A unifying identity for the work of cluster formation in heterogeneous and homogeneous nucleation theory

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Abstract

A unifying identity is derived relating the reversible work of cluster formation (W), and its molecular number content (n) and surface work (\(\Phi\)) components, each ratioed to the corresponding values for a spherical capillary drop of critical size in classical nucleation theory. The result is a relationship that connects these ratios: \(f_W = -2f_N + 3f_S\), where \(f_W = W/W_{\text{CNT}}\), \(f_N = n/n_{\text{CNT}}\), and \(f_S = \Phi/\Phi_{\text{CNT}}\). Shown to generalize two early thermodynamic relationships of Gibbs, the new result is demonstrated here for Fletcher’s model of heterogeneous nucleation, resulting in a unified treatment of condensation on flat and curved substrates and smooth passage to the homogeneous limit. Additional applications are made to clusters of non-critical as well as critical size, and to a molecular-based extension of classical nucleation theory based on the Kelvin relation. The new identity serves as a consistency check on complicated theoretical expressions and numerical calculations and can be used to guide construction of theory and interpretation of measurements.
1. Introduction

Nucleation is a ubiquitous phenomenon that manifests itself wherever there is a thermodynamic barrier to phase change - from the formation of bubbles in superheated liquids to new particle formation from the condensation of supersaturated vapor. Nucleation in the atmosphere is responsible for the formation of new particles that can subsequently grow to exert a significant impact on global climate directly, through the scattering and absorption of solar radiation, and indirectly by serving as sites for cloud droplet condensation [1]. There is evidence that both homogeneous and heterogeneous nucleation pathways contribute to this process [2,3]. Indeed, the interesting two-stage model of Kulmala and co-workers: heterogeneous nucleation of (most likely) oxidized organic vapors on stabilized 1-2 nm neutral cluster condensation sites formed from the gas phase [3], effectively eliminates distinction between heterogeneous and homogeneous nucleation mechanisms as the condensation sites approach molecular size.

The present analysis applies to nucleation models that separate the free energy of cluster formation into volume/number and surface work components, but the general method should be adaptable to inclusion of other free-energy terms such as solute effects in multicomponent nucleation, and molecular adsorption. The treatment is not limited to classical nucleation theory (CNT), but homogeneous nucleation in the CNT is used as the model of reference throughout this paper, as components of the true free energy are ratioed to their classical analogues.

2. Main Result
The reversible work of cluster formation takes the general form for a single-component condensate [4]:

$$W(n) = -n \Delta \mu + \Phi.$$  \hspace{1cm} (1)

with $\Delta \mu = kT \ln S$ where $S$ is saturation ratio, $n$ is the number of molecules in the cluster, $k$ is the Boltzmann constant and $T$ temperature. The lead term on the right is the ‘volume’ work – here the number of molecules present in the nucleus, rather than volume, is used to represent nucleus size. Under the assumption that the cluster is incompressible these are equivalent. The second term on the right is the surface work.

The CNT analogue to Eq. 1 for homogeneous nucleation has the form:

$$W_{\text{homo}}^* = -g^* \Delta \mu + \Phi_{\text{homo}}^* = -g^* \Delta \mu + 4\pi (r^*)^2 \sigma_{lv},$$  \hspace{1cm} (2)

where the asterisk refers to clusters of critical size and $\sigma_{lv}$ is the surface tension between the liquid drop and surrounding vapor phase. The critical radius of curvature, $r^*$, and number of molecules present in the nucleus, $g^*$, are connected under the assumption of incompressibility through the molecular volume of the fluid $v_i$ as: $4\pi (r^*)^3/3 = g^* v_i$. In the following, $g^*$ will refer to the number of molecules in a non-critical (critical) cluster modeled according to classical homogeneous nucleation theory. $n$ and $n^*$ will be used to distinguish clusters in other cases that will include heterogeneous nucleation on curved substrates and departures from the classical theory. The critical radius, $r^*$, is given by the Kelvin relation:
\[ r^* = \frac{2v^*}{\mu} \]  \hspace{1cm} (3)

