at fixed T we shall parametrize $f(\epsilon)$ by a fourth-order polynomial in ϵ . Owing to the pinning of the two local minima shown above, $f(\epsilon)$ will have its global minimum at $\epsilon_H(T)$ when $T > T_c$ and its global minimum at $\epsilon_L(T)$ when $T < T_c$. At the critical temperature the two minima of $f(\epsilon)$ are equal. Our parametrization is

$$\begin{aligned} f(\epsilon) = f_0 + \frac{f_0''(\epsilon - \epsilon_0)^2}{2} - \frac{(\epsilon_L + \epsilon_H - 2\epsilon_0)f_0''}{3(\epsilon_L - \epsilon_0)(\epsilon_H - \epsilon_0)}(\epsilon - \epsilon_0)^3 \\ + \frac{f_0''}{4(\epsilon_L - \epsilon_0)(\epsilon_H - \epsilon_0)}(\epsilon - \epsilon_0)^4 \end{aligned} \quad (13.52)$$

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 ($f_0'' < 0$). Let us define $\Delta\epsilon \equiv \epsilon_H - \epsilon_L > 0$ and $\Delta P \equiv P_L - P_H$. In terms of these variables,

$$\epsilon_0 = \frac{\epsilon_L + \epsilon_H}{2} + \frac{f_0''(\Delta\epsilon)^3}{12\Delta P} \pm \left[\left(\frac{f_0''(\Delta\epsilon)^3}{12\Delta P} \right)^2 + \frac{(\Delta\epsilon)^2}{4} \right]^{1/2} \quad (13.53)$$

where $+$ ($-$) corresponds to $\Delta P > 0$ ($\Delta P < 0$) and

$$f_0 = -P_H + \frac{f_0''(\epsilon_H - \epsilon_0)^2(\epsilon_H - 2\epsilon_L + \epsilon_0)}{12(\epsilon_L - \epsilon_0)} \quad (13.54)$$

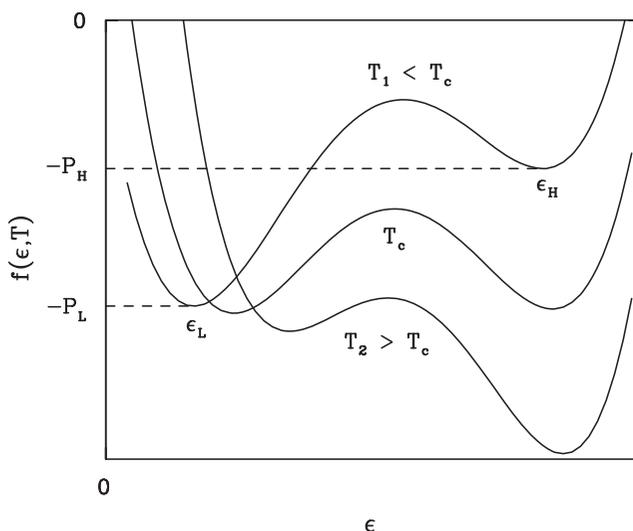


Fig. 13.2. Free-energy functional for extrapolating states away from equilibrium.

The first derivative of f is

$$f'(\epsilon) = \frac{\partial f}{\partial \epsilon} = \frac{f_0''(\epsilon - \epsilon_0)(\epsilon - \epsilon_L)(\epsilon - \epsilon_H)}{(\epsilon_L - \epsilon_0)(\epsilon_H - \epsilon_0)} \quad (13.55)$$

Thus, if the location of the two minima and their depths are given for fixed T then only one free parameter, f_0'' , remains. In particular, this parameter determines the barrier height, position, and curvature at all energy densities:

$$f''(\epsilon) = \frac{f_0''}{(\epsilon_L - \epsilon_0)(\epsilon_H - \epsilon_0)} \times [(\epsilon - \epsilon_0)(\epsilon - \epsilon_L) + (\epsilon - \epsilon_0)(\epsilon - \epsilon_H) + (\epsilon - \epsilon_L)(\epsilon - \epsilon_H)] \quad (13.56)$$

See Figure 13.2 for illustrations of $f(\epsilon)$ when T is greater than, equal to, or less than T_c . Unless we can extract this free-energy function from the Lagrangian in a more fundamental way we shall be content to use this parametrization in the following analyses.

