A LETTERS JOURNAL EXPLORING THE FRONTIERS OF PHYSICS

OFFPRINT

Reply to the Comment by Martin Rohloff et al.

MICHAEL WILKINSON

EPL, **108** (2014) 30006

Please visit the website
www.epljournal.org

Note that the author(s) has the following rights:
– immediately after publication, to use all or part of the article without revision or modification, **including the EPLA-formatted version**, for personal compilations and use only;
– no sooner than 12 months from the date of first publication, to include the accepted manuscript (all or part), **but not the EPLA-formatted version**, on institute repositories or third-party websites provided a link to the online EPL abstract or EPL homepage is included.
For complete copyright details see: https://authors.epletters.net/documents/copyright.pdf.

epl

A Letters Journal Exploring the Frontiers of Physics

AN INVITATION TO SUBMIT YOUR WORK

www.epljournal.org

The Editorial Board invites you to submit your letters to EPL

EPL is a leading international journal publishing original, innovative Letters in all areas of physics, ranging from condensed matter topics and interdisciplinary research to astrophysics, geophysics, plasma and fusion sciences, including those with application potential.

The high profile of the journal combined with the excellent scientific quality of the articles ensures that EPL is an essential resource for its worldwide audience. EPL offers authors global visibility and a great opportunity to share their work with others across the whole of the physics community.

Run by active scientists, for scientists

EPL is reviewed by scientists for scientists, to serve and support the international scientific community. The Editorial Board is a team of active research scientists with an expert understanding of the needs of both authors and researchers.

www.epljournal.org

OVER
560,000
full text downloads in 2013

24 DAYS
average accept to online publication in 2013

10,755
citations in 2013

"We greatly appreciate the efficient, professional and rapid processing of our paper by your team."

Cong Lin
Shanghai University

Six good reasons to publish with EPL

We want to work with you to gain recognition for your research through worldwide visibility and high citations. As an EPL author, you will benefit from:

1. **Quality** – The 50+ Co-editors, who are experts in their field, oversee the entire peer-review process, from selection of the referees to making all final acceptance decisions.
2. **Convenience** – Easy to access compilations of recent articles in specific narrow fields available on the website.
3. **Speed of processing** – We aim to provide you with a quick and efficient service; the median time from submission to online publication is under 100 days.
4. **High visibility** – Strong promotion and visibility through material available at over 300 events annually, distributed via e-mail, and targeted mailshot newsletters.
5. **International reach** – Over 2600 institutions have access to EPL, enabling your work to be read by your peers in 90 countries.
6. **Open access** – Articles are offered open access for a one-off author payment; green open access on all others with a 12-month embargo.

Details on preparing, submitting and tracking the progress of your manuscript from submission to acceptance are available on the EPL submission website **www.epletters.net**.

If you would like further information about our author service or EPL in general, please visit **www.epljournal.org** or e-mail us at **info@epljournal.org**.

EPL is published in partnership with:

European Physical Society | Società Italiana di Fisica | EDP Sciences | IOP Publishing

A Letters Journal Exploring the Frontiers of Physics

November 2014

EPL, **108** (2014) 30006 www.epljournal.org
doi: 10.1209/0295-5075/108/30006

Reply

Reply to the Comment by Martin Rohloff et al.

Michael Wilkinson

Department of Mathematics and Statistics, The Open University - Walton Hall, Milton Keynes, MK7 6AA, England, UK

received 17 August 2014; accepted in final form 20 October 2014
published online 7 November 2014

PACS 05.70.Fh – Phase transitions: general studies
PACS 82.40.Bj – Oscillations, chaos, and bifurcations
PACS 47.57.ef – Sedimentation and migration