The focus throughout the remainder of this paper will be on the following three non-dimensional ratios:

\[ f_w = \frac{W}{W_{\text{homo}}} \] (reversible work ratio)  
\[ f_s = \frac{\Phi}{\Phi_{\text{homo}}} \] (surface work ratio)  \hspace{1cm} (4)
\[ f_N = \frac{n}{g^*} \] (volume work/number ratio)

The numerators and denominators in Eqs. 4 are evaluated at the same chemical potential, \( \Delta \mu \), which then cancels in the last equality (see also Eq. 7 below). The denominators refer to CNT for homogeneous nucleation, which is the reference model.

The main result of this paper is the following identity, henceforth unifying identity, connecting the \( f \)-ratios appearing in Eqs. 4:

\[ f_w = -2f_N + 3f_s \]  \hspace{1cm} (5)

There is a surprising simple derivation of this result that lends insight into its origin, structure and generality well beyond classical nucleation theory, where \( f_w = f_N = f_s = 1 \) and Eq. 5 reduces to the trivial identity \( 1 = -2 + 3 \). The derivation makes use of the following thermodynamic relations for the work of critical droplet formation from a uniform surrounding vapor in the reference model:

\[ 2W_{\text{homo}} = g^* \Delta \mu \]
\[ 3W_{\text{homo}} = \Phi_{\text{homo}} = 4\pi(r^*)^2 \sigma_{lv} \]  \hspace{1cm} (6)

Equations 6, which are at the thermodynamic foundation of classical homogeneous nucleation theory, were obtained early on by Gibbs and can be found
in his collected works [5]. To obtain the main result, simply divide Eq. 1 by $W_{\text{homo}}^*$, and then make use of the Gibbs relations to obtain a more explicit form for the general unifying identity:

$$\frac{W}{W_{\text{homo}}^*} = \frac{-n\Delta\mu}{W_{\text{homo}}^*} + \frac{\Phi}{W_{\text{homo}}^*} = \frac{-2n\Delta\mu}{g\Delta\mu} + \frac{3\Phi}{\Phi_{\text{homo}}} = -2\frac{n}{g} + 3\frac{\Phi}{\Phi_{\text{homo}}}$$ \hspace{1cm} (7)

The second equality brings in the Gibbs relations and the third gives the desired result. Reflection shows that only the classical reference model denominators appearing in Eqs. 4 are involved in the derivation. As long as the application-specific numerators, which appear generally in Eq. 1, refer to a surrounding vapor at the same chemical potential as the reference model, Eqs. 5 and 7 remain valid.

The simplicity of its derivation, which incorporates no other physics beyond the separation of work terms in Eq. 1 and the Gibbs relations themselves, belies the utility of the unifying identity to a broad range of applications, some of which are sampled in Sec. 3. This range is limited only by Eq. 1. The great value of the Gibbs relations here lies in their determining both the reference denominators and the integer coefficients for the $f$-ratios appearing in the identity. Before discussing the applications, it is worthwhile establishing the special circumstance under which the Gibbs relations and the unifying identity are equivalent.

**The Gibbs relations and their equivalence to the special case of $f$-ratio equality:** It was shown above that the unifying identity follows from the Gibbs relations. The converse is not generally true as the new result is more general. But in the special case of $f$-ratio equality, which includes classical homogeneous nucleation theory,
and heterogeneous nucleation on flat substrates, the Gibbs relations and the unifying identity are equivalent as follows:

Inspection of Eq. 5 shows that if two $f$-ratios are equal, all three are equal. In the equality $f_w = f_N$, for example, the denominators are equal from the first Gibbs relation, $W_{homo}^* = g^* \Delta \mu / 2$, so the same must hold for the numerators, and this can only happen at the critical cluster size, to give $W^* = n^* \Delta \mu / 2$. This proves the converse for the first of Eqs. 6. Similarly for $f_w = f_S$ and the second Gibbs relation, $W^* = \Phi^* / 3$, again only at the critical size. But all three ratios are equal if any two of them are, so the converse is fully shown: the Gibbs relations and the unifying identity are equivalent in the special case that the $f$-ratios are equal.