13.4.3 Surface profile

We restrict ourselves to the case of idealized bubbles or droplets. That is, we consider only the limit in which the nucleating fluctuation described by $\{\bar{\eta}\}$ is, indeed, a well-defined sphere of the L-phase with radius R large compared with the interface thickness or the correlation length ξ (to be defined below). In principle we need not make this restriction in the

present theory. As we shall see, however, it is the appropriate one in the cases of interest here. By going to this limit we can do all our calculations analytically instead of having to resort to numerical methods.

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

$$\frac{\delta F_1}{\delta \bar{\epsilon}(r)} = -K \nabla^2 \bar{\epsilon} + \frac{\partial f}{\partial \bar{\epsilon}} = 0 \quad (13.57)$$

Given 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 will be ϵ_L ; far away from the bubble the energy density will be ϵ_H . The energy density profile $\bar{\epsilon}(r)$ then describes a smooth transition from one phase to the other. As discussed above, we will assume that the surface is located at a distance R from the center that is much greater than the surface thickness.

Using our parametrization of $f(\epsilon)$ the static profile equation becomes

$$-K \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) \bar{\epsilon} + f_0'' \frac{(\bar{\epsilon} - \epsilon_0)(\bar{\epsilon} - \epsilon_L)(\bar{\epsilon} - \epsilon_H)}{(\epsilon_L - \epsilon_0)(\epsilon_H - \epsilon_0)} = 0 \quad (13.58)$$

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

$$\frac{d^2 \bar{\epsilon}}{dr^2} + \frac{2}{r} \frac{d \bar{\epsilon}}{dr} + \frac{(\bar{\epsilon} - \epsilon_0)(\bar{\epsilon} - \epsilon_L)(\bar{\epsilon} - \epsilon_H)}{\xi_0^2 (\epsilon_L - \epsilon_0)(\epsilon_H - \epsilon_0)} = 0 \quad (13.59)$$

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

(i) In the interior of the bubble $\bar{\epsilon} = \epsilon_L + g_1(r)$; $g_1(r)$ is a small deviation from the equilibrium L-phase energy density satisfying

$$\frac{d^2 g_1}{dr^2} + \frac{2}{r} \frac{dg_1}{dr} - \xi_L^{-2} g_1 = 0 \quad (13.60)$$

where

$$\xi_L^2 = \xi_0^2 \frac{\epsilon_H - \epsilon_0}{\Delta \epsilon} \quad (13.61)$$

defines the correlation length in the L-phase. The solution of this equation is

$$g_1(r) = \frac{A_1}{r} \sinh \left(\frac{r}{\xi_L} \right) + \frac{B_1}{r} \cosh \left(\frac{r}{\xi_L} \right) \quad (13.62)$$

From the requirement that the solution be finite at the origin we get $B_1 = 0$. In order to match onto the interface region, A_1 must be very small, proportional to e^{-R/ξ_L} . Then $\bar{\epsilon}(r) \approx \epsilon_L$ throughout most of the interior.

(ii) Near R we can write $\bar{\epsilon} = \epsilon_0 + g_2(r)$. Linearizing in g_2 leads to

$$\frac{d^2 g_2}{dr^2} + \frac{2}{r} \frac{dg_2}{dr} + \xi_0^{-2} g_2 = 0 \tag{13.63}$$

The general solution is

$$g_2(r) = \frac{A_2}{r} \sin\left(\frac{r}{\xi_0}\right) + \frac{B_2}{r} \cos\left(\frac{r}{\xi_0}\right) \tag{13.64}$$

We require that $g_2(R) = 0$, which is equivalent to defining the location of the surface by the equation $\bar{\epsilon}(R) = \epsilon_0$. Thus the solution for $\bar{\epsilon}$ in the vicinity of the bubble's surface is

$$\bar{\epsilon} = \epsilon_0 + \frac{A_2}{r} \sin\left(\frac{r - R}{\xi_0}\right) \tag{13.65}$$

and $A_2 > 0$.

