Surface energy from heat content asymptotics

1993 J. Phys. A: Math. Gen. 26 823

(http://iopscience.iop.org/0305-4470/26/4/011)

J. Phys. A: Math. Gen. 26 (1993) 823–830. Printed in the UK

Surface energy from heat content asymptotics

D M McAvity

Department of Applied Mathematics and Theoretical Physics, Cambridge University, Silver Street, Cambridge, CB3 9EW, UK.

Received 13 August 1992

Abstract. The free energy associated with a bounding surface of an electrolytic solution is derived as an expansion in the screening length κ^{-1} with results for the first four orders. This new method makes use of a connection with heat content asymptotics, a recent development in the mathematics literature.

1. Introduction

A topic of current interest is the calculation of the free energy associated with a bounding membrane of an electrolytic solution [1–3]. The free energy may be derived directly from the electrostatic potential ϕ which in the weak field limit (linearized theory) is obtained as a solution to the Debye–Hückel equation

$$(-\nabla^2 + \kappa^2)\phi(x) = 0 \tag{1}$$

where κ is the inverse screening length of the electrolyte. Equation (1) is also supplemented with appropriate boundary conditions dictated by the particular physics of the bounding membrane. Exact solutions for arbitrary κ have only been found for certain highly symmetric boundary geometries. However, in the strong electrolyte regime when κ is assumed to be large compared to typical curvature of the membrane, it is possible to obtain results for more complex geometries and topologies [1]. Previously [3] solutions to the Debye–Hückel equation (1) were considered for an arbitrary curved d-dimensional manifold $\mathcal{M}$ with coordinates x^μ and metric $g_{\mu\nu}$ bounded by a smooth $(d-1)$-dimensional surface $\partial\mathcal{M}$ with coordinates $\hat{x}^i$. The boundary is embedded in $\mathcal{M}$ with the parametrization $x^\mu(\hat{x})$ and the induced metric of the boundary is therefore $\hat{g}_{ij} = g_{\mu\nu}\partial x^\mu/\partial\hat{x}^i\, \partial x^\nu/\partial\hat{x}^j|_{x=x(\hat{x})}$. Solutions in this general framework were found with the use of an asymptotic expansion of the heat kernel for the Laplacian which enabled the free energy to be expressed as an expansion in the screening length κ^{-1}. This reproduced earlier results obtained by Duplantier [1] for a three-dimensional flat manifold $\mathcal{M}$. In this article the free energy is related to heat content asymptotics which have been recently studied in the mathematics literature [4–6] and elsewhere [7]. As a result the first four terms in the free energy expansion are obtained.

2. Surface free energy

The free energy $\mathcal{E}$ may be written as a surface integral over the electrostatic potential ϕ and the surface charge density of the membrane $\hat{\rho}$ after using the Debye–Hückel equation (1)

$$\mathcal{E} = \alpha \int_{\mathcal{M}} \mathrm{d}v\, (\partial_\mu \phi \partial^\mu \phi + \kappa^2 \phi^2) = \alpha \int_{\partial\mathcal{M}} \mathrm{d}S\, \hat{\rho}\phi \tag{2}$$

where $\mathrm{d}S = \mathrm{d}^{d-1}\hat{x}\sqrt{\hat{g}}$ is the surface element and α is a constant which depends on the boundary conditions considered. The surface charge density $\hat{\rho}$ is given by

$$\hat{\rho}(\hat{x}) = -\partial_n \phi(x)|_{\partial\mathcal{M}} = -n^\mu(\hat{x})\partial_\mu \phi(x)|_{x=x(\hat{x})} \tag{3}$$

where n^μ is the inward pointing unit, normal to the surface.

The two types of membrane considered here are:

(i) Conducting membranes on which the field is fixed, $\phi(x)|_{\partial\mathcal{M}} = \hat{\varphi}(\hat{x})$, —giving rise to the Dirichlet problem for which we take $\alpha = -1/2$ in (2) and consequently $\mathcal{E}^D < 0$.