3. Applications

This section demonstrates applications that can benefit from the unifying identity. The identity itself was discovered in connection with heterogeneous nucleation studies and new results appear in Sec. 3.1. These include Eq. 10, which connects the rather complicated algebraic expressions for the work of spherical cap formation given in the Appendix (Eqs. A1-A3), and verifies the connection through algebraic reduction and numerical calculations summarized in Fig. 2. Sections 3.2 and 3.3 examine (mostly) known results in light of the new identity. Both examples cover ground between Eq. 10 and the much more general result obtained in Sec. 2. Sec. 3.2 is an application to clusters of non-critical size and Sec. 3.3 to a molecular based extension of classical homogeneous nucleation theory.
3.1 Heterogeneous nucleation in the Fletcher model: Consider, first, the specialization of Eq. 1 to heterogeneous nucleation of a spherical cap on a spherical substrate in the classical Fletcher model [6]. Geometric parameters of the model are indicated in Fig. 1. The reversible work of critical cap formation takes the following form:

\[ W_{hetero}^* = -n^* \Delta \mu + \Phi_{hetero}^*, \]  

where \( n^* \) is the number of liquid condensate molecules present in the critical-size cap. The subscript designates heterogeneous nucleation in the CNT.

The second term on the right-hand-side of Eq. 8 is the surface work, which in the Fletcher model is given as [6]:

\[ \Phi_{hetero}^* = \sigma^h \Omega_{lv} - (\sigma_{sv} - \sigma_{sl}) \Omega_{sl} = \sigma^h \Omega_{lv} - (\sigma^l \cos \theta) \Omega_{sl}. \]  

Here \( s, l, \) and \( v \) refer to solid substrate, liquid condensate, and surrounding vapor phases, respectively. \( \sigma_{ij} \) and \( \Omega_{ij} \) are the surface tension and interfacial area between phases \( i \) and \( j \). The second equality uses Young’s relation [7]: \( \sigma_{sv} - \sigma_{sl} = \sigma^l \cos \theta \).

The factor appearing before \( \Omega_{sl} \) includes contributions from molecular interactions between seed and condensate, parameterized in terms of the contact angle \( \theta \).

![Figure 1: Spherical cap geometry for heterogeneous nucleation in the Fletcher model. \( R \) and \( r^* \) are radii drawn from the centers of curvature of the seed and the cap, respectively. \( d \) is the distance between these centers. Note that \( r^* \), here the cap radius of curvature, has the same value, given by the Kelvin relation, for heterogeneous and homogeneous nucleation at the same driving free energy \( \Delta \mu \).](image-url)
The $f$-ratios, as defined according to Eqs 2 and 8, take the form: $f_W = W_{\text{hetero}}^*/W_{\text{homo}}^*$, $f_N = n^*/g^*$, and $f_S = \Phi_{\text{hetero}}^*/\Phi_{\text{homo}}^*$. These ratios are given explicitly in the Appendix for the Fletcher model with $f_W$ and $f_N$ from [8]. The surface work ratio, $f_S$, follows from Eqs. 9 and 2, and expressions for the interfacial areas (see the Appendix for a derivation of this quantity). Numerators and denominators are again evaluated at the same chemical potential difference, $\Delta \mu$, which then cancels in the final result to obtain the following expression for the unifying identity in heterogeneous nucleation:

$$\frac{W_{\text{hetero}}^*}{W_{\text{homo}}^*} = -2 \frac{n^*}{g} + 3 \frac{\Phi_{\text{hetero}}^*}{\Phi_{\text{homo}}^*} \tag{10}$$

