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# Generalized van der Waals theories and the asymptotic form of the density profile of a liquid-vapor interface

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Generalized van der Waals theories for the free energy and density profile of an inhomogeneous fluid are used to obtain an expression for the tails of the density profile of a liquid-vapor interface of an argon-like fluid. We find that the density profile decays asymptotically into the bulk regions as the inverse cubed power of the distance from the center of the interface. We estimate the effect to be too small to be quantitatively significant.

## I. INTRODUCTION

Abraham<sup>1,2</sup> and Ebner *et al.*<sup>3</sup> have constructed generalized van der Waals theories for the free energy and density profile of an inhomogeneous fluid. The important advance made on the modified van der Waals theories (e.g., Evans<sup>4</sup>) is that one no longer expands in powers of gradients of the density profile. The obvious qualitative error that is introduced by making a density gradient expansion is, for fluids in which the pair potential decays at long range as an inverse power law, that a liquid-vapor density profile will be predicted to decay exponentially into the bulk regions instead of as an inverse power of the distance from the center of the interface, which is the expected behavior (Plesner and Platz,<sup>5</sup> Toxvaerd,<sup>6</sup> and de Gennes<sup>7</sup>). In particular, in a planar liquid-vapor interface or an argon-like fluid, the long range part of the tails of the density profile  $n(z)$  vary as  $z^{-3}$  ( $z$  the distance from the center of the interface). In this paper, we use the generalized van der Waals theories to explore the importance, or otherwise, of the contribution to the density profile of a planar liquid-vapor interface of an argon-like fluid from the  $z^{-3}$  tails.

In Sec. II, we outline the generalized van der Waals theories of Abraham<sup>1,2</sup> and Ebner *et al.*<sup>3</sup> In Sec. III, we show that a true minimization of the free energy of an argon-like fluid with a planar liquid-vapor interface leads to a density profile that is both nonsymmetric and tends to its asymptotic bulk values with  $z^{-3}$  tails. The qualitative effect of the  $z^{-3}$  tails is estimated to be too small to be of any significance for the free energy, and it is unlikely that the  $z^{-3}$  tails could be detected by computer simulation or experiment. The nonsymmetric nature of the density profile is of more significance. Finally, in Sec. IV, we derive an exact expression for the density profile of a planar fluid interface, involving the direct correlation function of the inhomogeneous fluid. In the tails of the profile of a planar liquid-vapor interface, we show that the exact result reduces, under given approximations, to the results of Sec. III.

## II. GENERALIZED VAN DER WAALS THEORIES

We consider a single component inhomogeneous fluid with a planar liquid-vapor interface oriented parallel to the  $xy$  plane.

## A. Perturbation theory

This approach, due to Abraham,<sup>1,2</sup> is based on Toxvaerd's generalization of the Barker-Henderson liquid-state perturbation theory to inhomogeneous fluids<sup>6,8</sup>:

$$F[n] = F_r[n] + \frac{1}{2} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 n(z_1)n(z_2) \times g_r(r_{12}, z_1, z_2) u_p(r_{12}) + O(u_p^2). \quad (1)$$

Here, the free energy of the inhomogeneous fluid is expanded about a reference state (a hard sphere fluid in the Barker-Henderson prescription), with the small parameter  $u_p(r)$  being the difference between the true pair potential and the reference state pair potential (for inclusion of three-body terms see Ref. 8). To avoid problems concerning the existence of an inhomogeneous reference system, which for hard spheres would require an appropriate external field to create a liquid-vapor interface, it is natural to replace the inhomogeneous reference state pair correlation function  $g_r(r_{12}, z_1, z_2)$  by that of a uniform fluid with a density that is some symmetric average of the local values at  $z_1$  and  $z_2$ ,  $g_r[r_{12}, \bar{n}(z_1, z_2)]$ . Abraham<sup>1</sup> rewrites Eq. (1) in the following manner:

$$F[n] = F_r[n] + \frac{1}{2} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 n^2(z_1) g_r(r_{12}, z_1, z_2) u_p(r_{12}) + \frac{1}{2} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 n(z_1)[n(z_2) - n(z_1)] g_r(r_{12}, z_1, z_2) u_p(r_{12}) + O(u_p^2) \approx \int d^3\mathbf{r}_1 f_0[n(z_1)] + \frac{1}{2} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 n(z_1)[n(z_2) - n(z_1)] g_r[r_{12}, \bar{n}(z_1, z_2)] u_p(r_{12}), \quad (2)$$

