Phase transition of a finite quark-gluon plasma

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The deconfinement transition region between hadronic matter and quark-gluon plasma (QGP) is studied for finite volumes. Assuming simple model equations of state and a first order phase transition, we find that fluctuations in finite volumes hinder a sharp separation between the two phases around the critical temperature, leading to a *rounding* of the phase transition. For reaction volumes expected in heavy ion experiments, the softening of the equation of state is reduced considerably. This is especially true when the requirement of exact color singletness is included in the QGP equation of state. [S0556-2813(98)01102-9]

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I. MOTIVATION

A primary goal of relativistic nuclear collisions is the observation of a phase transition of confined, hadronic matter to a deconfined quark-gluon plasma (QGP). One of the proposed signatures, namely, hydrodynamic flow, is based on the presumed softening of the equation of state due to the rapid increase of the entropy density. It has been investigated in the framework of relativistic hydrodynamic models [1,2]. The expansion of once compressed matter is predicted to be delayed in the case of a QGP, which in turn leads to a reduction of the transverse (directed) flow [3,4].¹ This is mainly due to the fact that the sound velocity vanishes for energy densities in the mixed phase. A smooth crossover transition within an assumed interval of $\Delta T = 0.1T_C$, on the other hand, results in drastically reduced time delays as compared to a sharp transition [6].

As is well known, a rounding of sharp first order phase transitions is expected due to explicit finite size effects [7]. The importance of fluctuations of the coexisting phases in small volumes of strongly interacting matter has already been pointed out in [8] for the case of a liquid-gas phase transition and in [9] for the deconfinement phase transition. As a consequence, it was claimed that the observation of two separate phases in heavy ion collisions might be hindered. In this work we explore this behavior in more detail, starting from rather simple model equations of state. We put special emphasis on the question as to how the requirement of color singletness of the QGP phase affects the phase transition on top of the fluctuation effect.

The limited reaction size of a heavy ion collision is a generally ignored problem of the experimental search for a quark-gluon plasma. According to one-fluid dynamical model calculations, one expects to produce deconfined matter in volumes of about 10–50 fm³ at fixed target energies [3]. Similar values of typical QGP cluster sizes are found within a microscopic approach in combination with a percolation model [10]. At collider energies the relevant reaction volumes for heavy systems are estimated to be much larger: Assuming an initial interaction volume of $V_0 = \pi (1.15A^{1/3})^2 \tau_0$ with a formation time $\tau_0 \approx 1 \text{ fm/}c$ and subsequent expansion one may expect (at the onset of confinement) $V \approx 750 \text{ fm}^3$ for Au+Au collisions at Relativistic Heavy Ion Collider (RHIC) energies ($\sqrt{s} = 200A \text{ GeV}$) and $V \approx 1350 \text{ fm}^3$ for Pb+Pb at CERN Large Hadron Collider (LHC) energies ($\sqrt{s} \approx 5.5A \text{ TeV}$) [11].

However, the longitudinal flow velocities exceed the thermal motion by far. Thus, only subsystems of smaller volume can be regarded as being in approximate "global" thermal equilibrium. Only the latter are suitable for the study of finite size effects. Therefore, if we require the local thermal motion to be of the same order as the relative flow velocity, one must restrict the study of finite size effects to regions of about one unit of rapidity (cf. [12]). The volume of such (possibly multiple) subsystems would thus only be V<100 fm³ for both the RHIC and LHC.

Another motivation for the study of finite size effects is lattice QCD calculations, which have to be extrapolated from a finite lattice (although with periodic boundary conditions) to infinite matter [13,14]. Depending on the number of grid points in the spatial direction, the presently accessible volumes are in the range of $V \approx 50-100$ fm³. The extrapolation to infinity is not clear [14]. Our investigation can yield some insight into what can be phenomenologically expected when going from finite volumes to the infinite volume limit.

