PHYSICAL REVIEW A VOLUME 26, NUMBER 4 OCTOBER 1982

Derivation of the Ornstein-Zernike differential equation from the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy

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(Received 20 April 1982)

The theory of inhomogeneous fluids is applied to a d-dimensional system near its critical point to derive the probability of finding a particle at a distance r from a pair separated by a distance s, given that $r \gg \xi \gg s$, where ξ is the correlation length. When this result is used in the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy, an approximation-free equation is obtained, from which it follows that the pair correlations for $r \gg \xi$ satisfy the Ornstein-Zernike differential equation.

I. INTRODUCTION

Interest in the use of integral equations to describe critical phenomena in fluids has been rekindled following the report of nonclassical critical exponents from the Yvon-Born-Green (YBG) equation in $d=3$ dimensions.[1] This equation for the pair-correlation function $g_2(r)$ in terms of the intermolecular potential is obtained by truncating the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy with the Kirkwood superposition approximation (KSA).[2] After the report of novel critical exponents, a sagacious analysis[3,4] of the decay of the YBG net correlation function $h(r)=g_2(r)-1$ appeared; at the critical point, this decay is characterized by the exponent η as $1/r^{d-2+\eta}$. For $d=3$, two possibilities emerged: Either (a) the YBG equation has no critical point, in the sense that the isothermal compressibility K_T remains uniformly bounded, or (b) K_T diverges to $+\infty$, but $\eta=1$, which is much larger than the expected value $\eta \simeq 0.03$, and $h(r)<0$ for $r \to \infty$, which does not seem to be physical. Further numerical studies of the solutions to the YBG equation for $d=3$ support possibility (a).[5] On the positive side, the analysis of $h(r)$ for $d>4$ showed that $\eta=0$,[4] and numerical studies for $d=6$ strongly suggest that the YBG exponents are classical.[6] Both of these results are in agreement with current renormalization-group theory.[7]

The problem with the YBG equation, at least for $d<4$, is due to the use of the KSA, this being the only approximation in the theory. The question, then, is whether the KSA can be improved upon to provide a better description of the critical region for $d<4$. It would also be of interest to understand why the KSA seems to give the correct upper borderline dimensionality $d_{>}=4$. A beginning step in these directions is to derive the classical Ornstein-Zernike (OZ) form of $h(r)$ [i.e., the form of $h(r)$ for $r \gg \xi$, $\xi \to \infty$] from the BBGKY hierarchy without using the KSA or, indeed, without invoking any closure assumption. The purpose of this paper is to report such a derivation for arbitrary d.

To be more specific, the derivation requires only the first member of the BBGKY hierarchy for a uniform fluid:

$$-g_2'(r)=g_2(r)u'(r) +\rho \int d\vec{s}\, \hat{r}\cdot\hat{s}\, u'(s) g_3(r,s\,|\,\vec{r}-\vec{s}\,|\,) , \tag{1.1}$$

where ρ is the number density, $u(r)=\beta\phi(\,|\,\vec{r}\,|\,)$ is the dimensionless intermolecular potential ($\beta=1/k_BT$), and g_3 is the three-particle correlation function. From this, the OZ differential equation

$$\nabla^2 h(r) \equiv h''(r)+\frac{d-1}{r}h'(r)=\xi^{-2}h(r) \tag{1.2}$$

is then derived, with the correlation length ξ given by

$$\xi^2=(2d)^{-1}\rho \int d\vec{r}\, r^2 h(r) \Big/ \left[1+\rho\int d\vec{r}\, h(r)\right] . \tag{1.3}$$

Moreover, the entire analysis is done for pair potentials $u(r)$ of finite range, but the results could be extended to infinite-range potentials which decay sufficiently fast at large distances. The corresponding extension for the YBG equation has, in fact, already been carried out.[8]

The derivation shows that the OZ result (1.2) is correct to leading order in ξ/r for $r \gg \xi$, as expected. The treatment, in fact, breaks down when $r \lesssim \xi$, and this is discussed in Sec. III. One must, of course, extend the theory into the region $r \ll \xi$ in order to study properties *at* the critical point.

