Late-stage coarsening in off-critical vapour-liquid phase separation is re-examined. In the limit of bubbles of vapour distributed throughout a continuous liquid phase, it is argued that coarsening proceeds via inertial hydrodynamic bubble collapse. This replaces the Lifshitz-Slyozov-Wagner mechanism seen in binary liquid mixtures. The arguments are strongly supported by simulations in two dimensions using a novel single-component soft sphere fluid.

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Late stage coarsening kinetics in phase separating mixtures shows a wealth of interesting non-linear coupled phenomena. If dynamical scaling holds, the growth may be characterised by a scaling law relating the typical size of domains, \( L \), to the elapsed time \( t \), thus \( L \sim t^\alpha \). The standard picture of coarsening in a space dimension \( d = 3 \) critical quench (equal proportions of the two phases) is as follows. An initial diffusive regime (\( \alpha = 1/3 \)) is followed by accelerated growth when hydrodynamic modes become activated. If a fluid is characterised by its density \( \rho \), viscosity \( \eta \), and surface tension \( \sigma \), then hydrodynamically limited coarsening follows a law like \( L/H = f(t/H) \) on dimensional grounds, where \( L_H = \eta^2/\rho \sigma \) and \( T_H = \eta^3/\rho^2 \sigma^2 \) are hydrodynamic length and time scales. If scaling holds, \( f(x) \sim x^{\alpha} \). The expectation is that an initial viscous hydrodynamic (VH) regime (\( \alpha = 1 \)) crosses over to an inertial hydrodynamic (IH) regime (\( \alpha = 2/3 \)), since the Reynolds number \( Re = \rho L/H \eta = f' \sim x^{2\alpha-1} \) grows like \( x \) in the VH regime and eventually inertial effects must become important. The observation that \( Re \) continues to grow in the IH regime (as \( \sim x^{1/3} \)) has recently prompted Grant and Elder to argue that turbulent remixing will limit the asymptotic exponent to \( \alpha \leq 1/2 \). However the currently available numerical evidence suggests a breakdown of pure scaling is more likely, in the sense that coarsening is no longer dominated by a single length scale.

In an off-critical quench (unequal proportions of the two phases) the situation seems much clearer. For the case of a binary liquid mixture, one rapidly establishes a population of droplets of the minority phase distributed throughout the continuous phase. Such droplets can coarsen via the Lifshitz-Slyozov-Wagner (LSW) mechanism in which the larger drops grow at the expense of the smaller drops, as material diffuses through the continuous phase driven by weak chemical potential gradients. Diffusion limited droplet coalescence may additionally occur. Both mechanisms lead to \( \alpha = 1/3 \) in \( d = 3 \).

Up to now I have not drawn a clear distinction between coarsening in a single component system quenched into vapour-liquid coexistence, and demixing in a binary liquid mixture. Both have similar conserved order parameters, and one expects similar kinetic coarsening mechanisms to hold for critical quenches. In this Letter though, I argue that coarsening in vapour-liquid systems is fundamentally different from binary liquid mixtures in the limit of bubbles of vapour distributed throughout a continuous liquid phase. This reflects a fundamental difference in the way the conserved order parameter is transported, and is motivated by simulations of coarsening in a novel single-component soft sphere fluid described below.

Visual observation of the bubble coarsening regime shows that an LSW-like mechanism operates, but much faster than would be expected from diffusion of the order parameter. The large bubbles grow by bulk movement of fluid, at the expense of the small bubbles which collapse under the influence of their surface tension. This is strongly suggestive of a new hydrodynamically limited bubble coarsening regime, in which flow fields are generated by pressure gradients caused by a distribution of bubble sizes. These pressure gradients are analogous to the chemical potential gradients in the LSW mechanism, but in this case the continuous fluid phase responds hydrodynamically.

To gain insight, I consider the paradigmatic problem of an isolated bubble, initial radius \( R_0 \), which collapses from rest under the influence of its surface tension, in zero ambient pressure. Related problems of bubble growth and collapse under varying ambient pressure fields go back to Rayleigh and Elder, and are of great technological and military significance in cavitation phenomena. In these problems, the flow field is radial, \( v = (R^2 \dot{R}/r^2)\hat{r} \), where \( \dot{R}(t) \) is the drop radius. Incompressibility requires the \( 1/r^2 \) dependence, and the fluid velocity is matched to the bubble radius velocity at \( r = R \). This flow field is irrotational and can be derived from a velocity potential \( \phi = -R^2 \dot{R}/r \). The drop radius obeys the equation

\[
\rho(\dot{R} + 3\dot{R}^2/2) = p(R) - p(\infty)
\]

where \( p(r) \) is the pressure. This can be derived for example by applying Bernoulli’s principle to a streamline extending from the surface of the drop to infinity.
In our case \( p(R) = -2\sigma / R \) from the Laplace law (the pressure inside the droplet is \( \approx 0 \)), and \( p(\infty) = 0 \). The above equation can be integrated to find that the bubble collapses in a time

\[
t_{\text{collapse}} = \left( \frac{R_0^3 \rho}{\sigma} \right)^{1/2} \frac{1}{\sqrt{2}} \int_0^1 \frac{dx}{(x^{-3} - x^{-1})^{1/2}}
\]