(ii) Insulating membranes on which the surface charge density $\hat{\rho}(\hat{x})$ is fixed so that the boundary condition for ϕ is $\partial_n \phi(x)|_{\partial\mathcal{M}} = -\hat{\rho}(\hat{x})$, —giving rise to the Neumann problem for which we take $\alpha = 1/2$ in (2) and consequently $\mathcal{E}^N > 0$.

From standard potential theory the solution of (1) with boundary conditions (i) or (ii) may be expressed as a surface integral over the relevant Green function of the Debye–Hückel operator

(i) $$\phi(x) = \int_{\partial\mathcal{M}} \mathrm{d}S'\, G_D(x, x') \overleftarrow{\partial'_n} \Big|_{x'=x(\hat{x}')} \hat{\varphi}(\hat{x}') \tag{4}$$

(ii) $$\phi(x) = \int_{\partial\mathcal{M}} \mathrm{d}S'\, G_N(x, x') \Big|_{x'=x(\hat{x}')} \hat{\rho}(\hat{x}') \tag{5}$$

where $G_D(x, x')$ is the Dirichlet–Green function satisfying $G_D(x, x')\big|_{x=x(\hat{x})} = 0$ and $G_N(x, x')$ is the Neumann–Green function satisfying $\partial_n G_N(x, x')\big|_{x=x(\hat{x})} = 0$. Then at least formally the free energy may be obtained directly from the above equations via equation (2)

$$\begin{aligned} \mathcal{E}^D &= \frac{1}{2} \int_{\partial\mathcal{M}} \mathrm{d}S\, \mathrm{d}S'\, \hat{\varphi}(\hat{x})\, \mathcal{K}(\hat{x}, \hat{x}')\, \hat{\varphi}(\hat{x}') \\ \mathcal{K}(\hat{x}, \hat{x}') &= \partial_n G_D(x, x') \overleftarrow{\partial'_n} \big|_{x=x(\hat{x}), x'=x(\hat{x}')} \end{aligned} \tag{6}$$

$$\mathcal{E}^N = \frac{1}{2} \int_{\partial\mathcal{M}} \mathrm{d}S\, \mathrm{d}S'\, \hat{\rho}(\hat{x})\, G_N(x, x')\big|_{x=x(\hat{x}), x'=x(\hat{x}')} \hat{\rho}(\hat{x}'). \tag{7}$$

The free energies may be obtained as large κ expansions directly by employing the asymptotic form of the heat kernel $\mathcal{G}_{\nabla^2}(x, x'; \tau)$ as $\tau \to 0$. The Green function for the Debye–Hückel theory is related to this heat kernel by a Laplace transform

$$G(x, x') = \int_0^\infty \mathrm{d}\tau\, \mathrm{e}^{-\tau\kappa^2} \mathcal{G}_{\nabla^2}(x, x'; \tau)\ . \tag{8}$$

In the Dirichlet case (6) it is necessary to give a prescription for treating the non-integrable singularity of the kernel $\mathcal{K}(\hat{x},\hat{x}') = \partial_n G_D(x,x')\overleftarrow{\partial}'_n|_{x=x(\hat{x}),x'=x(\hat{x}')}$ for $\hat{x}\to\hat{x}'$ in a consistent fashion. A discussion of such a prescription, which makes use of the heat kernel $\mathcal{G}_{\nabla^2}(x,x';\tau)$ corresponding to the operator ∇^2, may be found in [3]†. This gives the regulated definition

$$\mathcal{K}(\hat{x},\hat{x}') = \lim_{\epsilon\to 0}\left\{\int_\epsilon^\infty \mathrm{d}\tau\, \mathrm{e}^{-\tau\kappa^2}\partial_n \mathcal{G}_{\nabla^2,D}(x,x';\tau)\overleftarrow{\partial}'_n|_{x=x(\hat{x}),x'=x(\hat{x}')} - \frac{1}{(\pi\epsilon)^{\frac{1}{2}}}\,\delta_{\partial\mathcal{M}}(\hat{x},\hat{x}')\right\} + \frac{1}{2}K(\hat{x})\,\delta_{\partial\mathcal{M}}(\hat{x},\hat{x}') \tag{9}$$