II. PHASE COEXISTENCE AND FLUCTUATIONS

Let us consider a finite volume of strongly interacting matter in the grand canonical ensemble with vanishing net baryon density. The model equation of state is constructed by matching a low energy density phase (a hadron gas) and a high energy density phase (the quark-gluon plasma): For infinite matter the system undergoes a first order phase transition at a critical temperature $T_{\rm C}$. However, when we assume

¹However, in a three-fluid hydrodynamical model [5] the directed nucleon flow is already lowered as compared to the usual one-fluid models (which assume instantaneous local thermalization between projectile and target). It will be exciting to learn whether the softening of the equation of state (EOS) is also signaled in this model.

a finite volume *V* of the system, statistical (thermodynamical) fluctuations are not negligible; they do not allow for a sharp transition between the two phases in this case. In general, the probability *p* of finding the system in a state **x** is given by $p(\mathbf{x}) \sim \exp[-\beta F(\mathbf{x})]$, where $F(\mathbf{x})$ is the free energy of the system [15,9] (see also the Appendix). Let us introduce an "order" parameter ξ for the quantitative characterization of the macroscopic state of the total system, such that $\xi = 1$ corresponds to the pure hadron phase and $\xi = 0$ corresponds to the pure quark-gluon phase. For the mixed phase the fractional volumes are defined as $V_h = \xi V$ and $V_q = (1 - \xi)V$.

It is now assumed that the partition function of the total system factorizes into the partition functions of the two individual phases for fixed ξ (see the Appendix). Then there are no correlations between the possible microscopic energy eigenstates of the two subsystems (the two phases). The free energy of the total system can thus be expressed in terms of the free energy densities of the individual phases f_q and f_h and the volume fraction of the hadron phase ξ :

$$F_{\xi}(T,V) = [f_{h}(T,\xi V)\xi + f_{q}(T,(1-\xi)V)(1-\xi)]V. \quad (1)$$

The normalized probability density is a function of the order parameter:

$$p(\xi) = \frac{\exp[-\beta F_{\xi}(T,V)]}{\int_0^1 d\xi \exp[-\beta F_{\xi}(T,V)]}.$$
(2)

The expectation value of any intensive thermodynamic quantity A(T,V) is then calculated as

$$A(T,V) = \int_{0}^{1} d\xi p(\xi;T,V) [A_{h}(T,\xi V)\xi + A_{q}(T,(1-\xi)V)(1-\xi)].$$
(3)

A reminder of a thermodynamic derivation of Eqs. (2) and (3) can be found in the Appendix.

As long as explicit finite size effects in the equations of state of the individual phases are ignored (i.e., the free energies F_i are linear functions of V_i), the free energy densities equal the negative pressure within the two phases:

$$P_i(T) = -\frac{\partial F_i}{\partial V_i} = -\frac{F_i}{V_i} = -f_i.$$
(4)

When inserting this into Eqs. (1) and (2), respectively, one sees immediately that for large volumes V of the total system and a given temperature T the occurrence of the phase with the lower pressure is strongly suppressed. For $V \rightarrow \infty$ the coexistence of both phases requires $P_h = P_q$, which is the Gibbs condition for mechanical two-phase equilibrium. This holds also for the case of explicit finite size modifications of the equation of state, because the correction terms vanish by definition in the limit $V \rightarrow \infty$.

III. EQUATIONS OF STATE FOR INFINITE MATTER

For illustration let us consider first the case of infinite matter equations of state, i.e., without explicit finite size corrections. The constituents of the low energy density phase are well-established nonstrange hadrons up to masses of 2 GeV. The system is treated as a mixture of relativistic, noninteracting Bose-Einstein and Fermi-Dirac gases. As the net baryon number is zero, the free energy reads

$$F(T,V) = -\sum_{i} \frac{g_{i}V}{6\pi^{2}} \int_{0}^{\infty} \frac{p^{4}}{\sqrt{p^{2} + m^{2}}} \frac{1}{e^{E_{i}/T} \pm 1} dp, \quad (5)$$

where the + stands for fermions, the – for bosons, and g_i denotes the spin and isospin degeneracies of particle species *i*. To take into account repulsive interactions, all thermodynamic quantities are corrected by the Hagedorn factor $1/(1 + \epsilon/4B)$ [16], where ϵ is the energy density of the point particles and *B* is the bag constant. The bag constant is chosen as $B = 200 \text{ MeV/fm}^3$ for all calculations presented here.