(iii) The exterior solution has the same functional form as in the interior except that $g_3(r \rightarrow \infty) = 0$ is required by the boundary condition. The exterior solution is therefore

$$\bar{\epsilon} = \epsilon_H - \frac{A_3}{r} e^{-r/\xi_H} \tag{13.66}$$

where

$$\xi_H^2 = \xi_0^2 \frac{\epsilon_0 - \epsilon_L}{\Delta\epsilon} \tag{13.67}$$

defines the correlation length in the H-phase and $A_3 > 0$.

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:

$$\bar{\epsilon}(x) = \frac{1}{2} \left[\epsilon_L + \epsilon_H + \Delta\epsilon \tanh\left(\frac{x}{2\xi_H}\right) \right] \tag{13.68}$$

Here the surface is located at $x = 0$ 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

$$\Delta F = \frac{4\pi}{3} (f_L - f_H) R^3 + 4\pi R^2 \sigma \tag{13.69}$$

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

$$\Delta F = \frac{4\pi}{3} [P_H(T) - P_L(T)] R^3 + 4\pi R^2 \sigma \tag{13.70}$$

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

$$P_L(T) - P_H(T) = \frac{2\sigma}{R(T)} \quad (13.71)$$

Thus the activation energy, in our approximation, is

$$\Delta F = \frac{4}{3}\pi\sigma R^2 \quad (13.72)$$

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 [12]:

$$\sigma = K \int_{-\infty}^{\infty} dx \left(\frac{d\bar{\epsilon}}{dx} \right)^2 \quad (13.73)$$

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

$$\sigma = K \left(\frac{\Delta\epsilon}{2} \right)^2 \frac{1}{2\xi_H} \int_{-\infty}^{\infty} dz \frac{1}{\cosh^4 z} = \frac{K(\Delta\epsilon)^2}{6\xi_H} \quad (13.74)$$

The correlation length and the surface free energy determine the parameters $-f_0''$ and K in the coarse-grained free energy. In principle these parameters are temperature dependent. Their temperature dependence is, however, generally difficult to obtain.

13.4.4 The prefactor

The prefactor is a product of two terms: the statistical prefactor and the dynamical prefactor. The statistical prefactor, Ω_0 , is a measure of both the available phase space as the system goes over the saddle and of statistical fluctuations at the saddle relative to the equilibrium states. The dynamical prefactor, κ , is the exponential growth rate of the bubble or droplet at the saddle point. This is the more difficult to calculate. We shall evaluate it using techniques exactly analogous to those employed by Turski and Langer [9, 10].

The general expression for the statistical prefactor was given in (13.36). To evaluate it, we first consider the eigenvalues of the matrix of second derivatives of F , the λ_α . The $\lambda_\alpha^{(0)}$ are eigenvalues of the operator

$$\left. \frac{\delta^2 F_I}{\delta\epsilon(\mathbf{x})\delta\epsilon(\mathbf{x}')} \right|_{\epsilon=\epsilon_H} = \left(-K \nabla^2 + \frac{\partial^2 f}{\partial\epsilon_H^2} \right) \delta(\mathbf{x} - \mathbf{x}') \quad (13.75)$$

Here by $\partial^2 f / \partial \epsilon_{\text{H}}^2$ 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 the fluctuations in the system and cannot be determined from knowledge of the equation of state alone. Since the right-hand side of (13.75) depends on \mathbf{x} only through ∇^2 , its eigenfunctions are plane waves, with wave vectors \mathbf{q} and eigenvalues

$$\lambda_{\mathbf{q}}^{(0)} = K \mathbf{q}^2 + \frac{\partial^2 f}{\partial \epsilon_{\text{H}}^2} \quad (13.76)$$

There is also a set of eigenvalues, formally to be included among the $\lambda_{\alpha}^{(0)}$, which come from the kinetic term F_{K} . In Langer and Turski [10] it was concluded that these eigenvalues are spurious; that is, they do not describe physically relevant fluctuations but only bulk motion of the system. Hence they do not appear in the final formula for any nucleation quantity.