where $K = \hat{g}^{ij}K_{ij}$ and $K_{ij}(\hat{x})$ is the extrinsic curvature of the boundary $\partial\mathcal{M}$ which may be defined by $\partial x^\mu/\partial\hat{x}^i\,\partial x^\nu/\partial\hat{x}^j\nabla_\mu n_\nu = -K_{ij}$. The limit in (9) may be shown to exist after integration over suitably smooth test functions on $\partial\mathcal{M}$.

An extended DeWitt ansatz for the small τ limit of $\mathcal{G}_{\nabla^2}(x,x';\tau)$ has been given which takes the form of an expansion for $x\approx x'$ near the boundary. In [3] this expansion, valid for an arbitrary d-dimensional curved manifold $\mathcal{M}$, was used directly via equations (6)–(8) to obtain the first three terms of the large κ expansion of the free energies. The results were found to be in agreement with previous calculations carried out by Duplantier *et al* [1] in the physically significant limit $d=3$, $\mathcal{M}$ flat and arbitrary smoothly curved two-dimensional boundary $\partial\mathcal{M}$.

Substituting the relation (8) into the free energy definitions (6) and (7) it is possible to express $\mathcal{E}$ in compact form. In the Dirichlet case in light of the regulation (9) one has

$$\mathcal{E}^D = \frac{1}{2}\lim_{\epsilon\to 0}\left\{\int_\epsilon^\infty \mathrm{d}\tau\,\mathrm{e}^{-\tau\kappa^2}\hat{\mathcal{T}}^D_{\nabla^2}[\hat{\varphi},\hat{\varphi};\tau] - \frac{1}{(\pi\epsilon)^{\frac{1}{2}}}\int_{\partial\mathcal{M}}\mathrm{d}S\,\hat{\varphi}^2\right\} + \frac{1}{2}\int_{\partial\mathcal{M}}\mathrm{d}S\,K\hat{\varphi}^2 \tag{10}$$

where $\hat{\mathcal{T}}^D_{\nabla^2}$ is defined by

$$\hat{\mathcal{T}}^D_{\nabla^2}[\hat{\varphi},\hat{\varphi};\tau] = \int_{\partial\mathcal{M}}\mathrm{d}S\mathrm{d}S'\,\hat{\varphi}(\hat{x})\,\partial_n\mathcal{G}^D_{\nabla^2}(x,x';\tau)\overleftarrow{\partial}'_n\Big|_{x=x(\hat{x}),x'=x(\hat{x}')}\hat{\varphi}(\hat{x}'). \tag{11}$$

In this prescription the non-integrable singularity of the Dirichlet case manifests itself in the limiting behaviour of $\hat{\mathcal{T}}^D_{\nabla^2}$ as $\tau\to 0$. In this limit $\hat{\mathcal{T}}^D_{\nabla^2}\sim 1/\tau^{3/2}$ and the singular term in (10) cancels. For Neumann boundary conditions

$$\mathcal{E}^N = \frac{1}{2}\int_0^\infty \mathrm{d}\tau\,\mathrm{e}^{-\tau\kappa^2}\hat{\mathcal{T}}^N_{\nabla^2}[\hat{\rho},\hat{\rho};\tau] \tag{12}$$

with

$$\hat{\mathcal{T}}^N_{\nabla^2}[\hat{\rho},\hat{\rho};\tau] = \int_{\partial\mathcal{M}}\mathrm{d}S\mathrm{d}S'\,\hat{\rho}(\hat{x})\mathcal{G}^N_{\nabla^2}(x,x';\tau)\Big|_{x=x(\hat{x}),x'=x(\hat{x}')}\hat{\rho}(\hat{x}'). \tag{13}$$

† In that paper the second equation in (26) should be $\mathrm{d}\Omega_d = (\sin\theta)^{d-2}\mathrm{d}\theta\,\mathrm{d}\Omega_{d-1}$.