where, at each value of  $z_1$ ,  $f_0[n(z_1)]$  is the free energy density of a uniform fluid of density  $n(z_1)$ . From the condition that the Grand potential

$$\Omega[n] = F[n] - \mu \int d^3\mathbf{r}_1 n(z_1), \quad (3)$$

( $\mu$  the chemical potential) be a minimum, with respect to density variations, we obtain by functional differentiation of Eq. (2) with respect to  $n(z_1)$ :

$$\mu[n] = \mu_0[n(z_1)] + \int d^3\mathbf{r}_2 [n(z_2) - n(z_1)] \times g_r[r_{12}, \bar{n}(z_1, z_2)] u_p(r_{12}) + \frac{1}{2} \int d^3\mathbf{r}_2 \int d^3\mathbf{r}_3 \times n(z_2)[n(z_3) - n(z_2)] u_p(r_{23}) \frac{\delta g_r[r_{23}, \bar{n}(z_2, z_3)]}{\delta n(z_1)}. \quad (4)$$

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To the relevant order of our starting point Eq. (2) we can neglect the last term in Eq. (4) and so, transforming coordinates

$$\mathbf{r}_2 \rightarrow (z, r_{12}); \quad z \equiv z_2 - z_1, \quad (5)$$

we obtain

$$\begin{aligned} \mu[n] - \mu_0[n(z_1)] &\simeq 2\pi \int_{-\infty}^{\infty} dz [n(z+z_1) - n(z_1)] \\ &\times \int_{|z|}^{\infty} dr r u_p(r) g_r[r, \bar{n}(z_1, z_2)]. \end{aligned} \quad (6)$$

From Eqs. (2) and (6), the minimized free energy is

$$F_{\min}[n] \simeq \int d^3\mathbf{r}_1 \left\{ f_0[n(z_1)] + \frac{n(z_1)}{2} \{\mu - \mu_0[n(z_1)]\} \right\}. \quad (7)$$

It is known from the work of Mermin,<sup>18</sup> that there exists a functional of the density which has the property that it is minimized by the exact  $n(z)$  at the true value of the free energy. The functional defined by Eq. (2) is of course not this exact functional, but it appears to be a useful approximation in view of the agreement between results to which it led and computer simulation results and experiment.<sup>1,2</sup> In the region of the critical point, where the density is slowly varying so that in the right side of Eq. (6) we may make the expansion

$$n(z+z_1) - n(z_1) = zn'(z_1) + \frac{z^2}{2!} n''(z_1) + \dots \quad (8)$$

The result [Eq. (7)] reduces to the van der Waals theory<sup>8</sup>

$$\begin{aligned} F_{\min}[n] &\simeq \frac{1}{(T-T_c)} \int d^3\mathbf{r} \{ f_0[n(z)] + \frac{1}{2} m [n'(z)]^2 \}, \\ mn''(z) &= \mu_0[n(z)] - \mu, \end{aligned} \quad (9)$$

where, from the density expansion of Eq. (6), we

identify the constant  $m$  as

$$m = -\frac{1}{6} \int d^3\mathbf{r} r^2 u_p(r) g_r(r, n_c). \quad (10)$$

## B. Direct correlation function expressions

Ebner, Saam, and Stroud<sup>3</sup> argue that, analogous to Eq. (2), one can write

$$\begin{aligned} F[n] &\simeq \int d^3\mathbf{r}_1 f_0[n(z_1)] \\ &- \frac{k_B T}{2} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 n(z_1) [n(z_2) - n(z_1)] c[r_{12}, \bar{n}(z_1, z_2)], \end{aligned} \quad (11)$$

where  $c[r_{12}, \bar{n}(z_1, z_2)]$  is the direct correlation function of a uniform fluid with a density that is some symmetric average of the local values of the real inhomogeneous density at  $z_1$  and  $z_2$ . Saam and Ebner<sup>10</sup> further obtain an exact expression that reduces to the result [Eq. (11)] after making reasonable approximations. Comparing Eq. (11) with Eq. (2), it follows from the results of Sec. IIA that minimization of the free energy [Eq. (11)], with respect to density changes gives [cf. Eq. (6)]