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

$$\frac{\delta^2 F_{\text{I}}}{\delta \epsilon(\mathbf{x}) \delta \epsilon(\mathbf{x}')} \Big|_{\epsilon = \bar{\epsilon}(r)} = \left(-K \nabla^2 + \frac{\partial^2 f}{\partial \bar{\epsilon}^2} \right) \delta(\mathbf{x} - \mathbf{x}') \quad (13.77)$$

is no longer translationally invariant because of the r -dependence of $\bar{\epsilon}$. As was discussed by Langer [13], 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

$$\bar{\lambda}_1 \approx -\frac{2K}{R^2} \quad (13.78)$$

This eigenstate is associated with the instability of the critical bubble against uniform expansion or contraction. 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 starting at $\bar{\lambda} = \partial^2 f / \partial \epsilon_{\text{H}}^2$. 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. As before, the eigenvalues associated with the kinetic part of F are spurious and can be disregarded.

We can recognize the products over α in (13.36) as representing fluctuation corrections to the mean field excess free energy of the bubble. If we were to evaluate ΔF using measured values of the surface energy and thermodynamic potential, it would be inconsistent to include fluctuation corrections to ΔF in the prefactor Ω_0 . Strictly speaking, the

nucleation formula used here requires that ΔF be first evaluated at the stationary point obtained from (13.57), and then corrected by the fluctuation terms in Ω_0 . But this procedure would imply that the radius of the critical droplet is determined by the expression for σ given in (13.73), which is not necessarily the same as the experimental surface free energy because of the fluctuation corrections. What we shall do, instead, is to delete the explicit fluctuation terms in Ω_0 and interpret σ everywhere as the true surface energy; we shall make a similar assumption concerning other thermodynamic quantities that appear. Possibly this procedure can be justified by going beyond the Gaussian approximations for η -space integrations which were used in deriving (13.36); that is, by constructing a renormalized perturbation expansion in the neighborhood of $\{\bar{\eta}\}$. If this program can be carried out, we might also be able to compute systematically curvature corrections to the surface energy. These corrections will be omitted here, and we shall focus our attention on other ingredients of the nucleation formula, particularly the dynamical prefactor.

Note that there are $\alpha_0 + 1 = 4$ more terms in the product over the $\lambda_\beta^{(0)}$ than in the product over the $\bar{\lambda}_\alpha$ in (13.36). This means that the logarithm of the combined products is not precisely a free-energy difference. To see what is happening here, it is useful to think in terms of a one-to-one pairing between the $\lambda_\beta^{(0)}$ and the $\bar{\lambda}_\alpha$. At the top of the spectra (large positive $\lambda^{(0)}$ and $\bar{\lambda}$) both kinds of eigenvalue correspond to short-wavelength fluctuations that extend throughout the volume of the system V . We can pair these eigenvalues so that their contributions cancel each other to the extent that the droplet volume is negligible compared with the total volume of the system. At the bottom of the continuum a finite set of $\bar{\lambda}$ values, which correspond to localized deformations of the bubble, fall appreciably below their associated $\lambda^{(0)}$ values. Thus, by pairing the λ 's as described, the correction to ΔF remains of order R^3 in the limit $V \rightarrow \infty$, as it must. This procedure leaves four unpaired $\lambda^{(0)}$'s at the bottom of the spectrum that are not accounted for by the revised ΔF . Specifically, we have

$$\lim_{V \rightarrow \infty} \prod_{\beta=1}^4 \left(\frac{\lambda_\beta^{(0)}}{2\pi T} \right)^{1/2} = \left(\frac{1}{2\pi T} \frac{\partial^2 f}{\partial \epsilon_H^2} \right)^2 \quad (13.79)$$

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

Having written down the value for $\bar{\lambda}_1$, we need only evaluate the factor \mathcal{V} to complete the calculation of Ω_0 . The formula for \mathcal{V} was given by

Langer [2, 13]:

$$\mathcal{V} = V \left[\frac{1}{3} \int dr (\nabla \bar{\epsilon})^2 \right]^{3/2} = V \left[\frac{4\pi R^2 \sigma}{3K} \right]^{3/2} \quad (13.80)$$

Here we have made use of the fact that $d\bar{\epsilon}/dr$ is appreciable only in a narrow region near $r = R$, where R is the radius of the bubble.