These definitions for $\hat{T}^D_{\nabla^2}$ and $\hat{T}^N_{\nabla^2}$ are special cases of a more general sesquilinear form on $\partial\mathcal{M}$ which will be defined later. To derive an expression for the free energy it is sufficient to obtain an asymptotic expansion of the quantities $\hat{T}^D_{\nabla^2}$ and $\hat{T}^N_{\nabla^2}$ either directly from the heat kernel expansion itself or by some other means.

In the following section $\hat{T}_{\nabla^2}$ will be derived from what are called heat content asymptotics, which have been analysed using functorial methods in the mathematics literature [4–6] which are closely related to the short-time transient of diffusion outside a conducting body [8].

3. Heat content asymptotics

Heat content asymptotics are concerned with the form of the double integral over the manifold of the heat kernel $\mathcal{G}_\Delta(x,x';\tau)$ associated with a general second-order elliptic operator Δ in the small τ limit.

$$\int_{\mathcal{M}} \mathrm{d}v\mathrm{d}v'\ \left(f^\dagger(x)\,\mathcal{G}_\Delta(x,x';\tau)\,f'(x')\right) \equiv \mathcal{T}_\Delta[f,f';\tau] \qquad (14)$$

where $\mathrm{d}v = \mathrm{d}^d x\sqrt{g}$ is the volume element. Assuming the operator Δ acts on sections of an n dimensional vector bundle V over $\mathcal{M}$ then f and f' are dimension n vectors of smooth test functions on $\mathcal{M}$.

The heat kernel $\mathcal{G}_\Delta(x,x';\tau)$ satisfies the generalized heat equation

$$\left(\frac{\partial}{\partial\tau}+\Delta_x\right)\mathcal{G}_\Delta(x,x';\tau)=0 \qquad \mathcal{G}_\Delta(x,x';0)=\delta^d(x,x'). \qquad (15)$$

where $\delta^d(x,x') = \delta^d(x-x')/g(x)^{1/2}$. This equation is supplemented with some appropriate linear boundary conditions expressed in terms of a linear operator $\mathcal{B}$ acting on sections of V so that $\mathcal{B}_x\,\mathcal{G}_\Delta(x,x';\tau)=0$, where the subscript x denotes operation on the argument x. If Δ is self-adjoint, as is assumed here, then $\mathcal{G}_\Delta$ will also satisfy the boundary condition $\mathcal{G}_\Delta(x,x';\tau)\overleftarrow{\mathcal{B}}_{x'}=0$, where the arrow indicates operating to the left.

The most general form for the second-order elliptic operator Δ is assumed here to be

$$\Delta = -D^2 + X \qquad D^2 = g^{\mu\nu}D_\mu D_\nu \qquad D_\mu = \nabla_\mu + A_\mu. \qquad (16)$$

Here A_μ and X are matrix-valued vector gauge and scalar fields respectively which satisfy the symmetry relations $A^\dagger_\mu = -A_\mu$ and $X^\dagger = X$. Note also that ∇_μ contains the usual Christoffel connection formed from $g_{\mu\nu}$.