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II. DERIVATION

The theory of inhomogeneous fluids can be used to derive an expression for the correlation function for three particles when one is far from the other two. Let $\rho_n = \rho^n g_n$ and consider

$$\rho_2(\vec{r}+\vec{s},\vec{r}-\vec{s}\mid n(\vec{x}))\,,$$

which is the probability density of finding particles at the positions $\vec{r}+\vec{s}$ and $\vec{r}-\vec{s}$ in a system with nonuniform density $n(\vec{x})$. Taking the latter quantity to be the density induced in the system by fixing a particle at the origin $\vec{0}$, one has

$$n(\vec{x})=\rho g_2(\vec{x})=\rho g_2(x) \tag{2.1}$$

so that

$$\rho_2(\vec{r}+\vec{s},\vec{r}-\vec{s}\mid n(\vec{x}))=\rho_3(\vec{0},\vec{r}+\vec{s},\vec{r}-\vec{s})/\rho\,, \tag{2.2}$$

where the right-hand side is the conditional probability density of finding particles at $\vec{r}+\vec{s}$ and $\vec{r}-\vec{s}$, given that there is one at the origin. Since the correlation functions for a uniform fluid are translationally and rotationally invariant, the triplet correlation function needed for Eq. (1.1) follows from the right-hand side of Eq. (2.2) by letting $\vec{r}\rightarrow\vec{r}-\vec{s}$ and $\vec{s}\rightarrow\vec{s}/2$, in succession; that is,

$$\rho_3(\vec{0},\vec{r},\vec{r}-\vec{s})=\rho^3 g_3(r,s,\mid\vec{r}-\vec{s}\mid)\,.$$

Now assume that the system is near a critical point, and consider configurations $(\vec{0},\vec{r}+\vec{s},\vec{r}-\vec{s})$ such that $r \gg \xi \gg s$. Since $n(\vec{x})$ may be expected to vary significantly only over distances of the order of the correlation length ξ, and $\xi \gg s$, the density in the neighborhood of the particles at $\vec{r}+\vec{s}$ and $\vec{r}-\vec{s}$ is essentially constant, and approximately equal to $n(\vec{r})=\rho g_2(\vec{r})$.[9] A reasonable estimate would therefore seem to be

$$\rho_2(\vec{r}+\vec{s},\vec{r}-\vec{s}\mid n(\vec{x}))=\rho_2^0(\vec{r}+\vec{s},\vec{r}-\vec{s})\,, \tag{2.3}$$

where the notation 0 indicates that the right-hand side is evaluated for a system with uniform density $\rho g_2(\vec{r})$. This is just the density in the nonuniform system at the point halfway between $\vec{r}+\vec{s}$ and $\vec{r}-\vec{s}$.

A systematic procedure for improving upon the result (2.3), whereby it is just the first term in a functional Taylor series, can be obtained using methods originally developed by Lebowitz and Percus.[10] The expansion parameter then becomes

$$\Delta n(\vec{x})=n(\vec{x})-n_0\,, \tag{2.4}$$

where n_0 is the density of the uniform reference system, i.e.,

$$n_0=\rho g_2(\vec{r})=n(\vec{r})\,. \tag{2.5}$$

This particular choice of n_0 optimizes the convergence of the functional expansion for any given value of $\vec{r}$.[10]

The computation of the coefficients in the functional Taylor series is facilitated by making use of the analogy in which the density deviation is thought of as having been produced by an externally imposed field $\beta\Phi(\vec{x})\equiv U(\vec{x})$; for Eq. (2.3), this is just the intermolecular potential $u(x)$. The variation of ρ_2 with respect to $n(\vec{r})$ can then be written formally by means of the chain rule as

$$\begin{aligned}\rho_3(\vec{0},\vec{r}+\vec{s},\vec{r}-\vec{s})/\rho &= \rho_2^0(\vec{r}+\vec{s},\vec{r}-\vec{s})+\int d\vec{r}\,'\left[\frac{\delta\rho_2(\vec{r}+\vec{s},\vec{r}-\vec{s}\mid n(\vec{x}))}{\delta n(\vec{r}\,')}\right]_{n(\vec{x})=n_0}\Delta n(\vec{r}\,')+\cdots\\ &= \rho_2^0(\vec{r}+\vec{s},\vec{r}-\vec{s})+\int d\vec{r}\,'\left[\int d\vec{r}\,''\frac{\delta\rho_2(\vec{r}+\vec{s},\vec{r}-\vec{s}\mid U(\vec{x}))}{\delta U(\vec{r}\,'')}\frac{\delta U(\vec{r}\,'')}{\delta n(\vec{r}\,')}\right]_{n(\vec{x})=n_0}\Delta n(\vec{r}\,')+\cdots\,,\end{aligned} \tag{2.6}$$