 Numerous studies have made use of one or more of the $f$-ratios for heterogeneous nucleation, going back to Fletcher’s pioneering work sixty years ago [6]. Despite this activity, the connection between them through Eq. 10 appears to have gone unnoticed until now. The identity, together with the ratios themselves, are displayed in Fig. 2. Equation 10 can be demonstrated to hold for Fletcher’s model by substitution from the detailed mathematical expressions given in Eqs. A1-A3, followed by considerable algebraic reduction. On the other hand, Eq. 10 follows immediately as a specialization of Eqs. 5 and 7. The fact that the parent theory makes no reference to geometric details of the spherical cap model, implies a broad applicability for the unifying identity, not only to the Fletcher model, but well beyond.
A physical example of $f$-ratio equality, discussed in the previous section, occurs in the case of heterogeneous nucleation on a flat substrate. For $m = \cos \theta$ (see Appendix):

$$f_w = f_N = f_S = \frac{1}{4} \left( 2 - 3m + m^3 \right).$$

(11)

Figure 2: Illustrative $f$-ratios at two different values of the seed particle radius, $R$, and same values of $S$ and cap radius of curvature, $r^*$. (a) $R = 1.0\text{nm}$, (b) $R = 6.0\text{nm}$ with curve labeling indicated in panel (a). These ratios depend only on $x = R/r^*$ and contact angle (see Appendix), but the latter is substance dependent. Note superposition of the solid curve and markers in agreement with Eqs. 5 and 10.
The merging of f-ratios with increasing substrate radius (decreasing curvature) is becoming evident when comparing Figs. 2a and 2b. The classical homogeneous nucleation is recovered from Eq. 11 in the non-wetting limit, \( m = -1 \).

A characteristic of systems with f-ratio equality is that nucleus shape is independent of nucleus size. In addition to homogeneous nucleation in the CNT (where \( f_w = f_n = f_s = 1 \)), shape preservation is seen to apply to heterogeneous nucleation on a flat substrate in the Fletcher model, in which case cap shape, including contact angle \( \theta \), are preserved with size. Note that line tension can cause the contact angle to become size dependent [9]; breaking the size-independent scaling described here. But in the Fletcher model (with flat substrate) the f-ratios follow Eq. 11, and the surface and volume numerators scale as \( g^{2/3} \) and \( g \), respectively. Such systems can be described by a further specialization of Eq. 1, with size-independent shape factor \( \alpha \):

\[
W_{CNT}(g) = -g\Delta \mu + \alpha g^{2/3}.
\]

**3.2 Clusters of non-critical size:** The general form of Eq. 1 forces no requirement on the numerators of the unifying identity that they apply only at critical size. With extension to clusters of non-critical size, the f-ratios in accord with the scaling exhibited in Eq. 12, can be written immediately:

\[
\begin{align*}
  f_w &= W_{CNT}(g) / W_{CNT}(g^*) \\
  f_n &= g / g^* \\
  f_s &= (g / g^*)^{2/3}.
\end{align*}
\]

Substitution into Eq. 7 gives a convenient scaling result valid for clusters of any size:
\[
\frac{W_{\text{CNT}}(g)}{W_{\text{CNT}}(g^*)} = -2 \left( \frac{g^*}{g} \right) + 3 \left( \frac{g^*}{g} \right)^{2/3}.
\]  

(14)

Equation 14 is a known result showing, for a broad class of systems satisfying Eq. 12, that the nucleation barrier has the same overall shape independent of substance and saturation ratio. See for example [10] for a conventional derivation of this result that first locates the critical cluster size and barrier height, \( W_{\text{CNT}}(g^*) \), from Eq. 12, and uses these to eliminate the substance- and saturation ratio-dependent parameters \( \alpha \) and \( \Delta \mu \).