For the equation of state of the high energy density phase (the quark-gluon plasma) we take a simple bag model EOS for massless quarks, their antiquarks, and gluons in a MIT bag of infinite volume, where the number of quark flavors is $N_q=2$:

$$F(T,V) = BV - \pi^2 \left(\frac{7}{60}N_q + \frac{8}{45}\right)T^4V.$$
 (6)

In this case the integration in Eq. (3) can be carried out easily, rendering

$$A(T,V) = \frac{e^{\{-\beta[f_h(T) - f_q(T)]V\}} \{-\beta[f_h(T) - f_q(T)]V - 1\} + 1}{[e^{\{-\beta[f_h(T) - f_q(T)]V\}} - 1] \{-\beta[f_h(T) - f_q(T)]V\}} \times [A_h(T) - A_q(T)] + A_q(T).$$
(7)

Note that $f_h(T_C) = f_q(T_C)$. The expectation value of an intensive thermodynamic quantity like pressure, entropy density, or energy density at a temperature $T \neq T_C$ can be calculated with this formula.

Figure 1 (top) shows the expectation value of the order parameter $\langle \xi \rangle$, the average hadronic volume fraction, as a function of the temperature for different system sizes. This quantity is calculated as

$$\langle \xi \rangle(T,V) = \int_0^1 d\xi p(\xi;T,V)\xi.$$
(8)

For volumes $V=100 \text{ fm}^3$ or less, $\langle \xi \rangle(T)$ deviates clearly from a simple step function. Even below T_C , the system is *not* purely hadronic. The quark phase has a finite probability (see also [17]). On the other hand, the hadronic phase contributes, with similar probability, even above T_C . Note that the order parameter in our model is simply the volume fraction of the hadronic phase. Thus, for a volume of 25 fm³ and a temperature of 10 MeV above T_C one can read off Fig. 1 that the system is composed of about 10% hadron gas and 90% QGP (this admixture for *finite* sizes is different from the predicted persistence of clusters in an *infinite* plasma [18]). The unfavorable phase is suppressed, according to Eq. (2), due to the differences of the free energy. However, any composition of the total system (any value of ξ) must correspond to a finite total free energy content, because the volume is



FIG. 1. The order parameter (expectation value of the volume fraction of the hadron gas, $\langle \xi \rangle$) vs the temperature for systems of different sizes (top). The energy density ϵ , divided by the temperature *T* to the power of 4 (middle), and the entropy density *s*, divided by the temperature to the power of 3 (bottom), are also shown. The bag constant is $B^{1/4}$ = 200 MeV. Equations of state for infinite matter (hadronic and QGP) are used.

finite. Thus, the suppression relative to the state with minimum free energy content is finite; i.e., the probability is nonzero.

Figure 1 also shows the energy density ϵ/T^4 and the entropy density s/T^3 as a function of temperature for different volumes of the system. In the case of an infinite volume, the first order phase transition is reflected by the sharp discontinuity of both quantities at $T_{\rm C}$ = 143 MeV. Because of the finite probability of fluctuations, the average values of the energy density and the entropy density at a temperature *T* are different for finite systems. Below $T_{\rm C}$, the presence of the quark phase, although a small fraction of the total volume, increases the energy density and the entropy density. Above $T_{\rm C}$, the contribution of the hadronic phase still lowers the



FIG. 2. Pressure *P* divided by the energy density ϵ vs the energy density for systems of different sizes. The bag constant is $B^{1/4}$ =200 MeV. Equations of state for infinite matter (hadronic and QGP) are used.

average values of ϵ and *s*, leading to the expected *rounding* of the phase transition. A functional form of thermodynamic quantities has been parametrized [6,19]; this was used to model the *assumed* smooth crossover transition and for studying the resulting physics. In any case, for finite size systems such a crossover has to be expected. Here we calculate such a behavior for strongly interacting, finite systems on the basis of a very simple model without free parameters.

Figure 2 now shows the (hydrodynamically relevant) ratio $P(\epsilon)/\epsilon$ vs ϵ for various system sizes. Here the "softest points" of the equation of state vs V are the respective minima of the curves. The thermodynamics of the system exhibits a very distinct volume dependence with respect to this quantity. Observe the strong influence of V over a wide range of energy densities. This could not be clearly seen in Fig. 1, where the transition appears within a rather narrow region of temperature.