The most general boundary conditions considered in this analysis are mixed boundary conditions, for which the operator $\mathcal{B}$ takes the form, for $\xi(x)$ a section of the bundle V over $\mathcal{M}$

$$\mathcal{B}\,\xi \equiv (1-\mathcal{P})\,\xi\Big|_{\partial\mathcal{M}} + \mathcal{P}(D_n+\psi)\,\xi\Big|_{\partial\mathcal{M}} \qquad (17)$$

and correspondingly

$$\xi^\dagger\overleftarrow{\mathcal{B}} = \xi^\dagger(1-\mathcal{P})\Big|_{\partial\mathcal{M}} + \xi^\dagger(\overleftarrow{D}_n+\psi)\mathcal{P}\Big|_{\partial\mathcal{M}} \qquad (18)$$

where $\overleftarrow{D}_n = \overleftarrow{\partial}_n - A_n$, $\mathcal{P}(\hat{x})$ is a self-adjoint projection operator; $\mathcal{P}^2 = \mathcal{P}$, $\mathcal{P}^\dagger = \mathcal{P}$ and $\psi(\hat{x})$ is a matrix valued scalar surface field for which $\psi^\dagger = \psi$ and $\psi\mathcal{P} = \mathcal{P}\psi = \psi$. The limit $\mathcal{P} \to 0$ corresponds to pure Dirichlet boundary conditions and $\mathcal{P} \to 1$ leads to pure Neumann boundary conditions (Neumann boundary conditions including the linear term ψ are often referred to as Robin boundary conditions).

In the asymptotic limit $\tau \to 0$ the heat content $\mathcal{T}_\Delta$ may be expanded as a power series in the parameter τ

$$\mathcal{T}_\Delta[f, f'; \tau] = \sum_{n \geqslant 0} \beta_n[f, f'] \tau^{n/2}. \tag{19}$$

In general the β_n are expressed as the sum of volume and surface integrals

$$\beta_n = \int_M \mathrm{d}v \, \beta_n^{\mathcal{M}} + \int_{\partial\mathcal{M}} \mathrm{d}S \, \beta_n^{\partial\mathcal{M}} \tag{20}$$

where the $\beta_n^{\mathcal{M}} = 0$ for odd n and are independent of the choice of boundary conditions. Results for β_n are given up to $n = 3$ for mixed boundary conditions in [5,7] and up to $n = 4$ for pure Dirichlet and $n = 6$ for pure Neumann boundary conditions in [6].

A more general definition for the purely surface quantity $\hat{\mathcal{T}}_\Delta$ that incorporates the special cases given in (11) and (13) is possible. Define a linear operator $\mathcal{B}^*$ acting on sections of the vector bundle V so that

$$\mathcal{B}^* \xi = (1 - \mathcal{P}) \, D_n \xi \Big|_{\partial\mathcal{M}} - \mathcal{P}\xi \Big|_{\partial\mathcal{M}}. \tag{21}$$

Then if $\hat{f}, \hat{f}'$ are n-dimensional vectors of test functions on $\partial\mathcal{M}$, a natural definition for $\hat{\mathcal{T}}_\Delta$ is

$$\hat{\mathcal{T}}_\Delta[\hat{f}, \hat{f}'; \tau] = \int_{\partial\mathcal{M}} \mathrm{d}S \mathrm{d}S' \left(\hat{f}^\dagger(\hat{x}) \, \mathcal{B}_x^* \mathcal{G}_\Delta(x, x'; \tau) \overleftarrow{\mathcal{B}}_{x'}^* \hat{f}'(\hat{x}') \right) \tag{22}$$

which in the appropriate Dirichlet and Neumann ($\psi = 0$) limits reduces to the definitions given in (11) and (13). The connection between $\hat{\mathcal{T}}_\Delta$ and $\mathcal{T}_\Delta$ may be derived in this general framework and the limit of physical interest $d = 3$, $\mathcal{M}$ flat, $\Delta = -\nabla^2$ and $\mathcal{P} \to 0, 1$ is only taken later to determine the free energy expansion through equations (10) and (12).