where

$$\begin{aligned}\left[\frac{\delta\rho_2(\vec{r}+\vec{s},\vec{r}-\vec{s}\mid U(\vec{x}))}{\delta U(\vec{r}\,'')}\right]_{n(\vec{x})=n_0} &= \rho_3^0(\vec{r}+\vec{s},\vec{r}-\vec{s},\vec{r}\,'')-n_0\rho_2^0(\vec{r}+\vec{s},\vec{r}-\vec{s})\\ &\quad +\rho_2^0(\vec{r}+\vec{s},\vec{r}-\vec{s})[\delta(\vec{r}+\vec{s}-\vec{r}\,'')+\delta(\vec{r}-\vec{s}-\vec{r}\,'')]\,,\end{aligned} \tag{2.7a}$$

$$\left[\frac{\delta U(\vec{r}\,'')}{\delta n(\vec{r}\,')}\right]_{n(\vec{x})=n_0}=\delta(\vec{r}\,'-\vec{r}\,'')/n_0-c^0(\mid\vec{r}\,'-\vec{r}\,''\mid)\,. \tag{2.7b}$$

As before, the notation 0 denotes functions evaluated at the uniform reference density n_0, and $c(r)$ is the uniform fluid direct correlation function, related to $h(r)$ by the OZ integral equation

$$h(r)=c(r)+\rho\int d\vec{s}\, c(s)h(|\vec{r}-\vec{s}|)\ . \tag{2.8}$$

The zeroth and second moments of this equation imply the following results, needed below, for the compressibility $\chi=\rho^{-1}(\partial\rho/\partial p)_\beta$ (p being the pressure) and correlation length ξ:

$$\begin{aligned}\frac{\rho\chi}{\beta}&\equiv 1+\rho\int d\vec{r}\, h(r)\\ &=\left[1-\rho\int d\vec{r}\, c(r)\right]^{-1}\end{aligned} \tag{2.9a}$$

$$\xi^2=(2d)^{-1}\rho\int d\vec{r}\, r^2 c(r)\Big/\left[1-\rho\int d\vec{r}\, c(r)\right]\ . \tag{2.9b}$$

Near (but not at) the critical point, the functions in Eq. (2.7) should decay exponentially on the scale of the correlation length, and an expansion of $n(\vec{r}\,')$ about $\vec{r}\,'=\vec{r}$ in Eq. (2.6) is justified. Since $\Delta n(\vec{r}\,')=n(\vec{r}\,')-n_0$ and $n_0=n(\vec{r})$, one has

$$\Delta n(\vec{r}\,')=(\vec{r}\,'-\vec{r})\cdot\vec{\nabla}n(\vec{r})+\tfrac{1}{2}[(\vec{r}\,'-\vec{r})\cdot\vec{\nabla}]^2 n(\vec{r})+\cdots\ , \tag{2.10}$$

whereupon Eq. (2.6) becomes, after integrating term-by-term and using the results (2.9),

$$\begin{aligned}\rho_3(\vec{0},\vec{r}+\vec{s},\vec{r}-\vec{s})/\rho=\rho_2^0(\vec{r}+\vec{s},\vec{r}-\vec{s})&+\frac{\beta}{n_0^2\chi_0}\rho_2^0(\vec{r}+\vec{s},\vec{r}-\vec{s})(\vec{s}\,\vec{s}-2\xi_0^2\underline{I}):\vec{\nabla}\,\vec{\nabla}n(r)\\ &+\frac{1}{2}\frac{\beta}{n_0^2\chi_0}\int d\vec{r}\,'[\rho_3^0(\vec{r}+\vec{s},\vec{r}-\vec{s},\vec{r}\,')-n_0\rho_2^0(\vec{r}+\vec{s},\vec{r}-\vec{s})]\\ &\times[(\vec{r}-\vec{r}\,')(\vec{r}-\vec{r}\,')-2\xi_0^2\underline{I}]:\vec{\nabla}\vec{\nabla}n(r)+\cdots\ .\end{aligned} \tag{2.11}$$