The resulting expression for Ω_0 is

$$\Omega_0 = V \left(\frac{4\pi R^2 \sigma}{3K} \right)^{3/2} \left(\frac{\pi T R^2}{K} \right)^{1/2} \left(\frac{1}{2\pi T} \frac{\partial^2 f}{\partial \epsilon_H^2} \right)^2 \quad (13.81)$$

Identifying the correlation length ξ_H in the H-phase by

$$\frac{1}{K} \frac{\partial^2 f}{\partial \epsilon_H^2} = \frac{1}{\xi_H^2} \quad (13.82)$$

we can write (13.81) in the form

$$\Omega_0 = \frac{2}{3\sqrt{3}} \left(\frac{\sigma}{T} \right)^{3/2} \left(\frac{R}{\xi_H} \right)^4 V \quad (13.83)$$

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 do mean the rate per unit volume and so Ω_0 will not include the factor V in subsequent discussion.

The dynamical prefactor κ should be obtained as the positive eigenvalue of the matrix given in (13.38). Using the mobility matrix and the fact that the bubble solution is spherically symmetric and satisfies (13.57), one finds that $\kappa = 0$. This means that the bubble does not grow. The reason was discussed by Langer and Turski [10]. In order for a bubble (or droplet) to grow, latent heat must be transported away from the surface region: for the nonrelativistic systems they were considering, they discovered that heat conduction was necessary to allow for growth. This eventually led to (13.39), which says that κ is proportional to the thermal conductivity λ . It is clear that to get our bubble to grow we must include the effects of dissipation in the dynamics.

We now want to determine the equations of motion of dissipative fluid dynamics (Section 6.9) 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} :

$$\partial_t \nu = -\nabla \cdot \mathbf{M} = -\nabla \cdot (\bar{w} \mathbf{v}) \quad (13.84)$$

$$\partial_t (\bar{w} \mathbf{v}) = \nabla \bar{\epsilon} [-K \nabla^2 \nu + f'' \nu] + \nabla [(\zeta + 4\eta/3) \nabla \cdot \mathbf{v}] \quad (13.85)$$

Hereafter 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

$$\nu(\mathbf{x}, t) = \nu(r)e^{\kappa t} \quad (13.86)$$

$$\mathbf{v}(\mathbf{x}, t) = v(r)\hat{r}e^{\kappa t} \quad (13.87)$$

These radial deviations are governed by the equations of motion

$$\kappa\nu(r) = -\frac{1}{r^2} \frac{d}{dr} [r^2 \bar{w}v(r)] \quad (13.88)$$

and

$$\begin{aligned} \kappa \bar{w}v(r) = & -\frac{d\bar{\epsilon}}{dr} \left[-K \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + f'' \right] \nu(r) \\ & + \frac{d}{dr} \left\{ \left(\zeta + \frac{4\eta}{3} \right) \frac{1}{r^2} \frac{d}{dr} [r^2 v(r)] \right\} \end{aligned} \quad (13.89)$$

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

$$\begin{aligned} \kappa^2 \bar{w}v(r) = & -\frac{d\bar{\epsilon}}{dr} \left[K \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) - f'' \right] \left\{ \frac{1}{r^2} \frac{d}{dr} [r^2 \bar{w}v(r)] \right\} \\ & + \frac{d}{dr} \left\{ \kappa \left(\zeta + \frac{4\eta}{3} \right) \frac{1}{r^2} \frac{d}{dr} [r^2 v(r)] \right\} \end{aligned} \quad (13.90)$$

Self-consistent solutions of this equation, together with the boundary conditions, should provide us with the allowed values of κ . Unfortunately, it is not a trivial equation to solve. Therefore we will first analyze the behavior of the solution in three regions: the interior of the bubble, the exterior of the bubble, and the surface region. We first note a constraint that follows from (13.88) and the conditions that $v(r)$ vanishes at the origin and at infinity, namely

$$\int_0^\infty dr 4\pi r^2 \nu(r) = 0 \quad (13.91)$$

In the interior region, from the origin to within a few correlation lengths of the surface, recall that $\bar{\epsilon} \approx \text{constant}$. Then the first term on the right-hand side of (13.90) vanishes, and the equation for $v(r)$ reduces to

$$r^2 v'' + 2rv' - (a_L^2 r^2 + 2)v = 0 \quad (13.92)$$

where $a_L^2 = \kappa w_L (\zeta_L + 4\eta_L/3)^{-1}$. The general solution of this differential equation is

$$v(r) = A \left(\frac{a_L}{r} - \frac{1}{r^2} \right) e^{a_L r} + B \left(\frac{a_L}{r} + \frac{1}{r^2} \right) e^{-a_L r} \quad (13.93)$$

where A and B are constants. We must require that v and v' vanish at $r = 0$. Consequently both A and B are zero, so that the velocity vanishes in the interior of the bubble. This is true to the extent that $\bar{\epsilon} = \text{constant}$ in this region.