It has been suggested [1,2] that a clear peak of the lifetime of the mixed phase as a function of the collision energy could signal the QCD phase transition in heavy ion reactions. This peak should be observable in a particular window of the initial energy density, around the softest point of the equation of state. The comparatively small pressure prevents a fast expansion of the system around that well-located point.

However, as can be seen in Fig. 2, the minimum of $P(\epsilon)/\epsilon$ is much less pronounced for finite volumes than for an infinite volume. At low temperatures — which correspond to low energy densities — the influence of a small admixture of quark matter on P and ϵ is particularly strong, because the absolute values of P and ϵ are very large in the quark phase in the simple MIT bag description $(-P = \epsilon = B \text{ for } T = 0)$ as compared to the values in the hadron phase $(P = \epsilon = 0 \text{ for } T = 0)$. In Fig. 2 solid circles on the curves indicate the values of the energy density, where the pressure of the pure quark phase would become zero according to the simple bag model equation of state, Eq. (6). Whether the concept of thermodynamic fluctuation theory is adequate for lower energy densities and how the equation of state for the super-

cooled quark matter phase might look like at temperatures considerably lower than $T_{\rm C}$ remain to be investigated.

IV. QUARK MATTER EQUATION OF STATE WITH COLOR SINGLET CONSTRAINT

In the following we consider a phenomenological model equation of state for the plasma phase including explicit finite size effects: A grand canonical partition function for a quark-gluon plasma droplet with the necessary requirement of color singletness was proposed in [20]. The internal SU(3)_C symmetry is accounted for by applying a grouptheoretical projection technique [21] on color singlet states to the grand canonical partition function of a noninteracting quantum gas of massless quarks and gluons. The authors find that, due to the color confinement, the internal degrees of freedom in a finite plasma droplet are effectively reduced as compared to the infinite matter equation of state. Also, the finite level density (in a finite system) for the single-particle eigenstates leads to an additional effective reduction. This is explicitly accounted for. In summary, these finite size corrections can be interpreted as surface (curvature) effects. We use the corresponding free energy as the equation of state for the high density phase. It reads [20]

$$F(T,V) = BV - T(X - Y) + \frac{3}{2}T[\ln(D) - \ln(\pi)] + T[4\ln(C) + \ln(2\sqrt{3}\pi)],$$

$$X = \pi^2 \left(\frac{7}{60}N_q + \frac{8}{45}\right)T^3V,$$

$$Y = \pi \left(\frac{1}{3}N_q + \frac{32}{9}\right)RT,$$

$$C = -\frac{1}{\pi} \left(\frac{2}{3}N_q - 8\right)RT + \left(\frac{1}{3}N_q + 2\right)T^3V,$$

$$D = -\pi \left(\frac{1}{9}N_q + \frac{32}{27}\right)RT + \pi^2 \left(\frac{7}{30}N_q + \frac{16}{45}\right)T^3V,$$
(9)

where $R = (3V/4\pi)^{1/3}$ is the radius of the spherical plasma drop and $N_q = 2$ denotes the number of (massless) quarks. This equation of state (for the quark-gluon plasma) incorporates an explicit volume dependence of the pressure at fixed T. In this case, $P_q(T) = -\partial F_q/\partial V_q \neq -F_q/V_q$. Therefore, Eqs. (2) and (3) have to be evaluated numerically. The partition function was derived in a saddle-point approximation which breaks down for $RT \rightarrow 0$. It agrees within $\approx 30\%$ with the exact value for $RT \approx 1$ [20]. Therefore, we approximate the free energy density by f(R) = f(1/T) for plasma volumes $(1 - \xi)V_{tot}$, which correspond to spherical droplets of sizes less than R < 1/T. The hadronic equation of state of Sec. III is used, without any explicit finite size modifications.

Figure 3 (top) shows the free energy density as a function of the order parameter ξ (the hadron volume fraction) using the color singlet equation of state for the quark phase. The temperature is chosen to be $T=T_{\rm C}$, where we *define* the critical temperature at the point where $\epsilon(T_{\rm C}) = [\epsilon_q(T_{\rm C}) + \epsilon_h(T_{\rm C})]/2$. Thus, $T_{\rm C}$ denotes the temperature for which



FIG. 3. Free energy density f as a function of the hadron fraction for systems of different sizes at $T_{\rm C}$ (top) and the resulting probability densities $p(\xi)$ (bottom). The bag constant is $B^{1/4}=200$ MeV. The color singlet constraint is taken into account for the QGP equation of state.

both phases contribute with equal probability to the state of the total system. In Sec. III the critical temperature was found to be independent of the volume — only the *width* of the transition was affected by the fluctuations.