$$\begin{aligned} \mu[n] - \mu_0[n(z_1)] &\simeq -2\pi k_B T \int_{-\infty}^{\infty} dz [n(z+z_1) - n(z_1)] \\ &\times \int_{|z|}^{\infty} dr r c[r, \bar{n}(z_1, z_2)], \end{aligned} \quad (12)$$

where we have neglected a higher order term involving  $\delta c[r_{23}, \bar{n}(z_2, z_3)]/\delta n(z_1)$ . That is, one may transform between the results of Secs. IIA and IIB by making the replacement

$$u_p(r_{12}) g_r[r_{12}, \bar{n}(z_1, z_2)] \rightarrow -k_B T c[r_{12}, \bar{n}(z_1, z_2)]. \quad (13)$$

We conclude this section by noting from the defining equation for the direct correlation function [Eq. (23)] that the result Eq. (12) is the first term of a functional Taylor series expansion<sup>19</sup>:

$$\begin{aligned} \mu_0[n(z_1)] &= \mu[n] + \int d^3\mathbf{r}_2 \delta n(z_2) \frac{\delta \mu}{\delta n(z_2)} + \frac{1}{2!} \int d^3\mathbf{r}_2 \int d^3\mathbf{r}_3 \delta n(z_2) \delta n(z_3) \frac{\delta^2 \mu}{\delta n(z_2) \delta n(z_3)} + \dots \\ &= \mu[n] - k_B T \int d^3\mathbf{r}_2 [n(z_1) - n(z_2)] c[r_{12}, z_1, z_2] - \frac{k_B T}{2} \int d^3\mathbf{r}_2 \int d^3\mathbf{r}_3 [n(z_1) - n(z_2)] [n(z_1) - n(z_3)] c[r_{12}, r_{23}, r_{31}] + \dots \\ &\simeq \mu[n] - k_B T \int d^3\mathbf{r}_2 [n(z_1) - n(z_2)] c[r_{12}, \bar{n}(z_1, z_2)]. \end{aligned} \quad (14)$$

Here,  $z_1$  is fixed and we have considered the difference between the chemical potential of a uniform fluid of density  $n(z_1)$  and that of an inhomogeneous system with density profile  $n(z_2)$ , at the same temperature. Formally, this type of argument requires that each density profile involved be the density of some equilibrium system, which is an assumption about the existence of a corresponding external field.<sup>4</sup>

## III. TAILS OF THE DENSITY PROFILE OF A LIQUID-VAPOR INTERFACE

The results [Eq. (6) or Eq. (12)] of the previous section can be used to analyze the manner in which the den-

sity profile tends to its asymptotic bulk values away from a liquid-vapor interface (we discuss the limiting case of negligible external field). First, note that far out in a tail of the profile where, writing

$$n(z) = n_b + \delta n(z), \quad (15a)$$

we have

$$|\delta n(z)/n_b| \ll 1, \quad (15b)$$

with  $n_b$  the limiting bulk liquid or bulk vapor value, the left side of Eq. (6) or Eq. (12) is

$$\int_{n(z_1)}^{n_b} dn \frac{d\mu_0(n)}{dn} = \int_{n(z_1)}^{n_b} dn \frac{1}{n^2 K_T(n)} \simeq -\frac{\delta n(z_1)}{(n^2 K_T)_b}. \quad (16)$$

Here,  $K_T(n)$  is the isothermal compressibility of a uniform fluid of density  $n$ , assumed not to be a rapidly varying function of  $n$  over the small range of density variation involved in Eqs. (15) and (16). So, in a tail of the density profile we may rewrite Eq. (6) or Eq. (12) as

$$\frac{\delta n(z_1)}{(n^2 K_T)_b} \simeq -2\pi \int_{-\infty}^{\infty} dz [n(z+z_1) - n(z_1)] \int_{|z|}^{\infty} dr r u_p(r) g_r(r, n_b), \quad (17a)$$

$$\simeq 2\pi k_B T \int_{-\infty}^{\infty} dz [n(z+z_1) - n(z_1)] \int_{|z|}^{\infty} dr r c(r, n_b). \quad (17b)$$