The quantities $\mathcal{T}_\Delta$ and $\hat{\mathcal{T}}_\Delta$ are related by making use of Green's theorem, expressing Δ as a symmetric operator

$$\begin{aligned} \int_{\mathcal{M}} \mathrm{d}v \, (\Delta f)^\dagger \, \mathcal{G}_\Delta(x, x'; \tau) - \int_{\mathcal{M}} \mathrm{d}v \, f^\dagger \Delta \mathcal{G}_\Delta(x, x'; \tau) \\ = \int_{\partial\mathcal{M}} \mathrm{d}S \, (D_n f)^\dagger \, \mathcal{G}_\Delta(x, x'; \tau) \Big|_{x = x(\hat{x})} \\ - \int_{\partial\mathcal{M}} \mathrm{d}S \, f^\dagger \, D_n \mathcal{G}_\Delta(x, x'; \tau) \Big|_{x = x(\hat{x})} \end{aligned} \tag{23}$$

and the heat equation (15). Hence one obtains

$$\begin{aligned}
\mathcal{T}_\Delta[\Delta f,\Delta f';\tau] &+ \frac{\partial}{\partial\tau}(\mathcal{T}_\Delta[\Delta f,f';\tau] + \mathcal{T}_\Delta[f,\Delta f';\tau]) + \frac{\partial^2}{\partial\tau^2}\mathcal{T}_\Delta[f,f';\tau] \\
&= \int \mathrm{d}S\mathrm{d}S'\,(f^\dagger D_n \mathcal{G}_\Delta \overleftarrow{D}'_n f' + (D_n f)^\dagger \mathcal{G}_\Delta D'_n f' \\
&\quad - (D_n f)^\dagger \mathcal{G}_\Delta \overleftarrow{D}'_n f' - f^\dagger D_n \mathcal{G}_\Delta D'_n f') \\
&= \hat{\mathcal{T}}_\Delta[\mathcal{B}f,\mathcal{B}f';\tau]. \qquad (24)
\end{aligned}$$

Equation (24) may be interpreted in two ways. On the one hand it provides an iterative procedure for generating the heat content asymptotics $\mathcal{T}_\Delta$ given a suitable expansion for $\hat{\mathcal{T}}_\Delta$. On the other hand given an expansion for $\mathcal{T}_\Delta$ it is possible to derive directly such an expansion for $\hat{\mathcal{T}}_\Delta$. The latter approach is the one taken in this article since $\mathcal{T}_\Delta$ has thus far been calculated to a higher order than $\hat{\mathcal{T}}_\Delta$. Following the second approach, equation (24) also gives an important consistency check on the asymptotic expansion of $\mathcal{T}_\Delta$ because all volume contributions on the left-hand side of the equation must cancel. In addition the derivatives of the test functions f and f' in the boundary terms must take on the required form dictated by the right-hand side of the equation.

Using the previous results [6] for $\mathcal{T}_\Delta$, specializing to pure Dirichlet and Neumann boundary conditions but retaining arbitrary dimension d and a curved manifold $\mathcal{M}$, the expansions for $\hat{\mathcal{T}}_\Delta$ are derived. Writing $\hat{\mathcal{T}}_\Delta$ as a power series in τ

$$\hat{\mathcal{T}}_\Delta[\hat{f},\hat{f}';\tau] = \tau^{-2}\int_{\partial\mathcal{M}} \mathrm{d}S \sum_{n\geqslant 0} \hat{\beta}_n[\hat{f},\hat{f}'](\hat{x})\tau^{\frac{n}{2}} \qquad (25)$$

then for Dirichlet boundary conditions the local coefficients $\hat{\beta}_n[\hat{f},\hat{f}'](\hat{x})$ are then determined to be

$$\hat{\beta}_0[\hat{f},\hat{f}'] = 0 \qquad (26)$$

$$\hat{\beta}_1[\hat{f},\hat{f}'] = \frac{1}{2\sqrt{\pi}}\hat{f}^\dagger\hat{f}' \qquad (27)$$