(2)

(the integral can be evaluated in terms of Euler’s B-function to be \( B(\frac{1}{4}, \frac{1}{2}) / 2 = 0.874 \)). This result can be rewritten as \( t_{\text{collapse}} / T_H^{2/3} \propto R_0 / L_H \). It is not surprising this coincides with the IH scaling law, since we are only considering a special case of the Navier-Stokes equations in which viscosity effects are absent.

This result for isolated bubble collapse suggests that in the LSW-like hydrodynamically limited bubble coarsening regime, the mean bubble size grows as \( L_H(t / T_H)^{2/3} \), identical to the growth law for IH coarsening. What is perhaps surprising is the indication that there is no VH regime, since isolated bubble collapse is purely inertial (but see discussion below). The above argument is for \( d = 3 \), but repeating the analysis in \( d = 2 \) obtains the same scaling law with additional logarithmic corrections.

I now describe the simulations which motivated the above arguments. These were undertaken with a novel soft sphere fluid based on the dissipative particle dynamics (DPD) method [2]. Two features make DPD attractive for phase ordering studies: firstly one has a fluid of soft spheres which allows comparatively large time steps to be taken in the integration algorithm, secondly a momentum-conserving thermostat is used which preserves hydrodynamic modes.

The soft spheres in DPD interact with short-range forces of the form \( f_{ij} = A(1 - r_{ij} / r_c) F_{ij} \), acting between all pairs of particles \( i \) and \( j \) for which \( r_{ij} < r_c \), where the positions are \( \mathbf{r}_i \) and \( \mathbf{r}_j \), \( r_{ij} = |\mathbf{r}_j - \mathbf{r}_i| \) and \( r_c = \mathbf{r}_j / r_{ij} \). Such a force law leads to a predominantly quadratic equation of state (EOS) which cannot be engineered conveniently to have a van der Waals loop. Phase ordering studies, using DPD in its original form, are therefore limited to binary fluid mixtures where it has been applied with some success [3].

Usually a van der Waals loop results from a hard core repulsion combined with a long range attraction, for example in previous studies using Lennard-Jones potentials [2,10]. However, introducing hard cores into DPD spoils the attractiveness of the method. Therefore an alternative method was pursued which may perhaps be termed many-body DPD.

In many-body DPD, the amplitude of the interaction between a pair of particles \( i \) and \( j \) is made to depend symmetrically on \( \mathbf{r}_i \) and \( \mathbf{r}_j \). In this way, almost completely arbitrary density dependence can be introduced into the EOS, including a van der Waals loop. Many-body DPD in this form has been described by Pagonabarraga and Frenkel [3], and was also invented independently by Groot [18]. Such density-dependent potentials have featured recently in coarse-grained models of polymers [17], and in principle can be constructed to have arbitrary phase behaviour [3].

The specific model used in the simulations comprises DPD with an additional interaction force of the form \( f_{\text{extra}} = B(\bar{p}_i + \bar{p}_j)(1 - r_{ij} / r_d) F_{ij} \) \( (r_{ij} < r_d) \). The \( d = 2 \) weight function is \( w(r) = (6/\pi r^2_d)(1-r/r_d)^3 \) \( (r < r_d) \) [9]. The EOS for this model is then predominantly cubic. By making \( A < 0 \), \( B > 0 \) and \( r_d < r_c \), one can produce a van der Waals loop and induce vapour-liquid coexistence with a sharp interface of width \( \sim r_c \) (see Fig. 1). Three suitable parameter sets were identified for \( d = 2 \) simulations, and are given in Table 1 along with the density and viscosity of the liquid phase, and interfacial tension computed by separate simulations. In common with previous studies, I fix the units by setting \( m = r_c = kT = 1 \) (\( \rho \) is the mass of the particles).