For the finite-size-corrected equation of state, however, the critical temperature shifts to higher values at finite volumes (see below). As one expects, the finite size modifications of the equation of state affect the free energy density most strongly for small systems. The infinite volume limit converges to a constant free energy density. Figure 3 (bottom) shows the resulting probability densities as functions of the order parameter ξ . A "two-hump" structure is observed, thus favoring the dominance of one of the phases against a two-phase composition with equal volume fractions for both phases. Such a two-hump structure is generally expected to occur for first order phase transitions [7].

One should emphasize that the peaks at $\xi=0$ and $\xi=1$ are most pronounced for the *largest* volume. This is because the free energy, and not the free energy density, enters Eq. (2) for the calculation of the probability density. The physics of large systems is therefore extremely sensitive to small variations of the free energy density. Because of this very distinct hump structure, either one phase or the other is present at $T_{\rm C}$. This basically reflects the barrier in the free energy density functional due to the explicit surface effects between the two seperate phases. Then, a first order phase



FIG. 4. The order parameter (expectation value of the volume fraction of the hadron gas, $\langle \xi \rangle$) vs the temperature for systems of different sizes (top). The energy density ϵ , divided by the temperature *T* to the power of 4 (middle), and the entropy density *s*, divided by the temperature to the power of 3 (bottom), are also shown. The bag constant is $B^{1/4}$ = 200 MeV. The color singlet constraint is taken into account for the QGP equation of state.

transition occurs dynamically in a way that the high temperature phase (or the low temperature phase, respectively) is supercooled (or superheated, respectively), up to a point where bubble nucleation starts to convert the now unstable phase to the more stable phase [22].

Figure 4 shows the temperature dependence of the order parameter, the energy density, and the entropy density, as in Fig. 1, but now for the quark matter equation of state with the color singlet constraint. The main difference is the shift of the critical temperature to higher values for smaller volumes. For systems of finite size the modified equation of state yields a lower pressure at a given temperature, because the internal degrees of freedom are gradually "frozen" with decreasing volume [20]. Thus, even when flucuations are neglected, the mechanical Gibbs equilibrium between the



FIG. 5. Shift of the critical temperature $\Delta T_{\rm C}$ vs the systems size V. The bag constant is $B^{1/4}$ = 200 MeV. The color singlet constraint is taken into account for the QGP equation of state.

two pressures would be reached for temperatures $T_C > T_C^{\infty}$. Here T_C^{∞} stands for the critical temperature of the *infinite* system.

Important consequences follow for the bulk quantities ϵ/T^4 and s/T^3 : The latent heat and the jump in the entropy density are considerably reduced for small systems. First, the effective number of degrees of freedom in the hadron phase increases with temperature: The rest masses become more and more negligible as compared to the kinetic energies. Secondly, as mentioned before, the effective number of degrees of freedom in the quark phase is reduced for finite volumes due to the requirement of color singletness. As stated in [19], the active degrees of freedom, which are "'quantified" as s(T), determine completely the gross behavior of the thermodynamics near the phase transition. Figure 4 also shows that the smearing due to the fluctuations is less pronounced than for the infinite matter equation of state in Sec. III. The rounding effect of a fluctuating phase composition of the system appears to be counteracted by the effect of the volume-dependent reduction of the quark-gluon degrees of freedom.

Figure 5 depicts the volume dependence of the shift of the critical temperature, $\Delta T_{\rm C} = T_{\rm C} - T_{\rm C}^{\infty}$. The temperature shift exhibits an approximate power law $\Delta T_{\rm C} \sim 1/V^{\alpha}$ with $\alpha \approx 0.7$. The analysis of Binder and Landau [7,14], who examined the first order phase transition of a finite system in the Ising ferromagnet model, advocates a coefficient $\alpha = 1$ [14].