### 3.3 Nucleation near a spinodal

A major limitation of classical homogeneous nucleation theory is its failure to predict a spinodal, the locus of states at the boundary between the metastable (nucleation) and unstable (spontaneous spinodal decomposition) regions of the phase diagram. Talanquer [11] obtained the following expression for nucleation barrier height; accommodating a spinodal while significantly improving agreement with cloud chamber studies of the temperature dependence of nucleation rates closer to the coexistence curve:

\[
\frac{W^*}{W_{\text{ homo}}} = 1 - \left( \frac{\Delta \mu}{\Delta \mu_S} \right)^2.
\]  

(15)

\( \Delta \mu_S \) is the temperature-dependent driving free energy for nucleation at the spinodal, at which location the barrier height \( W^* \) vanishes. Molecular features of the underlying (nonclassical) theory [12] are based on its use of the nucleation theorem [4]:

\[
\frac{dW^*}{d\Delta \mu} = -\Delta n^* = -n^*,
\]  

(16)
which has been shown from a molecular-based derivation to follow as a direct consequence of the law of mass action [13]. The approximate equality neglects subtracting the small number of molecules present in a volume, equal to the nucleus volume, of displaced vapor phase [4].

A key assumption of the underlying theory is the validity of the Kelvin relation to obtain the molecular content of the critical nucleus, \( n^* \) [12]. In other words, the assumption is made that \( n^* = g^* \) where \( g^* \) is given by the Kelvin relation:

\[
g^* = C(T)\Delta \mu^{-3},
\]

which is consistent with the last of Eqs. 4 for \( f_N = 1 \). \( C(T) \) is a substance dependent prefactor that is otherwise a function of temperature alone. In this context it is noteworthy that the Kelvin relation has been shown experimentally to hold for homogeneous and heterogeneous nucleation down to a few nanometers [14, 15].

The objective here is to derive Eq. 15 from the unifying identity to demonstrate the latter as an analysis tool. With the Kelvin assumption expressed compactly as \( f_N = n^*/g^* = 1 \), the identity becomes:

\[
f_w = -2 + 3f_S.
\]

At the spinodal \( f_w = 0 \), as the nucleation barrier vanishes there, and \( f_S = 2/3 \). Multiplication of Eq. 18 by \( g^* \Delta \mu / 2 \) gives:

\[
W^* = -g^* \Delta \mu + \frac{3}{2} g^* \Delta \mu f_S.
\]
To obtain \( f_s \), differentiate both sides of Eq. 19 with respect to \( \Delta \mu \) using the nucleation theorem (Eq. 16) on the left side, followed by replacement of \( n^* \) with \( g^* \) (per Kelvin assumption). Next use the Kelvin relation - in the form given by Eq. 17, from which follows the identity \( dg^*/d\Delta \mu = -3g^*/\Delta \mu \). Collecting terms yields the following differential equation for \( f_s \):

\[
\frac{3}{2} \Delta \mu \frac{df_s}{d\Delta \mu} - 3f_s + 3 = 0.
\]  

(20)

Integration of Eq. 20 using the boundary condition \( f_s = 2/3 \) at the spinodal, where \( \Delta \mu = \Delta \mu_S \), gives:

\[
f_s = 1 - \frac{1}{3} \left( \frac{\Delta \mu}{\Delta \mu_S} \right)^2.
\]  

(21)

Substituting this new expression into Eq. 18 recovers Talanquer’s result. While the connection between Eqs. 15 and 21 is not immediately apparent otherwise, they are immediately connected through the new identity.

We conclude this section with an application of the unifying identity to surface excess quantities using this same model.