Terms nonlinear in $\Delta n(\vec{x})$ in Eq. (2.6) are neglected in deriving this result, as are terms involving fourth- and higher-order derivatives of $n(\vec{r})$. In view of the anticipated exponential decay of $n(\vec{r})$, terms of the first type lead to entirely negligible corrections in the regime $r\gg\xi$; terms of the second type are also negligible in this limit, as they ultimately lead to corrections to the OZ differential equation of, at most, relative order l^2/ξ^2 [l is given in Eq. (3.1)]. The quantity $\underline{I}$ is the unit dyadic.

Since the triplet function in Eq. (1.1) is required at the density ρ, all quantities evaluated at the density n_0 on the right-hand side of Eq. (2.11) must be expanded about $n_0=\rho$, and all nonlinear terms in $n_0-\rho$ and its gradients may be neglected. When the resulting expression is simplified using the isothermal density derivative[11]

$$\frac{\partial\rho_2(\vec{s},-\vec{s})}{\partial\rho}=\frac{\beta}{\rho^2\chi}\left[2\rho_2(\vec{s},-\vec{s})+\int d\vec{r}\,'[\rho_3(\vec{s},-\vec{s},\vec{r}\,')-\rho\rho_2(\vec{s},-\vec{s})]\right]\ , \tag{2.12}$$

and the result that

$$\int d\vec{r}\,'[\rho_3(\vec{s},-\vec{s},\vec{r}\,')-\rho\rho_2(\vec{s},-\vec{s})]\vec{r}\,'\vec{r}\,'=f_1(s)\underline{I}+f_2(s)\hat{s}\hat{s}\ , \tag{2.13a}$$

where

$$f_1(s)=\frac{1}{d-1}\int d\vec{r}\,'[\rho_3(\vec{s},-\vec{s},\vec{r}\,')-\rho\rho_2(\vec{s},-\vec{s})]\,|\vec{r}\,'-\vec{r}\,'\cdot\hat{s}\hat{s}|^2 \tag{2.13b}$$

and

$$f_2(s)=\int d\vec{r}\,'[\rho_3(\vec{s},-\vec{s},\vec{r}\,')-\rho\rho_2(\vec{s},-\vec{s})](\vec{r}\,'\cdot\hat{s})^2-f_1(s)\ , \tag{2.13c}$$

the following equation is then obtained:

$$\begin{aligned}\rho_3(\vec{0},\vec{r},\vec{r}-2\vec{s})/\rho=\rho_2(\vec{0},2\vec{s})&+\frac{\partial\rho_2(\vec{0},2\vec{s})}{\partial\rho}\rho[g_2(|\vec{r}-\vec{s}|)-1]\\ &+\frac{\beta}{\rho\chi}[\rho_2(\vec{0},2\vec{s})s^2+\tfrac{1}{2}f_2(s)]\hat{s}\hat{s}:\vec{\nabla}\vec{\nabla}g_2(|\vec{r}-\vec{s}|)\\ &+\left[\frac{1}{2}\frac{\beta}{\rho\chi}f_1(s)-\xi^2\rho\frac{\partial\rho_2(\vec{0},2\vec{s})}{\partial\rho}\right]\nabla^2 g_2(|\vec{r}-\vec{s}|)+\cdots\ .\end{aligned} \tag{2.14}$$

It is convenient at this point to rewrite Eq. (1.1) in the form

$$-g_2'(r)=g_2(r)u'(r)+\rho\int d\vec{s}\, u'(s)\langle g_3(r,s,|\vec{r}-\vec{s}|)\cos\theta\rangle \,, \tag{2.15a}$$

with $\hat{r}\cdot\hat{s}=\cos\theta$ and

$$\langle g_3\cos\theta\rangle=\int d\Omega\, g_3\cos\theta\Big/\int d\Omega \,, \tag{2.15b}$$