As in Fig. 2, Fig. 6 shows the ratio $P(\epsilon)/\epsilon$ vs ϵ within the present scenario. Again, those values of the energy density are marked which correspond to zero pressure of the pure quark phase. In clear contrast to Fig. 2, the "softest point" is now characterized by less pronounced minima of $P(\epsilon)/\epsilon$ for reasonably small system sizes. For volumes of V < 25 fm³, the minimum of the curve vanishes completely. Hence, the lifetime signal [1,2], which is based on hydrodynamic considerations and infinite matter equations of state, will be considerably damped in a more realistic scenario of heavy ion collisions.



FIG. 6. Pressure *P* divided by the energy density ϵ vs the energy density for systems of different sizes. The bag constant is $B^{1/4} = 200$ MeV. The color singlet constraint is taken into account for the QGP equation of state.

Figure 7 shows the speed of sound (squared), $c_s^2 = \partial p / \partial \epsilon$, as a function of the energy density for three different cases. For infinite volume, the phase transition is truly first order. This can be seen from the vanishing speed of sound in the mixed phase. This is the cause of the pronounced time delay in hydrodynamical simulations: Even if there are strong gradients in the energy density, the mixed phase cannot perform mechanical work. Therefore, it does not expand on its own account. Deflagration fronts with small velocities convert the mixed phase into hadrons, leading to slow cooling and expansion [6].

A finite system of volume $V = 100 \text{ fm}^3$ is also depicted in Fig. 7 for the two different equations of state of the QGP.



FIG. 7. Speed of sound (squared) c_s^2 as a function of energy density ϵ for three different cases: (1) infinite volume of the system (solid line), (2) $V = 100 \text{ fm}^3$ using the infinite matter EOS (dotted line), and (3) $V = 100 \text{ fm}^3$ using the EOS with color singlet constraint (dashed line).

Neglecting the color singlet constraint (but including the effect of thermodynamic fluctuations in finite volumes) leads to a strong reduction of the speed of sound in the transition region. Thus, one still might expect a moderatively long-lived fireball of the mixed phase. However, the speed of sound does not vanish in a sharp region of energy density. Rather, it is smoothly damped in the large ϵ domain between 20 MeV/fm³ and 200 MeV/fm³. This effect would vastly smear out the lifetime signal if one scans the flow excitation function over a wide range of collision energies.

After the requirement of color singletness is included, c_s^2 is much less reduced. The dip is shifted to higher (factor ~2) energy densities. Although the rather sharp breakdown of the speed of sound in a well-located energy density domain is recovered, the hydrodynamical expansion solutions will now look much different from the infinite matter scenario: The rather high values of c_s^2 must lead to a much more rapid expansion than for infinite matter equations of state. The implementation of the present results, based on finite volumes and global equilibrium and also supercooling, into hydrodynamical calculations, remains a difficult enterprise for future investigations.

V. CONCLUSION

We have discussed the thermodynamic bulk properties for finite systems at the phase transition and the detailed behavior of the free energy density as a function of the temperature. In our investigations we have employed rather simple model equations of state. For finite volumes, $V < 100 \text{ fm}^3$, corresponding to the expected plasma volumes, there is a considerable rounding in the variables ϵ/T^4 and s/T^3 around $T_{\rm C}$. As a consequence, the speed of sound does not vanish in the mixed phase. This is inferred, under simple assumptions, from basic thermodynamic considerations. Fluctuations of the two phases in a finite system lead to a smooth transition between the low temperature regime — where the hadronic phase dominates the system — and the high temperature regime — where the pure quark phase is most probable.

In one scenario we have investigated the implications of a model equation of state including explicit finite size effects and the requirement of exact color singletness within the quark phase. This model exhibits a barrier in the free energy between the two phases near the phase transition. The existence of a barrier results in a double-hump structure of the probability distribution for the actual phase composition at the critical point. In addition, it leads to a shift of the critical temperature to higher temperatures for finite volumes. The speed of sound is considerably increased in the mixed phase. The significance of the time delay signal [1,2] for the experimental detection of a QGP phase in heavy ion collisions becomes questionable.

We expect that other (more realistic) models with a similar barrier between the two stable phases in a first order phase transition will generally yield qualitatively the same and quantitatively similar results in small systems. In addition, our investigations also show intuitively that the extrapolation from the behavior of a finite system to its infinite volume limit may, in fact, be rather model dependent.