In the exterior region, far outside the surface, the energy and enthalpy densities approach their equilibrium values in the bulk H-phase, $\bar{\epsilon} \rightarrow \epsilon_{\text{H}}$ and $\bar{w} \rightarrow w_{\text{H}}$. Then the first term on the right-hand side of (13.90) can again be neglected as a first approximation. The solution with the correct large- r behavior is

$$v(r) = C \left(\frac{a_{\text{H}}}{r} + \frac{1}{r^2} \right) e^{-a_{\text{H}} r} \quad (13.94)$$

where C is a constant and $a_{\text{H}}^2 = \kappa w_{\text{H}} (\zeta_{\text{H}} + 4\eta_{\text{H}}/3)^{-1}$.

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. Therefore, unlike in the deep interior or the exterior of the bubble, the first term on the right-hand side of (13.90) cannot be dropped. In fact, as we shall see, κ is proportional to the viscosity, which we assume to be very small. Then the other two terms in the equation are of second order in the viscosity, and we shall ignore them. Thus, to good approximation, in the surface region $\nu(r)$ satisfies

$$(-K\nabla^2 + f'') \nu(r) = 0 \quad (13.95)$$

Given that $\bar{\epsilon}(r)$ satisfies (13.57) and that $\nu(r)$ must go to zero at the origin and at infinity, the solution to the above equation is

$$\nu(r) \sim \frac{d\bar{\epsilon}}{dr} \quad (13.96)$$

Together with (13.88) this implies that in the surface region

$$v(r) = \frac{D}{r^2 \bar{w}(r)} \int_0^r dr' r'^2 \frac{d\bar{\epsilon}}{dr'} \quad (13.97)$$

where D is a constant. For distances r which exceed the bubble radius R by more than a few correlation lengths but which are less than $2R$, (13.97) can be integrated to give

$$v(r) \approx \frac{D\Delta\epsilon}{w_{\text{H}}} \frac{R^2}{r^2} \quad (13.98)$$

Remember that, as always, we are assuming weak to moderate supercooling, so that $R \gg \xi$.

It is necessary to distinguish between the actual radius of the bubble, R , and the radius of the bubble in the stationary or metastable configuration, R_* , determined by Laplace's formula. If the stationary bubble is perturbed only slightly then the energy-density profile will change by only a minute

amount. The transport of heat away from the surface will be a very slow process because of the assumed smallness of the viscosity. As the bubble slowly begins to expand, the energy-density profile will not change much, but the profile moves out a small distance dR in a time dt . The energy flux density (the energy per unit area per unit time) that must be transported outwards is $\Delta w dR/dt$. Here we do not distinguish between the difference in energy densities and the difference in enthalpy densities of the two bulk phases because the pressure difference is small compared with the energy-density differences; we shall refer to them interchangeably as the latent heat. This energy flux must be balanced by that due to dissipation, which is $-(\zeta + 4\eta/3)v dv/dr$. We will evaluate the flow velocity just outside the surface of the bubble. According to (13.98) the derivative is $dv/dr \approx -2v/R$. Therefore energy balance gives us the relation

$$\Delta w \frac{dR}{dt} = 2 \left(\zeta_{\text{H}} + \frac{4\eta_{\text{H}}}{3} \right) \frac{v^2}{R} \quad (13.99)$$

The outward momentum flux density (the momentum per unit area per unit time) is $\Delta w v^2$. (This neglects a small contribution from viscous terms that can be considered to be a higher-order effect.) The momentum flux density must be equated to the force per unit area, which comes from the Laplace formula

$$\Delta w v^2 = 2\sigma \left(\frac{1}{R_*} - \frac{1}{R} \right) \quad (13.100)$$

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 :

$$\frac{dR}{dt} = \frac{4(\zeta_{\text{H}} + 4\eta_{\text{H}}/3)\sigma(R - R_*)}{(\Delta w)^2 R^2 R_*} \quad (13.101)$$

This is a differential equation for $R(t)$, from which we can read off the value of κ . It is

$$\kappa = \frac{4\sigma(\zeta_{\text{H}} + 4\eta_{\text{H}}/3)}{(\Delta w)^2 R_*^3} \quad (13.102)$$

This may be considered the principal result of this section.

