Comment on "Comparison between solutions of the general dynamic equation and the kinetic equation for nucleation and droplet growth" [J. Chem. Phys. 130, 014102 (2009)]

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In a recent journal,[1] the Becker–Döring equation (BDE) was solved numerically for large cluster numbers n, giving the time-dependent distributions of nuclei far into the growth region. This provides a unique opportunity of a high-precision verification of the matched asymptotic solution (MAS) of Refs. [2] and [3], which, due to computational challenges of the large-n BDE, was previously tested only for modest $R \lesssim 2R_*$, the critical size. Comparison is especially interesting since large supersaturations S were considered in Ref. [1], leading to strong discreteness effects with significant deviations from the continuous "Zeldovich–Frenkel" limit.

A dimensionless radius $r = R/R_*$ will be used. To adjust the time scale, consider the Hertz–Knudsen growth law, which is associated with the BDE and which can be written as

$$\dot{r} = \frac{1}{a\tau}(1 - e^{-a\zeta}), \quad \zeta \equiv 1 - 1/r, \quad a \equiv \ln S. \tag{1}$$

This can serve as a definition of $\tau \simeq 2.788/C_1$ for parameters used in Fig. 2 of Ref. [1]. The growth-region flux in the MAS has the form

$$j(r,t) = J \exp(-e^{-x}), \quad x = [t - t_i(r)]/\tau. \tag{2}$$

Here, $t_i(r)$ is the "incubation time"[3]

$$t_i(r) = \tau \ln\left(\frac{6W_*}{kT}\right) + \mathbf{P} \int_0^r \frac{dr}{\dot{r}} - 2\tau C(a),$$

$$\tag{3}$$

$$C(a) = \int_0^1 dr\left(\frac{1}{\tau\dot{r}} - \frac{1}{r-1}\right)$$

with the barrier $W_*/kT = (4/27)\Theta^3/a^2$ in units of dimensionless interfacial tension Θ used in Ref. [1], and $\mathbf{P}$ indicating the principal value of the integral. With the above flux, the distribution is given by

$$f(r,t) = j(r,t)/\dot{r} \tag{4}$$

and, at least for not too small times, successfully reproduces the numerical data of Ref. [1] (see Fig. 1).[4]

The authors of Ref. [1] also considered the "general dynamic equation" with a stationary nucleation source placed at some small size $r_n > 1$ (in present notations) and turned on at $t = 0$. Such a source leads to a sharp front of the distribution, while the location of that front is sensitive to the selection of r_n. The MAS, on the other hand, suggests that the

source should be both time-dependent and r_n-dependent, with intensity given by Eq. (2) evaluated for $(r_n - 1) \to 0$, i.e., with an asymptote

$$\frac{1}{\tau}t_i(r_n) \sim \ln\left(\frac{6W_*}{kT}\right) - C(a) + \ln(r_n - 1). \tag{5}$$

(This source appears on the intermediate stages of the derivation.[2,3]) Distribution at larger sizes is then insensitive to selection of r_n, provides the latter remains close to 1, and this distribution is characterized by a smooth front, as in Fig. 1, with a finite width $-(\partial \ln f/\partial r|_{x=0})^{-1} \simeq \tau\dot{r}$. Inclusion of the diffusion component of the flux in the growth region is not required.

An interesting suggested way to avoid ambiguity in selecting the location of a stationary source is to request that the resulting sharp front give asymptotically the proper number of nuclei.[1] In terms of Eq. (2) this corresponds to $x = \gamma$, the Euler constant, quite similarly to the time-lag ("induction time") problem.[3] Evaluating the related position r_n, one obtains

$$r_n - 1 = \left(\frac{6W_*}{kT}\right)^{-1} e^{-\gamma + C(a)}. \tag{6}$$

This gives a Θ^{-3} dependence, close to empirical $\Theta^{-2.9}$ in the
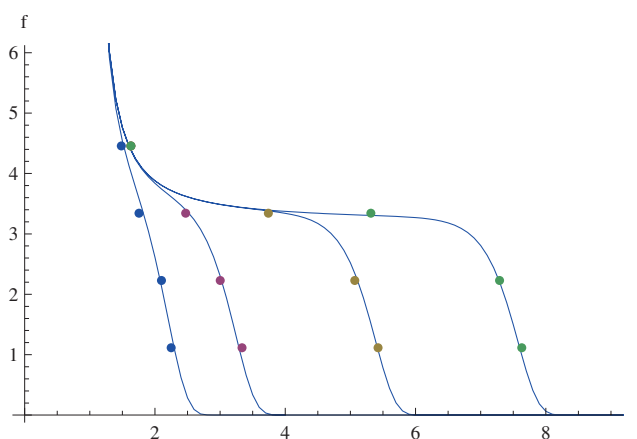

FIG. 1. Reduced distribution $f(r,t)/\tau J$ as a function of $r = R/R_*$ at different times. From left to right: $t/\tau \simeq 7.2, 10.8, 17.9, 25.1$ (equivalently, dimensionless "time" in Fig. 2 of Ref. [1] is 20, 30, 50 and 70). Symbols—numerics (Ref. [1]); lines—Eqs. (2)–(4). No matching parameters were used.

lower part of Fig. 4 in Ref. 1. The dependence on $a = \ln S$ also appears reasonably accurate on the logarithmic scale considered.

ACKNOWLEDGMENTS

I would like to thank the authors of Ref. 1 for very useful correspondence.

APPENDIX A: EVALUATION OF THE INTEGRAL IN EQUATION (3)

The presence of **P**, the principal value integration, was met with certain caution in the past, which limited the application of the MAS. In fact, an alternative representation of Eq. (3) in more conventional terms of decay and growth integrals is possible [see Eq. (9) of Ref. 3]. However, in a situation when $\int dr / \dot{r}$ cannot be evaluated in elementary functions, Eq. (3), which splits off the barrier-dependence, can be more convenient for actual calculations, especially since modern computational packages can evaluate **P** automatically. For example, one can use built-in numerical integration in the latest versions of *Mathematica*, with the extra option Principal Value → True. This was done for $a = \ln 20.57$ of Ref. 1 for a set of sizes r ranging between 1.1

and 10, and was used to plot solid lines in Fig. 1 at different times.

Alternatively, one could place the burden of **P** on $\tau / \zeta = \lim_{a \to 0}(1 / \dot{r})$, which can be integrated explicitly, while the correction $1 / \dot{r} - \tau / \zeta$ is finite near $r = 1$ and allows integration in conventional sense. One has

$$\frac{1}{\tau} t_i(r) = \ln\left[\frac{6W_*(r-1)}{e^2 kT}\right] + r + \int_0^r dr\left(\frac{1}{|\tau \dot{r}|} - \frac{1}{|\zeta|}\right) \quad \text{(A1)}$$

with the elementary part corresponding to the Zeldovich–Frenkel limit.[3] The above form is more amenable to various analytical approximations, as discussed in connection with large-r fluxes observed by Granasy and James[5] for the Turnbull–Fisher alternative of the BDE.

[1] V. Holten and M. E. H. van Dongen, J. Chem. Phys. **130**, 014102 (2009).
[2] V. A. Shneidman, Sov. Phys. Tech. Phys. **32**, 76 (1987).
[3] V. A. Shneidman, Sov. Phys. Tech. Phys. **33**, 1338 (1988).
[4] Minor scatter of symbols is due to limited accuracy of reading data from the original Fig. 2 of Ref. 1; For a precise recent comparison, see V. Holten, Ph.D. dissertation, Eindhoven University of Technology, 2009.
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