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APPENDIX: THERMODYNAMIC DERIVATION OF THE MODEL

For a canonical ensemble all thermodynamic quantities like the free energy F, the entropy S, the pressure P, and the energy E are determined by the partition function Z:

$$Z = \operatorname{Tr}\{e^{-\beta \hat{H}}\} = \sum_{n} e^{-\beta E_{n}}, \quad F = -T \ln Z.$$
 (A1)

Once F(T,V) is fixed, S, P, and E follow from standard relations.

The main assumption for the case of two coexisting phases is the *separability* of the energy spectra $E_{n_i}^{(i)}$ of the single phases *i*. It is assumed that the energy eigenvalues of the total system E_n^- factorize:

$$E_{\overline{n}}(\xi) = E_{n_1}^{(1)}(\xi) + E_{n_2}^{(2)}(\xi).$$
 (A2)

Here ξ is a not yet specified order parameter which characterizes the configuration of the total system, i.e., the relative importance of the individual phases. The partition function for a given ξ of the two-phase system then reads

$$Z(\xi) = \operatorname{Tr}_{n} \{ e^{-\beta \hat{H}} \} = \sum_{n_{1}} e^{-\beta E_{n_{1}}} \sum_{n_{2}} e^{-\beta E_{n_{2}}} = Z^{(1)}(\xi) Z^{(2)}(\xi),$$

$$F(\xi) = -T \ln Z(\xi) = F^{(1)}(\xi) + F^{(2)}(\xi).$$
(A3)

Equation (A2) guarantees that the simple factorization in Eqs. (A3) holds. Since ξ is a (continuous) order parameter, any value of ξ corresponds to a different state of the twophase system. As in our intuitive choice for ξ in the main text, we now assume that, without loss of generality, ξ can take any number in the range between 0 and 1. The total partition function of the system for a discretized spectrum of the order parameter and a given total volume V^{tot} reads

$$Z \equiv Z(\xi_1) + Z(\xi_2) + \dots + Z(\xi_n)$$
 with $\xi_i = \frac{(i-1)}{n}$.
(A4)

The probability for the system being in the state ξ_i is then given by

$$\Delta p(\xi_i) = \frac{Z(\xi_i)}{Z}, \quad \sum_{i=1}^n \Delta p(\xi_i) \equiv 1.$$
 (A5)

From this we infer the probability density of the continuous case:

$$p(\xi) = \frac{Z(\xi)}{\int_0^1 Z(\xi) d\xi}.$$
 (A6)

We now evaluate the free energy of the total system F^{tot} as well as the other thermodynamic quantities S^{tot} , P^{tot} , and E^{tot} . In the discretized case we have

$$Z = \sum_{i=1}^{n} Z(\xi_i) = \sum_{i=1}^{n} e^{-\beta F(\xi_i)} \equiv e^{-\beta F^{\text{tot}}}.$$
 (A7)

Differentiating with regard to β (as an independent paramter) yields

$$F^{\text{tot}} = \sum_{i=1}^{n} \frac{e^{-\beta F(\xi_i)}}{\sum_{j=1}^{n} e^{-\beta F(\xi_j)}} F(\xi_i) \to \int_0^1 p(\xi) F(\xi) d\xi. \quad (A8)$$

The entropy is readily obtained as

$$S^{\text{tot}} = -\left(\frac{\partial F^{\text{tot}}}{\partial T}\right) \bigg|_{V} = \ln \mathbb{Z} + \frac{T}{\mathbb{Z}} \left(\frac{\partial \mathbb{Z}}{\partial T}\right) \bigg|_{V}$$

$$= \ln \mathbb{Z} + \frac{T}{\sum_{j=1}^{n} \mathbb{Z}(\xi_{j})} \sum_{i=1}^{n} \left(\frac{\partial \mathbb{Z}(\xi_{i})}{\partial T}\right) \bigg|_{V}$$

$$= \ln \mathbb{Z} + \frac{T}{\sum_{j=1}^{n} \mathbb{Z}(\xi_{j})} \sum_{i=1}^{n} \left[e^{-\beta F(\xi_{i})} \frac{F(\xi_{i})}{T^{2}} - \beta e^{-\beta F(\xi_{i})} \left(\frac{\partial F(\xi_{i})}{\partial T}\right) \bigg|_{V}\right]$$