Copyright © EPLA, 2014

Introduction. – Reference [1] discusses a theory describing experiments on a binary mixture of liquids close to a miscibility transition, with critical temperature T_c. In these experiments periods of turbidity are observed as the system is driven away from the critical point by a slow change of the temperature T. The turbidity is caused by precipitation of droplets which drift towards the interface between the two phases due to their difference in density. Reference [1] presents a theory for the time period Δt between these precipitation events, as a function of the rate of change of the temperature of the system, described by a parameter ξ with dimensions of inverse time. The theory assumes that the initial growth of droplets is by Ostwald ripening (as discussed in [2]), and that this crosses over to collisional growth driven by gravitational settling. The theory predicts that

$$\Delta t \sim K\,\xi^{-3/7}. \tag{1}$$

The coefficient K is a function of the reduced temperature, $\theta = |T - T_c|/T_c$:

$$K(\theta) = \alpha\left(D\Lambda\kappa^3\right)^{-1/7}, \tag{2}$$

where α is a dimensionless constant, D is the interdiffusion coefficient, Λ is a Kelvin length for the phase boundary and the settling speed of a droplet of radius a is $u = \kappa a^2$. The quantities Λ and κ are defined in terms of tabulated material parameters of the mixture, such as the interfacial tension γ and the density difference between the phases, $\Delta\rho$. Because $\Delta\rho$, γ and D all approach zero as a power law in θ at the critical point, it is predicted that $K \sim \theta^{-\eta}$. Using standard critical exponents gives $\eta \approx 0.5$ [1].

In [1] it is asserted that (1) is a good description of the experimental data, for the water/isobutoxyethanol system. This statement is based upon a plot in the PhD Thesis of Lapp [3], fig. 3.26, which is a scatter plot of $\Delta t\xi^{3/7}$ against temperature. The experimental points collapse onto a curve which shows good agreement with eqs. (1) and (2), over a wide range of values of ξ and θ, with the dimensionless number α close to unity.

The comment by Rohloff, Lapp, and Vollmer, however, is phrased so as to suggest that their experimental results do not support the theory. In the following I argue that the data which they present are fully in accord with the theory as described in [1]. Furthermore, the basis of the claim that there is a disagreement results from an attempt to extend the theory in [1] by arguing that it can be used to determine a bound on the oscillation period. I give two arguments indicating that this proposed extension of the theory is unsound.

Comparison with experimental data. – Figure 1 of the Comment is a version of fig. 3.26 in [3]. I am grateful to the authors of the Comment for making this available in a widely disseminated journal, because it lends experimental support to [1].

In particular, the experimental data in fig. 1 of the Comment indicate that $\Delta t\xi^{3/7}$ is a function of temperature, as the theory predicts, with both ξ and θ varying over approximately two decades. Furthermore, the scatter of data points for different values of ξ appears to be random, indicating that there is no residual systematic dependence upon ξ. This is very strong support for the scaling relation, eq. (1).

Concerning the temperature dependence of $K = \Delta t\xi^{3/7}$, the experimental data points in fig. 1 differ from the theoretical prediction (dotted green curve) by what appears to be a constant offset. This constant offset on a logarithmic scale corresponds to the unknown dimensionless constant α in (2). Moreover, the fact that the data points follow a line of constant slope in

this double-logarithmic plot is an indication that the prefactor K has a power-law dependence on the reduced temperature, $K \sim \theta^{-\eta}$, with $\eta \approx 0.5$. These observations show that $K(\theta)$ is well approximated by eq. (2).

The presentation of the experimental data described in the Comment is a non-trivial test of the theory, and the data in fig. 1 of the Comment are entirely consistent with the prediction in [1].

One aspect of the presentation of fig. 1 of the Comment should to be remarked upon. The theoretical curve is not quite the same as that proposed in [1], namely eq. (1) above: an additional factor of $2.4396 \times (4^3/3^4)^{1/7} \approx 2.4$ has been included in the theoretical expression used in the Comment, namely eq. (3) of that work. This exaggerates the apparent "disagreement" with the experimental data, as presented in fig. 1 of the Comment.