Armed with this model, \( d = 2 \) simulations of vapour-liquid phase ordering were undertaken by preparing a random distribution of particles in a square domain at a density \( \phi \rho \) where \( \phi \) is the desired liquid phase area fraction. Typical simulations comprised 5–10 runs of \( 10^4–10^5 \) particles in a domain of side 100\( r_c \), at \( \phi = 0.9 \). These were run out to times of order 150 (DPD units) where only one or two large vapour bubbles remain. The progress of the simulation was monitored by overlaying a grid at a resolution 0.5\( r_c \), computing the local density in each grid element (pixel), and determining connected sets of pixels where the density is less than a critical value (usually \( \rho = 1 \)) by cluster analysis (see Fig. 3). These clusters are identified with bubbles, and statistics on the bubble size distribution were obtained. Most attention was paid to how the mean bubble area \( \langle A \rangle \) grows with time; very similar results were obtained with \( \langle A^1/2 \rangle \).

Fig. 3 shows data from runs for all three parameter sets, reduced using the hydrodynamic length and time scales. There are two key points to note. Firstly the data collapses onto a single curve despite the order of magnitude variation in \( L_H \) and \( T_H \) across the sets. This is a strong indication that bubble coarsening is hydrodynamically limited. Secondly the data follows a scaling law virtually indistinguishable from that expected in an IH regime over nearly four decades in reduced time. This is a strong indication that the above arguments concerning inertia-dominated bubble collapse are correct. To be precise, the scaling law found by fitting across all data sets is \( \langle A \rangle = (4.2 \pm 0.5)L_H^2(t/T_H)^{1.30 \pm 0.02} \). The barely significant deviation of the exponent from \( 2 \alpha = 4/3 \) may
be due to the logarithmic corrections expected in $d = 2$

By way of comparison I have also done some corresponding simulations on a binary liquid mixture. This is achieved in regular DPD by introducing two species of particle with an additional repulsion between them [7]. The parameter sets in Table II were used, and the results are also shown in Fig. 3. The growth exponent is that expected for diffusion-limited droplet coalescence in $d = 2$ as has been seen in previous work [8]. Note the absence of a scaling collapse between the two parameter sets in this case.

It may be worthwhile to interject a brief comment about the opposite limit to the bubble coarsening regime, namely a dispersion of drops in a vapour phase. If the vapour is sufficiently dilute, coarsening can proceed by ballistic drop coalescence, as has been reported previously for a Lennard-Jones fluid [10]. Following Bray [1], simple scaling arguments suggest a growth law 
$$\left(\frac{\phi t \sqrt{kT}}{\rho}\right)^{2/(d+2)}.$$  
I have confirmed the validity of various aspects of this growth law in $d = 2$ at $\phi = 0.1$ and 0.05.

In summary therefore, I have presented arguments which show a fundamental difference in phase coarsening between binary liquid demixing and vapour-liquid phase separation. Simulations of a soft sphere fluid strongly support the idea of an inertial hydrodynamic (IH) bubble coarsening regime for an off-critical vapour-liquid quench. The relevance of the critique of Grant and Elder [2] is not immediately apparent in this case, nevertheless there has to be a mechanism to dissipate the interface energy. It may be that it is converted to kinetic energy in the fluid, and subsequently lost in viscous dissipation by a turbulent cascade, as suggested for the critical quench in a binary liquid mixture [9]. But, in real cavitation, a significant amount of the interface energy is converted into pressure waves [12]. Thus another possibility is that fluid compressibility plays a role, and the interface energy is (partly) dissipated through sound waves. The subtleties of these mechanisms do not show up in the statistics of the bubble size distribution since the data in Fig. 5 indicates the mean bubble size follows the IH growth law very closely indeed, but the signature may perhaps be sought in the statistics of the flow fields.