*Surface excess quantities in the Kelvin scaling model:* Comparison of Eqs. 15 and 21 reveals that \( f_w \) and \( f_s \) have different forms consistent with the identity and \( f_N = 1 \). The latter equality is just the Kelvin scaling assumption [12] that underlies the spinodal-compatible nucleation model [11]. Interpretation of the Kelvin assumption and its allowance of departure from CNT were also developed in [12] using the Gibbs concept of superficial density [4]. Departure from CNT is described by the following equation:
\[ W^* = W_{CNT}^* - D(T) \] (22)

where \( D \) is a temperature-dependent parameter that describes departure from the classical theory. Two relationships involving surface excess quantities were also obtained in [12]. These are:

\[ W^* = n_L^* \Delta \mu / 2 \] (23)

and

\[ D(T) = n_S^* \Delta \mu / 2 \] (24)

where \( n_L^* \) is defined as the number of molecules contained within the volume bounded by the surface of tension (of radius \( R_S \)) for uniform interior density of the drop, and \( n_S^* \) divided by \( 4\pi R_S^2 \) is the superficial density. Thus Eq. 24 frames the departure from CNT in terms of the superficial density. Neglecting the displaced vapor component (c.f. Eq. 16) the molecular occupation numbers are related as:

\[ g^* = n^* = n_L^* + n_S^* \] (25)

where the first equality expresses the Kelvin scaling assumption, \( f_N = 1 \). From Eqs. 23, 25, and the first of the Gibbs relations (Eqs. 6), \( f_w = n_L^* / g^* \) and two of the \( f \)-ratios are determined. The new identity (Eq. 5) can be used immediately to obtain the third ratio:

\[ f_S = \frac{\Phi^*}{\Phi_{CNT}^*} = \frac{1}{3}(3n_L^* + 2n_S^*) / g^* \] (26)

Combine the Gibbs relations, to obtain \( \Phi_{CNT}^* = (3/2)g^* \Delta \mu \), and use Eq. 26 to obtain a new result for the surface free energy component in the model:
$$\Phi^* = \frac{3}{2} n_L^* + n_S^* \Delta \mu.$$  

(27)

Though inspired by the new identity, Eq. 27 can of course be validated by other methods. This is particularly easy to do here: returning to general expression, Eq. 1, and making substitutions from Eqs. 23 and 25, yields the desired result.

4. Summary and outlook

A unifying identity connecting the surface and volume work components of the reversible work of general cluster formation has been derived using a fundamental result, due to Gibbs, for the work of forming a spherical liquid drop from vapor in classical homogeneous nucleation theory. The new result yields productive insights into much broader applications that include Fletcher’s model of heterogeneous nucleation, extension to clusters of non-critical size, and molecular-based extensions of classical nucleation theory. It can be expected that the new identity will hold for extensions of the Fletcher model that include line tension and microscopic contact angle [9], and molecular adsorption [16]. Moreover, its power as an analysis tool that enables heterogeneous and homogeneous nucleation to be examined within the same unified theoretical framework has been demonstrated. As has its potential to serve as a consistency check on mathematical formulas and numerical calculations, and as a guide to the interpretation of theory and measurements.

The examples provided in Sec. 3 demonstrate versatility in how the new unifying identity can be used. While its denominators are referenced to classical expressions, its numerators are adaptable to any application that is compatible with
the generic cluster model of Eq. 1. New fundamental insights can be expected on this basis into a range of current active topics including nucleation on ions and ionic clusters [15], ice nucleation [17], and Köhler/nano-Köhler theory describing the processes by which water vapor condenses on cloud condensation nuclei (CCN) and forms cloud droplets [18] or organic vapors condense on nano-clusters to form CCN. The only requirements are: (1) that the work of cluster formation be separable into surface and volume components and (2) that the parent phase chemical potential be the same in the application and reference models.