Proposed bound on the period. – The model developed in [1] includes a "collision efficiency" ϵ, which was assumed to be of order unity. The authors of the Comment argue that $\epsilon < 1$, and that this inequality leads to a lower bound on the period Δt. They argue that the resulting bound is violated by their experimental data.

There are two flaws in this argument. First, droplet growth in a system which combines gravitational settling and Ostwald ripening is an extremely complicated problem, involving a population of droplets with a distribution of radii $P(a,t)$. This distribution is determined by a supersaturation field satisfying an advection diffusion equation with moving boundaries (due to gravitational settling of the droplets). The simplified model described in eq. (11) of [1], equivalently eq. (1) of the Comment, is a caricature of this complex system in terms of the evolution of the radius of a single droplet, $a(t)$. While this has proven sufficient to surmise scaling properties (as was done in [1]), it is not adequate to establish quantitative bounds on the oscillation period (as proposed in the Comment). Adapting eq. (1) of the Comment to yield a precise bound on the period is an unsound procedure.

Secondly, the argument is based upon the notion that a collision efficiency ϵ cannot exceed unity. This inequality cannot be guaranteed for the collision efficiency which is defined in [1]. The value of ϵ is defined by considering a droplet of radius a falling through a gas of much smaller droplets with volume fraction Φ at a relative speed u. The rate of increase of the volume v_{d} of the droplet is defined to be

$$\dot{v}_{\mathrm{d}} = \epsilon \pi a^2 u \Phi. \tag{3}$$

In the case where the large droplet grows by coalescence upon contact, the collision efficiency cannot exceed unity (and it may be substantially smaller, as is thought to be the case for water droplets in clouds [4]). In [1], however, droplets grow by Ostwald ripening, which is effected by diffusive transfer of material between droplets which need not be in contact. A large droplet creates a reduction of the supersaturation field in its neighbourhood, which causes material to evaporate from smaller droplets and condense on the larger droplet [2]. This mechanism allows a falling droplet to collect material from a cylindrical region which has a greater area than its geometrical cross-section, implying that it is possible, in principle, for the collision efficiency defined in (3) to exceed unity.

While the collision efficiencies for water droplets in air have been extensively investigated, those of small droplets in the water/isobutoxyethanol system do not appear to have been studied. Moreover, the physics is fundamentally different (as discussed in [1]) because the experiments are performed close to the critical point (down to $\theta \approx 10^{-3}$). There is, however, an argument supporting the assumption that the collision efficiency ϵ is of order unity. If ϵ were very small or very large, it is unlikely that it would be a constant. Instead, ϵ would be expected to have a systematic dependence upon parameters of the model, which would imply that the predicted scaling relations (1) and (2) would be expected to fail. The success of these predictions is indirect evidence that $\epsilon \approx 1$.

Summary. – The experimental data presented in the Comment are fully consistent with the theory in [1]. Figure 1 of the Comment confirms the $\Delta t \propto \xi^{-3/7}$ scaling, and that the temperature dependence of the prefactor is in accord with the theory. The dimensionless prefactor α would be close to unity if a comparison were made with the theory in the form presented in [1].

The claim that the theory in [1] does not agree with the experimental results is a consequence of an inappropriate attempt to extend it. In particular, the model used in [1] is not sufficiently accurate to support quantitative bounds on the period, and the physics of the growth process does not guarantee that $\epsilon = 1$ is an upper bound on the "collision efficiency".

REFERENCES

[1] Wilkinson M., *EPL*, **106** (2014) 40001.
[2] Lifshitz E. M. and Slyozov V. V., *J. Phys. Chem. Solids*, **19** (1961) 35.
[3] Lapp T., *Evolution of droplet distributions in hydrodynamic systems*, PhD Thesis, Georg-August-University, Göttingen (2011).
[4] Mason B. J., *The Physics of Clouds* (University Press, Oxford) 1957.