Putting it all together gives the nucleation rate

$$I = \frac{4}{\pi} \left(\frac{\sigma}{3T} \right)^{3/2} \frac{\sigma(\zeta_{\text{H}} + 4\eta_{\text{H}}/3)R_*}{\xi_{\text{H}}^4 (\Delta w)^2} e^{-\Delta F/T} \quad (13.103)$$

where $\Delta F = 4\pi\sigma R_*^2/3$ and R_* is given by the Laplace formula (13.71). This is the probability per unit volume per unit time of nucleating an L-phase bubble out of the H-phase. If one considers nucleating an H-phase

droplet in the L-phase instead, one just needs to evaluate the correlation length and the viscosities in the L-phase rather than the H-phase. At the critical temperature, $R_* \rightarrow \infty$, and the rate vanishes because of the exponential. The system must supercool a minute amount at least in order that the rate attain a finite value. Note that at the critical temperature the pre-exponential factor is linearly divergent in R_* , which is qualitatively unlike the simple dimensionless estimate of a constant I_0 .

Venugopalan and Vischer [7] extended the calculation of κ to incorporate a net baryon number and therefore the effect of thermal conduction. The result is

$$\kappa = \frac{2\sigma[\lambda_{\text{H}}T + 2(\zeta_{\text{H}} + 4\eta_{\text{H}}/3)]}{(\Delta w)^2 R_*^3} \quad (13.104)$$

This is proportional to a linear combination of the three dissipation coefficients. It reduces to the expression derived above when thermal conduction can be neglected and to the expression of Langer and Turski in the nonrelativistic limit and when shear and bulk viscosities are small.

This completes our calculation and analysis of the thermal nucleation rate for systems with zero or negligibly small baryon number. In a subsequent chapter we shall use it in a set of rate equations for the time evolution of phase transitions in the early universe and in ultrarelativistic nuclear collisions.

13.5 Black hole nucleation

In a beautiful and original work Gross, Perry, and Yaffe [14] calculated the nucleation rate for black holes in a thermal bath of gravitons. Their result is

$$I = 1.752 T \left(\frac{M_0}{T} \right)^{212/45} \left(\frac{m_{\text{P}}}{4\pi} \right)^3 \exp \left(\frac{-m_{\text{P}}^2}{16\pi^2 T^2} \right) \quad (13.105)$$

where $m_{\text{P}} \equiv G^{-1/2}$ is the Planck mass and G is Newton's constant. The quantity M_0 is a regulator mass, undetermined in the pure Einstein theory but supposed to be of the order of m_{P} in a more complete quantum theory of gravitation. Physically the reason for this instability of flat space is that statistical fluctuations will produce small black holes. According to Hawking [15] the effective temperature of a black hole is $m_{\text{P}}^2/8\pi M$ where M is its mass. If the mass is too large then the black hole temperature will be smaller than that of its surroundings and it will accrete matter. If the mass is too small, the black hole temperature will be greater than its surroundings and it will evaporate and eventually explode. The critical mass for this unstable equilibrium is $M_* = m_{\text{P}}^2/8\pi T$.

The calculation of the nucleation rate by Gross, Perry, and Yaffe is based upon small fluctuations about a Schwarzschild instanton in a path-integral formulation of Einstein's theory. There is one negative eigenvalue, which gives rise to the instability of flat space. The calculation is at the same time elegant and lengthy. However, the main features of the result can be obtained from the classical theory of nucleation [16].