**Appendix 1: f-ratios in Fletcher’s spherical cap model**

With reference to Fig. 1, define \( x = R / r^* \) where \( R \) is seed radius, \( r^* \) is the critical radius of curvature of the liquid-vapor interface of the cap, and \( m = \cos(\theta) \) for contact angle \( \theta \). In terms of the additional non-dimensional quantity,

\[
g_F = \frac{d}{r^*} = \frac{\sqrt{R^2 + (r^*)^2} - 2Rr^* m}{r^*} = \sqrt{1 + \left( \frac{R}{r^*} \right)^2 - 2m \left( \frac{R}{r^*} \right)} = \sqrt{1 + x^2 - 2xm},
\]

the \( f \)-ratios take the following forms:

\[
f_w = \frac{W_{\text{hetero}}}{W_{\text{homo}}} = \frac{1}{2} \left\{ 1 + \left( \frac{1-mx}{g_F} \right)^3 \right\} + x^3 \left\{ 2 - 3 \left( \frac{x-m}{g_F} \right) + \left( \frac{x-m}{g_F} \right)^3 \right\} + 3mx^2 \left( \frac{x-m}{g_F} - 1 \right), \tag{A1}\]

\[
f_v = \frac{V_{\text{hetero}}}{V_{\text{homo}}} = \frac{1}{4} \left\{ 2 + 3 \left( \frac{1-mx}{g_F} \right) - \left( \frac{1-mx}{g_F} \right)^3 \right\} - x^3 \left\{ 2 - 3 \left( \frac{x-m}{g_F} \right) + \left( \frac{x-m}{g_F} \right)^3 \right\} = f_N, \tag{A2}\]

\[
f_s = \frac{\Phi_{\text{hetero}}}{\Phi_{\text{homo}}} = \frac{1}{2} \left\{ 1 + \left( \frac{1-mx}{g_F} \right) - mx^2 \left[ 1 - \left( \frac{x-m}{g_F} \right) \right] \right\}, \tag{A3}\]
The expressions in A1 and A2 follow Vehkamäki et al. [8]. A derivation of A3 is given below. In the limit that $R \to \infty$, $x \to \infty$, with l'Hôpital's rule used to evaluate indeterminate products involving powers of $x$, Eqs. A1-A3 reduce to:

$$f_W = f_N = f_S \to \frac{1}{4} \left( 2 - 3m + m^2 \right),$$

(A4)

which is the result for cap formation on a flat substrate, discussed as a special case in the text. For $R = x = 0$, or for $m = -1$, the homogeneous nucleus is recovered and $f_W = f_N = f_S = 1$. In this case Eq. 5 becomes a trivial identity: $1 = -2 + 3$.

**Derivation of Eq. A3 for $f_S$:** The interfacial areas appearing in Eq. 9 take the explicit forms [6]:

$$\Omega_{lv} = 2\pi r^* (1 - \cos \psi) = 2\pi r^* \left( 1 + \frac{1 - xm}{g_F} \right)$$

(A5)

and

$$\Omega_{sl} = 2\pi R^2 (1 - \cos \phi) = 2\pi R^2 \left( 1 - \frac{x - m}{g_F} \right)$$

(A6)

where the equalities (see Fig. 1 for relevant angles): $\cos \phi = (R - r^* m) / d = (x - m) / g_F$

and $\cos \psi = -(r^* - Rm) / d = -(1 - mx) / g_F$ have been used. Substitution using the last equality of Eq. 9 gives:

$$f_S = (\Omega_{lv} - \Omega_{sl} m) / (4\pi r^* ) = \frac{1}{2} \left[ 1 + \left( \frac{1 - mx}{g_F} \right) - m^2 \left[ 1 - \left( \frac{x - m}{g_F} \right) \right] \right].$$

(A7)

**References:**


**Acknowledgements:** RLM acknowledges support by the Atmospheric Systems Research (ASR) Program of the US Department of Energy (DE-SC0012704). PMW and PEW acknowledge support by the European Research Council under the European Community’s Seventh Framework Programme (FP7/2007–2013)/ERC grant agreement No. 616075, and the Austrian Science Fund (FWF) (project no. P19546, L593).