where Ω is the d-dimensional solid angle. The potential $u(r)$ is assumed to be of finite range, so the first term on the right-hand side of Eq. (2.15a) vanishes for sufficiently large r. Furthermore, this finite range limits s to finite values so that, for $r \gg s$, $g_2(|\vec{r}-\vec{s}|)$ may be expanded about $s=0$ in Eq. (2.14). Since this expansion is simply

$$\begin{aligned} g_2(|\vec{r}-\vec{s}|)=g_2(r)-sg_2'(r)\cos\theta+\tfrac{1}{2}s^2\left[g_2''(r)\cos^2\theta+g_2'(r)\frac{\sin^2\theta}{r}\right] \\ -\tfrac{1}{6}s^3\{g_2'''(r)\cos^3\theta+[g_2'(r)/r]'3\sin^2\theta\cos\theta\}+\cdots \,, \end{aligned} \tag{2.16}$$

the quantity $\langle g_3\cos\theta\rangle$ becomes

$$\langle g_3(r,s,|\vec{r}-\vec{s}|)\cos\theta\rangle=-\frac{1}{2\rho d}\frac{\partial\rho_2(\vec{0},\vec{s})}{\partial\rho}sg_2'(r)-\{g_2'''(r)+(d-1)[g'(r)/r]'\}\psi(s)+\cdots \,, \tag{2.17a}$$

where $\psi(s)$ is a function with dimension (length)^3 given by

$$\begin{aligned} \psi(s)=\frac{3}{d(d+2)}\left[\frac{s^3}{48\rho}\frac{\partial\rho_2(\vec{0},\vec{s})}{\partial\rho}+\frac{\beta s^3}{8\rho^3\chi}\rho_2(\vec{0},\vec{s})+\frac{\beta s}{4\rho^3\chi}f_2(s/2)\right] \\ +\frac{s}{2d}\left[\frac{\beta}{2\rho^3\chi}f_1(s/2)-\frac{\xi^2}{\rho}\frac{\partial\rho_2(\vec{0},\vec{s})}{\partial\rho}\right] . \end{aligned} \tag{2.17b}$$

Only every other term in the expansion (2.16) survives the angular integration; the higher-order terms in Eq. (2.16) would therefore lead to corrections in Eq. (2.17a) involving fifth- and higher-order derivatives of $g_2(r)$.

Substitution of the result (2.17a) into Eq. (2.15a) now leads, upon using the virial theorem for the pressure,[12] to the following differential equation:

$$\left[g_2''(r)+\frac{d-1}{r}g_2'(r)\right]' l^2=\beta\left[\frac{\partial p}{\partial\rho}\right]_\beta g'(r) \,, \tag{2.18a}$$

where the length parameter l is defined by

$$l^2=\rho\int d\vec{s}\, u'(s)\psi(s) \,. \tag{2.18b}$$

Letting $h(r)=g_2(r)-1$ and integrating, we therefore obtain

$$h''(r)+\frac{d-1}{r}h'(r)=l^{-2}\beta\left[\frac{\partial p}{\partial\rho}\right]_\beta h(r) \,, \tag{2.19}$$

which is identical in form to the OZ differential equation (1.2).

To complete the derivation, the relationship between $l^2/\beta(\partial p/\partial\rho)_\beta$ and the correlation length must be established. This is most easily accomplished by multiplying Eq. (1.1) by r^3 and integrating by parts. This leads, after further manipulation, to the identity

$$l^2\Big/\beta\left[\frac{\partial p}{\partial\rho}\right]_\beta=\xi^2 \,. \tag{2.20}$$

Upon substitution of this in Eq. (2.19), the desired result is thereby obtained

$$h''(r)+\frac{d-1}{r}h'(r)=\xi^{-2}h(r) \,, \tag{2.21}$$

whose solution for $r \gg \xi$ has the well-known form

$$h(r)\sim\exp(-r/\xi)/r^{(d-1)/2} \,. \tag{2.22}$$

III. CONCLUSIONS

A notable quantity in the preceding derivation is the length l^2 defined in Eq. (2.18b); from Eqs. (2.9) and (2.20) and the fact that $\chi=\rho^{-1}(\partial\rho/\partial p)_\beta$, it follows that