If we insert the density expansion (8) into the right side of Eqs. (17), we are led to an exponential form for the tails of the density profile

$$\frac{\delta n(z_1)}{(n^2 K_T)_b} \simeq m_b n''(z_1), \quad (18a)$$

which has the physical solution [with  $n(+\infty) = n_v$ ,  $n(-\infty) = n_l$ ]

$$\delta n(z_1) = \text{sgn}(z_1) a_b(T) (n_l - n_v) \exp(-|z_1|/\lambda_b), \quad (18b)$$

$$\lambda_b^2 = m_b (n^2 K_T)_b,$$

where  $m_b$  is given by, from Eq. (6)

$$m_b = -\frac{1}{6} \int d^3 r r^2 u_p(r) g_r(r, n_b), \quad (19a)$$

or from Eq. (12)

$$m_b = \frac{k_B T}{6} \int d^3 r r^2 c(r, n_b). \quad (19b)$$

However, as noted by Plesner and Platz,<sup>5</sup> Toxvaerd,<sup>6</sup> and most recently de Gennes,<sup>7</sup> exponential tails are not the correct behavior for the density profile of a liquid-vapor interface of most fluids, where the force between two molecules decays at long range as some inverse power of the distance between the molecules. This fact is often not appreciated, especially in theories of the van der Waals type which will always predict exponential tails for the density profile. The reason for this is that van der Waals theories are based on the result (9) which, like Eq. (18), follows from a density expansion of a more exact expression and it is this density expansion which breaks down for power law dependent interactions.<sup>21</sup> For example, for argon-like fluids where the potential between two molecules falls off at large separation as

$$u(r) \xrightarrow{(r \gg d)} \frac{C_6}{r^6}, \quad (20)$$

the coefficients of the density expansion of  $F[n]$  or  $\mu - \mu_0$  involve moments of the potential

$$\int_d^\infty dr r^{n+2} u(r),$$

which diverge for  $n > 2$ .

We can use the expression (17a) or (17b) to estimate the contribution to the tails of the density profile from a long range  $r^{-6}$  interaction [Eq. (20)]. The simplest approach, valid away from the critical point, is to consider  $\delta n(z_1)$  at  $z_1$  far enough out into a tail so that the contribution to the integrand of Eqs. (17) from the longest range part of the potential comes from interactions with the bulk phase on the other side of the interface. The long range parts of Eqs. (17a) and (17b) are identical since for large  $r$  we have

$$g_r[r, \bar{n}(z_1, z_2)] \rightarrow 1, \\ -k_B T c[r, \bar{n}(z_1, z_2)] \rightarrow u(r),$$

and so if we begin iterating Eqs. (17), starting on the right side with a sharp discontinuous trial profile situated at  $z_1 = 0$ , the lowest order solution at large  $|z_1|$  is

$$\frac{\delta n(z_1)}{(n^2 K_T)_b} \simeq -2\pi C_6 (n_l - n_v) \int_{-\infty \text{ sgn}(z_1)}^{-z_1} dz \int_{|z|}^{\infty} dr r^{-5} \\ = -\frac{\pi}{6} (n_l - n_v) \frac{C_6}{z_1^3}; \quad \text{large } |z_1|. \quad (21)$$

This result was obtained from a different approach by Rusanov and Kuni.<sup>22</sup> Insertion of Eq. (21) back into the right side of Eqs. (17) leads to a correction term varying as  $z_1^{-5}$ , and so we have rigorously shown that in argon-like fluids the density profile of a liquid-vapor interface tends to its asymptotic values as a  $z^{-3}$  power law ( $z$  the distance from the center of the interface). As pointed out by de Gennes,<sup>7</sup> in the vapor tail, this behavior is what is expected by analogy with the system of a gas interacting with a wall; i.e., where the liquid has solidified. In the liquid tail, it is the nature of the absence of interactions with the vapor side that is responsible for the  $z^{-3}$  behavior.