$$= \underbrace{\ln \mathbb{Z} + \frac{1}{T} \sum_{i=1}^{n} \frac{e^{-\beta F(\xi_{i})}}{\sum_{j=1}^{n} \mathbb{Z}(\xi_{j})} F(\xi_{i})}_{\equiv 0} - \sum_{i=1}^{n} \frac{e^{-\beta F(\xi_{i})}}{\sum_{j=1}^{n} \mathbb{Z}(\xi_{j})} \left(\frac{\partial F(\xi_{i})}{\partial T}\right) \bigg|_{V}$$

$$\longrightarrow \int_{0}^{1} p(\xi) \left(-\frac{\partial F(\xi)}{\partial T}\right) \bigg|_{V} d\xi \equiv \int_{0}^{1} p(\xi) S(\xi) d\xi \quad , \quad (A9)$$

and similarly for the pressure,

$$P^{\text{tot}} = -\left(\frac{\partial F^{\text{tot}}}{\partial V}\right)\Big|_{T} = \frac{T}{Z}\left(\frac{\partial Z}{\partial V}\right)\Big|_{T}$$

$$= \frac{T}{\sum_{j=1}^{n} Z(\xi_{j})} \sum_{i=1}^{n} \left(-\beta \frac{\partial F(\xi_{i})}{\partial V}\right)\Big|_{T} e^{-\beta F(\xi_{i})}$$

$$= \sum_{i=1}^{n} \frac{e^{-\beta F(\xi_{i})}}{\sum_{j=1}^{n} Z(\xi_{j})} \left(-\frac{\partial F(\xi_{i})}{\partial V}\right)\Big|_{T}$$

$$\to \int_{0}^{1} p(\xi) \left(-\frac{\partial F(\xi)}{\partial V}\right)\Big|_{T} d\xi \equiv \int_{0}^{1} p(\xi) P(\xi) d\xi,$$
(A10)

and the energy,

$$E^{\text{tot}} = F^{\text{tot}} + T^{\text{tot}}S^{\text{tot}} = \sum_{i=1}^{n} \Delta p(\xi_{i}) \left[F(\xi_{i}) - T\left(\frac{\partial F(\xi_{i})}{\partial T}\right) \Big|_{V} \right]$$
$$\rightarrow \int_{0}^{1} p(\xi) \left[F(\xi) - T\left(\frac{\partial F(\xi)}{\partial T}\right) \Big|_{V} \right] d\xi \equiv \int_{0}^{1} p(\xi) E(\xi) d\xi.$$
(A11)

Equations (A8)–(A11) do correspond to the prescription, Eq. (3), stated within the main text.

We now choose the order parameter ξ as the volume fraction of one of the two phases. The free energy of the system as a function of the order parameter thus becomes [refer to Eq. (1)]

$$F(\xi) = \{f^{(1)}(\xi V^{\text{tot}})\xi + f^{(2)}((1-\xi)V^{\text{tot}})(1-\xi)\}V^{\text{tot}},$$
(A12)

where $f^{(i)}$ is the free energy density of phase *i*. Note that the individual free energy densities can depend on the volume explicitly. For infinite matter equations of state, however, this is not the case. We now get, for the other quantities,

$$S(\xi) = -\left(\frac{\partial F(\xi)}{\partial T}\right)\Big|_{V}$$

= {s⁽¹⁾(\xi V^{tot})\xi + s⁽²⁾((1-\xi)V^{tot})(1-\xi)}V^{tot},
(A13)

where $s^{(i)}$ denotes the entropy densities

$$P(\xi) = -\left(\frac{\partial F(\xi)}{\partial V}\right)\Big|_{T}$$

= { $P^{(1)}(\xi V^{\text{tot}})\xi + P^{(2)}((1-\xi)V^{\text{tot}})(1-\xi)$ } (A14)

and

$$E(\xi) = F(\xi) + T(\xi)S(\xi)$$

= { $e^{(1)}(\xi V^{\text{tot}})\xi + e^{(2)}((1-\xi)V^{\text{tot}})(1-\xi)$ }V^{\text{tot}},
(A15)

where $e^{(i)}$ are the energy densities.

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