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1. A. J. Bray, Adv. Phys. 43, 357 (1994).
2. M. Grant and K. R. Elder, Phys. Rev. Lett. 82, 14 (1999).
3. V. M. Kendon, J.-C. Desplat, P. Bladon and M. E. Cates, Phys. Rev. Lett. 83, 576 (1999)
4. A. J. Wagner and J. M. Yeomans, Phys. Rev. Lett. 80, 1420 (1998); Int. J. Mod. Phys. C 9, 1373 (1998).
5. V. M. Kendon, Phys. Rev. E 61, R6071 (2000).
6. Additional mechanisms may operate for near critical quenches: H. Tanaka, Phys. Rev. Lett. 72, 1702 (1994); A. J. Wagner and M. E. Cates, cond-mat/0101140.
7. P. V. Coveney and K. E. Novik, Phys. Rev. E 54, 5134 (1996); S. I. Jury, P. Bladon, S. Krishna and M. E. Cates, Phys. Rev. E 59, R2535 (1999).
8. K. E. Novik and P. V. Coveney, Phys. Rev. E 61, 435 (2000).
9. S. W. Koch, R. C. Desmai and F. F. Abraham, Phys. Rev. A 27, 2152 (1983); E. Velasco and S. Toxværd, Phys. Rev. Lett. 71, 388 (1993).
10. G. Leptoukh, B. Strickland and C. Roland, Phys. Rev. Lett. 74, 3636 (1995).
11. Lord Rayleigh, Phil. Mag. 34, 94 (1917).
12. Section 6.12 in G. K. Batchelor, An Introduction to Fluid Dynamics, (CUP, Cambridge, 1967); problem 7 in §10, L. D. Landau and E. M. Lifshitz, Fluid Mechanics 2nd edn, (Pergamon, Oxford, 1987).
13. See §9 in Landau and Lifshitz referred to in [12].
14. For an overview see P. B. Warren, Curr. Opinion Coll. Int. Sci. 3, 620 (1998). The Verlet-like integration algorithm of R. D. Groot and P. B. Warren, J. Chem. Phys. 107, 4423 (1997), was used here. Recent improvements are described by C. P. Lowe, Europhys. Lett. 47, 145 (1999), and W. K. den Otter and J. H. R. Clarke, Europhys. Lett. 53, 426 (2001).
15. I. Pagonabarraga and D. Frenkel, Mol. Sim. 25, 167 (2000).
16. R. D. Groot, private communications.
17. A. A. Louis, P. G. Bolhuis, J.-P. Hansen and E. J. Meijer, Phys. Rev. Lett. 85, 2522 (2000).
18. N. G. Almarza, E. Lomba, G. Ruiz and C. F. Tejero, Phys. Rev. Lett. 86, 2038 (2001).
19. Many-body DPD is described in terms of forces here, but a Hamiltonian formulation is also possible which indicates the link between the weight function and the many-body force law [12].
FIG. 1. Interface density profiles for the three many-body DPD parameter sets in Table I. The origin of the z-axis is arbitrary. In all cases there is a fairly sharp interface between a liquid of moderate density on the left, and an extremely dilute vapour phase on the right.

FIG. 2. Density maps in bubble coarsening regime for set ‘6’ in Table I at reduced times \( t/T_H \approx 30 \) (left) and 120 (right). Grey scale runs linearly between \( \rho = 0 \) (black) and \( \rho \geq 6 \) (white).

FIG. 3. Scaling collapse of mean bubble area \( \langle A \rangle \) as a function of time, non-dimensionised by the hydrodynamic length and time scales, for the three many-body DPD parameter sets in Table I (upper data curves). Also shown is the corresponding reduced data for droplet area growth in binary liquid demixing, for the two conventional DPD parameter sets in Table II (lower data curves; the lowest being set ‘4b’).
\[
\rho \frac{\sigma}{\eta} L = \eta^2 / \rho \sigma \\
\frac{\eta}{\rho} = \rho \sigma^2 / T
\]

TABLE I. Parameter sets for many-body DPD, for vapour-liquid coexistence, and properties of the liquid phase determined by simulation (in all cases, the figure in brackets is an estimate of the error in the final digit). The vapour phase density is vanishingly small. The final two columns show the hydrodynamic length and time scales. Units are DPD units, where \( m = r_c = kT = 1 \).

| Set | \( A \) | \( B \) | \( r_d \) | \( \rho \) | \( \eta \) | \( \sigma \) | \( L_H = \eta^2 / \rho \sigma \) | \( T_H = \eta^3 / \rho \sigma^2 \) |
|-----|-------|-------|--------|------|------|------|----------------|----------------|
| '4' | -40   | 27    | 0.75   | 3.954(1) | 3.19(3) | 2.83(7) | 9.09 \times 10^{-1} | 1.03 \times 10^0 |
| '5' | -40   | 18    | 0.75   | 4.950(1) | 2.53(3) | 5.29(8) | 2.44 \times 10^{-1} | 1.17 \times 10^{-1} |
| '6' | -40   | 12    | 0.75   | 6.333(1) | 1.69(2) | 9.44(6) | 4.78 \times 10^{-2} | 8.55 \times 10^{-3} |

TABLE II. Parameter sets for ordinary DPD, for symmetric binary liquid mixtures.

| Set | \( A_{11} = A_{22} \) | \( A_{12} \) | \( \rho \) | \( \eta \) | \( \sigma \) | \( L_H = \eta^2 / \rho \sigma \) | \( T_H = \eta^3 / \rho \sigma^2 \) |
|-----|---------------------|--------|------|------|------|----------------|----------------|
| '4a' | 5       | 40     | 4    | 1.15(5) | 3.90(4) | 8.48 \times 10^{-2} | 2.50 \times 10^{-2} |
| '4b' | 20      | 50     | 4    | 1.10(3) | 6.55(4) | 4.62 \times 10^{-2} | 7.76 \times 10^{-3} |