Towards the center of the interface the contribution to  $\delta n(z_1)$  from short range interactions will dominate the  $z_1^{-3}$  tails. At an intermediate stage, it is plausible that an approximate solution to Eqs. (17) is obtained by assuming that one can make the density expansion (8) to take account of the short range interactions without significantly affecting the long range contribution [Eq. (21)]. Then, the profile is given by a superposition of the exponential form (18) with the  $z_1^{-3}$  form (21):

$$\delta n(z_1) = \text{sgn}(z_1) (n_l - n_v) \left[ a_b(T) \exp(-|z_1|/\lambda_b) + \frac{b_b(T)}{|z_1|^3} \right] \left\{ \begin{array}{l} \text{intermediate } |z_1| \end{array} \right. \quad (22)$$

$$\lambda_b^2 = m_b (n^2 K_T)_b, \quad b_b(T) = -\frac{\pi}{6} C_6 (n^2 K_T)_b$$

TABLE I. Evaluation of parameters in Eq. (22), appropriate to argon. Vapor compressibilities were estimated from values of the second virial coefficient<sup>a</sup> and vapor densities were obtained from Ref. 16. Liquid compressibilities and densities were obtained from Ref. 17. Values of  $b$  were calculated taking  $C_6$  to be that of the Lennard-Jones 12-6 fluid with parameters appropriate to argon.<sup>b</sup> The core diameter was assumed to be  $\sigma = 3.405 \text{ \AA}$ .

$T/K$	$(n^2 k_B T K_T)_l$ $\times 100\sigma^3$	$b_l/(2\sigma)^3$ $\times 100$	$(n^2 k_B T K_T)_v$ $\times 100\sigma^3$	$b_v/(2\sigma)^3$ $\times 100$
85	4.4	1.6	0.3	0.1
90	5.0	1.7	0.5	0.2
95	5.7	1.9	0.8	0.3
100	6.7	2.1	1.2	0.4
110	9.6	2.7	2.7	0.8

<sup>a</sup>Reference 15.

<sup>b</sup>Reference 13.

Here, remembering from Eq. (15b) that we require  $|z_1| \gg \lambda_b$ , it follows that as the temperature tends to the critical point the relative importance of the  $z_1^{-3}$  tails decreases. From estimates of the value of  $m_b(T)$ , as for example in Evans and Sluckin,<sup>11</sup> one finds that  $m_b$  is a slowly varying function of density, at least for the form (19b). So, from Eq. (22), the symmetry of the profile is largely determined by the difference between the values of  $(n^2 K_T)_b$  in the liquid and vapor phase. From Table I we conclude that near the triple point the density profile is significantly nonsymmetric, with the density rising more steeply from the vapor side than it falls from the liquid side.<sup>12</sup> Using the value of  $C_6$  for the Lennard-Jones 12-6 fluid with parameters appropriate to argon,<sup>13</sup> we calculated the contribution of the  $z^{-3}$  tails to  $\delta n(z)$  at  $z = 2\sigma$ ,  $\sigma$  the core diameter (see the table). The contribution is of the order of a few percent of  $(n_l - n_v)$  and so is probably too small to be detected, even in computer simulations. The effect of the  $z^{-3}$  tails on the minimized free energy is likely to be even smaller.

We conclude that a true minimization of the free energy of a liquid-vapor interface of an argon-like fluid near its triple point leads to a profile that is both nonsymmetric and tends to its asymptotic bulk values with  $z^{-3}$  tails. (Toxvaerd's<sup>6</sup> failure to achieve a lower free energy when using trial profiles with the correct asymptotic form must therefore be due, as Toxvaerd states, to his choice of profile being inappropriate well inside the interface, rather than in the tails.) However, the effect of the  $z^{-3}$  tails is only of the order of a few percent of  $(n_l - n_v)$  for the density profile, and probably has much less significance for the free energy. Away from the critical point, the nonsymmetric nature of the density profile is significant and profiles obtained by minimization of the free energy, with respect to simplified trial forms that are forced to be symmetric could be seriously inaccurate.