Consider a volume V with gravitons at temperature T . The probability that a fluctuation will produce a black hole of critical mass is $\exp(-\Delta F)$, where ΔF is the change in free energy of the system with T and V held fixed. Now $\Delta F = F_* - F_g$, where F_* is the free energy of the black hole and F_g is the free energy of the thermal gravitons displaced by the black hole. The black hole free energy F_* is related to M_* by

$$M_* = F_* - T \frac{dF_*}{dT} \quad (13.106)$$

or

$$F_* = \frac{M_*}{2} = \frac{m_{\text{P}}^2}{16\pi T} \quad (13.107)$$

whereas F_g is given by

$$F_g = -\frac{\pi^2}{45} T^4 \frac{4\pi}{3} r^3 \quad (13.108)$$

where r is of the order of or slightly greater than the Schwarzschild radius. Thus F_g/T is of the order of 10^{-2} to 10^{-3} and will be neglected.

Knowing the probability for one statistical fluctuation, we can estimate the density for fluctuations to occur. Consider quantum density fluctuations on the smallest scale possible, namely, the Planck wavelength $\lambda_{\text{P}} = 2\pi/m_{\text{P}}$. Imagine a cube with fluctuations spaced $\lambda_{\text{P}}/2$ apart. The quantum density of fluctuations necessary to produce a black hole of critical mass is then estimated to be

$$n_* = \left(\frac{m_{\text{P}}}{\pi}\right)^3 \exp\left(\frac{-m_{\text{P}}^2}{16\pi T^2}\right) \quad (13.109)$$

The rate of change of n_* can be calculated as

$$\frac{dn_*}{dt} = \frac{1}{T} \left| \frac{dM_*}{dt} \right| n_* = \frac{m_{\text{P}}^2}{8\pi T^3} n_* \quad (13.110)$$

The rate of increase in the black hole mass may be estimated by the rate at which gravitons cross the Schwarzschild radius R_{S} :

$$\frac{dM_*}{dt} = 2 \times 4\pi R_{\text{S}}^2 \int_{\text{hemisphere}} \frac{d^3p}{(2\pi)^3} \frac{p}{\exp(p/T) - 1} = \frac{\pi}{120} T^2 \quad (13.111)$$

Putting everything together we get

$$I = \frac{8\pi}{15} T \left(\frac{m_{\text{P}}}{4\pi} \right)^3 \exp \left(\frac{-m_{\text{P}}^2}{16\pi T^2} \right) \quad (13.112)$$

Comparing (13.105) and (13.112) we see that in the former there still remains a factor $(M_0/T)^{212/45}$ to interpret. The origin of this term is a quantum correction to the free energy of the black hole [17]:

$$\frac{F_*^{\text{quantum}}}{T} = -\frac{106}{45} \chi \ln \left(\frac{M_0}{T} \right) \quad (13.113)$$

The factor χ is a topological invariant of the space, being 2 for the Schwarzschild metric and 0 for flat space. The final formula derived heuristically is

$$I = \frac{8\pi}{15} T \left(\frac{M_0}{T} \right)^{212/45} \left(\frac{m_{\text{P}}}{4\pi} \right)^3 \exp \left(\frac{-m_{\text{P}}^2}{16\pi T^2} \right) \quad (13.114)$$

It is remarkable that not only the functional dependence on T and m_{P} is reproduced, but also the absolute normalization is very close. This is more than could reasonably be expected.

13.6 Exercises

- 13.1 Show that the functions $\phi_\mu = b\partial_\mu\bar{\phi}$ are solutions to the equation of motion given in Section 13.1 and that they have one node.
- 13.2 Write down the false vacuum decay rate including explicitly Planck's constant.
- 13.3 Make a numerical estimate of the nucleation rate for a critical-sized water droplet in an atmosphere that is oversaturated by 10% at 10 degrees C.
- 13.4 Derive (13.40) along the same lines used to derive the vacuum decay rate.
- 13.5 Derive (13.88)–(13.90) and from them patch together an approximate solution for $v(r)$ valid from $r = 0$ to $r = \infty$.
- 13.6 Calculate the black hole formation rate with the inclusion of N_{f} massless spin-1/2 fermions and N_{b} massless spin-0 bosons.

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Bibliography

A nice review of nucleation theory in nonrelativistic and condensed matter systems is the following:

- Gunton, J. D., San Miguel, M., and Sahni, P. S. (1983). In *Phase Transitions and Critical Phenomena*, eds. Domb, C., and Lebowitz, J. L. (Academic Press, London) Vol. 8.