Reply to "Comment on 'Transient kinetics of nucleation'"

G. Shi and J. H. Seinfeld
Department of Chemical Engineering, California Institute of Technology, Pasadena, California 91125

K. Okuyama
Department of Chemical Engineering, University of Hiroshima, Higashi-Hiroshima 724, Japan
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The results obtained in our previous paper [Phys. Rev. A **41**, 2101 (1990)] are extended to obtain $N(g_d,t)$, the total accumulated number concentration of nucleated clusters at the detectable size, g_d. It is shown that $N(g_d,t)$ obtained by Shneidman [preceding Comment, Phys. Rev. A **44**, 8441 (1991)] is incorrect since the time lag associated with $N(g_d,t)$ suffers a singularity at $\ln(-1)$.

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In our previous paper [1] we derived an expression for the total number concentration of clusters at the critical size, g_*, during transient nucleation, $N(g_*,t)$, by using the singular perturbation approach developed for transition layers [2]. Shneidman [3–5] attempted to solve for $N(g_d,t)$ without using $N(g_*,t)$, where g_d is the detectable cluster size and $g_d > g_*$. We agree with the preceding Comment [3] that we obtained similar results for the Laplace-transformed cluster-size distribution near g_*, even though the aim of work [1] was to obtain $N(g_*,t)$ and Shneidman's goal was to obtain $N(g_d,t)$. To discuss the other issues raised [1], it is necessary for us to extend our previous results [1] to the case considered by Shneidman [3–5]. In doing so, we can show that the total time lag associated with $N(g_d,t)$ obtained by Shneidman suffers from a singularity. It also will be shown that the correct expression for $N(g_d,t)$ and its associated time lag can be easily obtained by extending our previous result based on the conservation of total number concentration of nucleated clusters. Here the nucleated clusters are those with size equal to or larger than g_0, the size at which the true nucleation rate is defined, i.e., at g_0 the probability of decay is much smaller than that of growth [6].

From our previous work [1] the cluster flux $J(g,t)$, valid strictly in the entire critical region, $g_* - \delta < g < g_* + \delta$, is

$$J(g,t) = J_s(g)\exp\left\{-\left[\frac{g-g_*}{\delta} + \exp\left[-\frac{t-\lambda\tau}{\tau}\right]\right]^2\right\}, \tag{1}$$

where the steady-state cluster flux is given by

$$J_s(g) = \beta(g)n(g)Z .$$

The expressions for the critical cluster size g_*, the flux of monomer to a g-sized cluster $\beta(g)$, the equilibrium cluster number concentration $n(g)$, the Zeldovich factor Z, and λ are in our previous paper [1]. (Note that λ presented in Ref. [1] is for $\beta(g) \propto g^{2/3}$. λ for other cases can be obtained accordingly.)

Equation (1) can be rewritten as

$$J(g,t) = J_s(g)\exp(-z^2)\exp\left[-\exp\left[-\frac{t-t'}{\tau}\right]\right] \times \exp\left[-\exp\left[-2\frac{t-\lambda\tau}{\tau}\right]\right], \tag{2}$$

where

$$z = \frac{g-g_*}{\delta}, \quad t' = (\lambda + \ln 2z)\tau .$$

When

$$-\frac{t-t'}{\tau} \gg -2\frac{t-\lambda\tau}{\tau},$$

i.e.,

$$t \gg (\lambda - \ln 2z)\tau = 2\lambda\tau - t' , \tag{3}$$

Eq. (2) reduces to

$$J(g,t) = J_s(g)e^{-z^2}\exp\left[-\exp\left[-\frac{t-t'}{\tau}\right]\right] . \tag{4}$$

Since $2z$ in Eq. (3) must be larger than zero, Eq. (4) is thus strictly valid only in the right critical region, i.e., $0 < z < 1$ or $g_* < g < g_* + \delta$.

In obtaining the cluster-size distribution [and thus Eq. (1)] in the critical region, we found [1] that the right outer solutions are asymptotically zero, but that does not imply that the right outer solutions just outside the right critical region are also zero. Indeed, for example, the cluster flux in the immediate region just outside the right critical region can be asymptotically described by Eq. (4) for $z \ll 1/\epsilon$ or $g \ll 2g_*$, where $\epsilon = \delta/g_*$.

Equation (4) can be rewritten as

$$J(g_0,t) = J_s(g_*)\exp\left[-\exp\left[\frac{t-t'}{\tau}\right]\right] , \tag{5}$$

since $J_s(g_0)e^{-z_0^2} \cong J_s(g_*)$. If Eq. (1) is exactly valid in the region of interest, $J_s(g_0)e^{-z_0^2}$ should exactly equal $J_s(g_*)$ since the steady-state rate of nucleation should be equal at all sizes [6].

Upon further examination of Shneidman's work, it can be shown that the time lag associated with $N(g_d,t)$ obtained by Shneidman [3,5], $t_i(g_d)$, has a singularity at $\ln(-1)$, as shown below for $\beta(g)=\beta(g_*)x^{2/3}$, $x=g/g_*$.