$$l^2=(2d)^{-1}\rho\int d\vec{r}\,r^2c(r)\,, \tag{3.1}$$

so l^2 is essentially the second moment of the direct correlation function. Whether this quantity diverges at the critical point is of central importance in the theory of critical phenomena.[13] If $l^2<\infty$ at the critical point, as is believed to be the case for $d>4$, the OZ differential equation should be valid not only for $r\gg\xi$, but also for $r\ll\xi$, in which case Eq. (2.21) would imply $\eta=0$. It would therefore be of considerable interest to provide a convincing derivation for $r\ll\xi$, perhaps by including quadratic nonlinearities and analyzing the resulting equation along lines similar to Fisher and Fishman's analysis of the YBG equation.[4] If l^2 diverges at the critical point, as is expected for $d<4$, the OZ differential equation describes the correlations only for $r\gg\xi$, i.e., it breaks down as the critical point is approach for any fixed, large (but finite) value of r. Indeed, terms nonlinear in the density difference $\Delta n(\vec{x})$ cannot be neglected when $r\ll\xi$, as they lead to terms of the same order as the left-hand side of Eq. (2.18a). This difficulty has not yet been circumvented, and the extension of Eq. (2.21) into the region $r\ll\xi$ thereby obtained. Within the context of the Lebowitz-Percus theory of inhomogeneous fluids, perhaps a different reference density, one depending nonlinearly on $\rho g_2(r)$, should be considered. Alternatively one might attempt, at least formally, to identify and resum the dominant nonlinear terms.

The YBG theory also gives rise to an equation for $h(r)$ of OZ form (for $r\gg\xi$), but due to the use of the KSA, ξ^2 in Eqs. (2.21) and (2.22) must be replaced by[3]

$$\xi^2_{\mathrm{YBG}}=u_2/(1-u_0)\,, \tag{3.2a}$$

where

$$u_0=\frac{\rho}{d}\int d\vec{s}\,su'(s)g_2^{\mathrm{YBG}}(s)\,, \tag{3.2b}$$

$$u_2=\frac{\rho}{2d(d+2)}\int d\vec{s}\,s^3u'(s)g_2^{\mathrm{YBG}}(s)\,. \tag{3.2c}$$

This result may best be compared to the exact ξ by writing ξ^2_{YBG} in the form

$$\xi^2_{\mathrm{YBG}}=l^2_{\mathrm{YBG}}\Big/\beta\left[\frac{\partial p}{\partial\rho}\right]^{\mathrm{YBG}}_{\beta}\,, \tag{3.3}$$

where the YBG compressibility must be calculated from the compressibility integral (rather than from the virial pressure). Since the first moment of the YBG equation yields, after an integration by parts, the result

$$1-u_0=(1+A)\beta\left[\frac{\partial p}{\partial\rho}\right]^{\mathrm{YBG}}_{\beta}\,, \tag{3.4a}$$

where

$$A=\frac{\rho^2}{2d}\int d\vec{s}\,su'(s)g_2^{\mathrm{YBG}}(s)\times\int d\vec{r}\,h^{\mathrm{YBG}}(r)h^{\mathrm{YBG}}(|\vec{r}-\vec{s}|)\,, \tag{3.4b}$$

the YBG analog of Eq. (2.18b) is

$$l^2_{\mathrm{YBG}}=u_2/(1+A)\,. \tag{3.5}$$

This quantity plays the same role in the YBG theory as does l^2 in the exact theory. Finally, it should be noted that the third moment of the YBG equation yields, through the definition (1.3), yet another correlation length ξ'_{YBG} which differs from ξ_{YBG}:

$$\xi'^2_{\mathrm{YBG}}=\xi^2_{\mathrm{YBG}}+B/(1+A)\,, \tag{3.6a}$$

where

$$B=\frac{\rho^2}{4d(d+2)}\int d\vec{s}\,su'(s)g_2^{\mathrm{YBG}}(s)\int d\vec{r}\,h^{\mathrm{YBG}}(|\vec{r}+\tfrac{1}{2}\vec{s}|)h^{\mathrm{YBG}}(|\vec{r}-\tfrac{1}{2}\vec{s}|)(r^2+2r^2\hat{r}\cdot\hat{s}+\tfrac{1}{4}s^2)\,. \tag{3.6b}$$

The physically relevant length, however, is ξ_{YBG} since it characterizes the decay of the correlation function explicitly through the OZ differential equation.

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