#### IV. EXACT EXPRESSION FOR THE DENSITY PROFILE

In the previous section, the density profile was defined by minimization of the free energy. It is also possible to start from an exact expression for the gradient

of the density profile derived by Lovett, Mou, and Buff,<sup>20</sup> which follows from the translational invariance of the defining equation for the direct correlation function

$$\frac{\delta[\mu[n] - v(z_1)]}{\delta n(z_1)} = k_B T \left[ \frac{\delta(r_{12})}{n(z_1)} - c(r_{12}, z_1, z_2) \right], \quad (23)$$

where  $v(z_1)$  is the external field that uniquely determines the density profile  $n(z_1)$ .<sup>18,4</sup> That is, for the particular case of an infinitesimal uniform translation in the  $z$  direction (i.e., normal to the plane of the interface), Eq. (23) implies

$$\frac{d}{dz_1} \log n(z_1) = - \frac{v'(z_1)}{k_B T} + \int d^3 r_2 n'(z_2) c(r_{12}, z_1, z_2). \quad (24)$$

Kalos, Percus, and Rao<sup>12</sup> show that a density expansion of this equation leads directly to the result (18). Let us integrate Eq. (24) from a point in the interface  $z_0$  to a point in a bulk phase (say,  $z \rightarrow \infty$ ), to obtain

$$\log \left[ \frac{n(z_0)}{n_b} \right] = \frac{[v(\infty) - v(z_0)]}{k_B T} - 2\pi \int_{z_0}^{\infty} dz \int_{-\infty}^{\infty} dz' n'(z + z_1) \times \int_{|z|}^{\infty} dr r c(r, z_1, z_1 + z). \quad (25)$$

Integration by parts, with respect to  $z_1$ , in the last term gives us

$$\log \left[ \frac{n(z_0)}{n_b} \right] = \frac{[v(\infty) - v(z_0)]}{k_B T} + 2\pi \int_{-\infty}^{\infty} dz [n(z + z_0) - n_b] \times \int_{|z|}^{\infty} dr r c(r, z_0, z_0 + z) + 2\pi \int_{z_0}^{\infty} dz_1 \int_{-\infty}^{\infty} dz [n(z + z_1) - n_b] \times \int_{|z|}^{\infty} dr r \frac{\partial}{\partial z_1} c(r, z_1, z_1 + z). \quad (26)$$

The last term of Eq. (26) can be rewritten

$$2\pi \int_{z_0}^{\infty} dz_1 \int_{-\infty}^{\infty} dz [n(z + z_1) - n(z_1)] \int_{|z|}^{\infty} dr r \frac{\partial}{\partial z_1} c(r, z_1, z_1 + z) + 2\pi \int_{z_0}^{\infty} dz_1 n'(z_1) \int_0^{\infty} dr r \times \int_{-\infty}^{\infty} dz [c(r, z_0, z_0 + z) - c(r, z_1, z_1 + z)]. \quad (27)$$

Since the value of the direct correlation function is expected to be weakly dependent on the local densities, Eq. (27) is generally small and to a first approximation can probably be neglected, giving

$$\frac{n(z_0)}{n_b} \approx \exp \left\{ \frac{[v(\infty) - v(z_0)]}{k_B T} \right\} + 2\pi \int_{-\infty}^{\infty} dz [n(z + z_0) - n_b] \times \int_{|z|}^{\infty} dr r c(r, z_0, z_0 + z). \quad (28)$$

This result is also derivable from the approach due to Saam and Ebner<sup>10</sup> discussed in Sec. II B, as for example in Grimson and Rickayzen,<sup>14</sup> who derive Eq. (28) and use it, with  $c(r_{12}, z_1, z_2) \approx c(r_{12}, n_b)$ , to study fluid-wall interfaces. Finally, we note that Eq. (12) is an approximation to the exact result [Eq. (26)], and in the tails of the profile it is straightforward to show that Eq. (28) reproduces Eq. (17b). Namely, when Eq. (15b) holds, the log of Eq. (28) reduces to

$$\frac{\delta n(z_0)}{n_b} \left[ 1 - 2\pi n_b \int_{-\infty}^{\infty} dz \int_{|z|}^{\infty} dr r c(r, n_b) \right] \approx \frac{[v(\infty) - v(z_0)]}{k_B T} + 2\pi \int_{-\infty}^{\infty} dz [n(z + z_0) - n(z_0)] \int_{|z|}^{\infty} dr r c(r, n_b), \quad (29)$$

where the left side can be rewritten, using the identity

$$n_b \int d^3r c(r, n_b) = 1 - 1/(nk_B TK_r)_b, \quad (30)$$

as  $\delta n(z_0)/(n^2 k_B TK_r)_b$ , and so we regain Eq. (17b) in the limit of negligible external field.

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