In this case, the average growth rate for clusters with size $g \gg g_* + \delta$ can be approximated as [5,6]

$$\dot{g}_m=\frac{3g_*}{\tau}x^{2/3}(1-x^{-1/3}) \tag{6}$$

and

$$\int dg\frac{1}{\dot{g}_m}=\tau\{x^{1/3}+\ln[(x^{1/3}-1)]\} \ . \tag{7}$$

The total time lag τ_t associated with $N(g_d,t)$ obtained by Shneidman is [3,5]

$$\begin{aligned}\tau_t&=t_i(g_d)+\gamma\tau\\&=\tau\left\{\left[\frac{g}{g_*}\right]^{1/3}+\ln\left[\left[\frac{g}{g_*}\right]^{1/3}-1\right]\right\}\Bigg|_0^{g_d}\\&\quad+\tau\left[-2+\gamma+\ln\frac{2}{\epsilon^2}\right] ,\end{aligned} \tag{8}$$

where $\gamma=0.5772$ is Euler's constant. Shneidman's result for $t_i(g_d)$ given by Eq. (8) suffers from a singularity at $\ln(-1)$. That is why Shneidman had to introduce the assumption that the integral

$$\int_0^{g_d}dg\frac{1}{\dot{g}_m}$$

has to take its "principle value" [3,5].

A correct approach to "match" the "growth region" and the "nucleation region" is to use the fact that the total accumulated number concentration of nucleated clusters is conserved, i.e.,

$$N(g_d,t)\equiv N(g_0,t-t_{md}) \ . \tag{9}$$

Here g_0 must be larger than $g_*+\delta$, since the probability of growth outside the right critical region is much larger than that of decay and thus clusters of size larger than $g_*+\delta$ will grow to be large enough to be detected [6]. Since

$$N(g_0,t)\equiv\int_0^t J(g_0,t)dt \ , \tag{10}$$

and $J(g_0,t)$ is given by Eq. (5), which is approximately valid for $0<g_0 \ll 2g_*$ and $t \gg (\lambda-\ln 2z_0)\tau$, then

$$N(g_0,t)=J_s(g_*)\tau[E_1(e^{-t-t'/\tau})-E_1(e^{t'/\tau})] \ , \tag{11}$$

which is only valid for $g_*+\delta \ll g_0 \ll 2g_*$, where $t'=(\lambda+\ln 2z_0)\tau$, $\lambda=g_*^{-1/3}-1+\ln[3(1-g_*^{-1/3})/\epsilon]$, and E_1 is the exponential integral. For $t \gg (t'/\tau+1)\tau$, Eq. (11) reduces to

$$N(g_0,t)=J_s(g_*)(t-\tau_{me}) \ . \tag{12}$$

The effective time lag associated with $N(g_0,t)$ is then given by

$$\tau_{me}=\tau[\gamma+t'/\tau+E_1(e^{t'/\tau})] \ . \tag{13}$$

Using Eq. (9), we obtain from Eq. (11)

$$N(g_d,t)=J_s(g_*)\tau[E_1(e^{-(t-t_{md}-t')/\tau})-E_1(e^{t'/\tau})] \ , \tag{14}$$

which for $t \gg (t'/\tau+1+t_{md})\tau$ reduces to

$$N(g_d,t)=J_s(g_*)(t-t_{md}-\tau_{me}) \ . \tag{15}$$

Here t_{md} is given by

$$t_{md}=\int_{g_0}^{g_d}dg\frac{1}{\dot{g}_m} \ , \tag{16}$$

which is free of any singularity by using Eq. (7). Thus the total time lag associated with $N(g_d,t)$ is given by

$$\begin{aligned}\tau_t&=t_{md}+\tau_{me}\\&=\tau\left\{\left[\frac{g}{g_*}\right]^{1/3}+\ln\left[\left[\frac{g}{g_*}\right]^{1/3}-1\right]\right\}\Bigg|_{g_0}^{g_d}\\&\quad+\tau[t'+\gamma+E_1(e^{t'/\tau})] \ ,\end{aligned} \tag{17}$$

which is quite different from Eq. (8) even in the limit of very large g_*. More importantly Eq. (17) is free of any singularity.

Equation (4) and Eqs. (8)–(14) represent the solution to a problem attempted to be solved by Shneidman [3–5], which is important in interpreting nucleation experimental data.

Since g_0 is bounded by $g_*+\delta \ll g_0 \ll 2g_*$, a natural choice for g_0 is

$$g_0=\tfrac{1}{2}(g_*+\delta+2g_*)=\tfrac{1}{2}(3g_*+\delta) \ .$$

It should be noted that only for clusters of $g \geq g_0$ can the probability of decay be neglected. Shneidman's statement [3] that critical clusters of g_* "do not grow macroscopically" is not strictly correct, since a cluster of size g_* has at least equal probability to decay and grow [6].

We will conclude by pointing out that we employed the singular perturbation approach developed for transition layers [1,2], while Shneidman used the approach for conventional boundary layers. In treating the critical region as a transition layer, two unknowns in the inner solution can be obtained by matching the inner solution with two outer solutions. In Shneidman's treatment, there is only one outer solution available to match with the inner one. Another unknown was assumed to be zero. While the two treatments result in a similar expression for the Laplace-transformed cluster-size distribution in the critical region because of the present particular right outer boundary condition, for a different boundary condition, or for solving the barrier-crossing problem in general, only the approach developed for transition layers is correct.

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