$$\hat{\beta}_2[\hat{f},\hat{f}'] = 0 \qquad (28)$$

$$\hat{\beta}_3[\hat{f},\hat{f}'] = \frac{1}{2\sqrt{\pi}}(\hat{f}^\dagger(\tfrac{1}{2}K_{ij}K^{ij} - \tfrac{1}{4}K^2 + \tfrac{1}{2}R_{nn} - X)\hat{f}' - (\hat{D}^i\hat{f})^\dagger \hat{D}_i\hat{f}') \qquad (29)$$

$$\begin{aligned}
\hat{\beta}_4[\hat{f},\hat{f}'] = \hat{f}^\dagger(&\tfrac{1}{4}K_{ij}K^{ik}K_k{}^i - \tfrac{1}{8}K_{ij}K^{ij}K + \tfrac{1}{4}R_{injn}K^{ij} - \tfrac{1}{8}R_{ij}K^{ij} \\
&- \tfrac{1}{4}\partial_n X + \tfrac{1}{16}\partial_n R + \tfrac{1}{8}\hat{D}_i\hat{D}_j K^{ij})\hat{f}' - \tfrac{1}{2}K^{ij}(\hat{D}_i\hat{f})^\dagger \hat{D}_j\hat{f}' \\
&+ \tfrac{1}{4}((\hat{D}^i\hat{f})^\dagger F_{in}\hat{f}' - \hat{f}^\dagger F_{in}\hat{D}^i\hat{f}') \qquad (30)
\end{aligned}$$

and for Neumann boundary conditions

$$\hat{\beta}_0[\hat{f},\hat{f}'] = \hat{\beta}_1[\hat{f},\hat{f}'] = \hat{\beta}_2[\hat{f},\hat{f}'] = 0 \qquad (31)$$

$$\hat{\beta}_3[\hat{f},\hat{f}'] = \frac{1}{\sqrt{\pi}}\hat{f}^\dagger\hat{f}' \qquad (32)$$

$$\hat\beta_4[\hat f,\hat f'] = \hat f^\dagger\,(\psi+\tfrac{1}{2}K)\hat f' \tag{33}$$

$$\hat\beta_5[\hat f,\hat f'] = \frac{1}{\sqrt{\pi}}\Big(\hat f^\dagger\Big(\tfrac14 K^2+\tfrac12 K_{ij}K^{ij}+\tfrac12 R_{nn}+2\psi^2+2\psi K-X\Big)\hat f' - (\hat D^i\hat f)^\dagger\,\hat D_i\hat f'\Big) \tag{34}$$

$$\begin{aligned}\hat\beta_6[\hat f,\hat f'] = \hat f^\dagger\,\big(&\tfrac14 K_{ij}K^{ik}K_k{}^i+\tfrac18 K_{ij}K^{ij}K+\tfrac14 R_{injn}K^{ij}-\tfrac18 R_{ij}K^{ij}+\tfrac14 R_{nn}K\\&+\tfrac1{16}\partial_n R+\tfrac12\psi K^2+\tfrac12\psi K_{ij}K^{ij}+\tfrac32\psi^2K+\tfrac12\psi R_{nn}-\tfrac14\partial_n X\\&-\tfrac12 XK-\tfrac12(X\psi+\psi X)+\psi^3+\hat D^2\psi+\tfrac18\hat D_i\hat D_jK^{ij}\big)\,\hat f'\\&-\tfrac12 K^{ij}(\hat D_i\hat f)^\dagger\,\hat D_j\hat f'-(\hat D^i\hat f)^\dagger(\psi+\tfrac12K)\,\hat D_i\hat f'\\&+\tfrac14((\hat D^i\hat f)^\dagger\,F_{in}\,\hat f'-\hat f^\dagger\,F_{in}\,\hat D^i\hat f').\end{aligned} \tag{35}$$

In the above equations the coefficients $\hat\beta_n$ are expressed in general as a sum of contractions of various tensors associated with the manifold $\mathcal{M}$, the boundary $\partial\mathcal{M}$, the operator Δ and the boundary conditions. The tensor $R_{\mu\nu\sigma\rho}$ is the Riemann tensor on $\mathcal{M}$ for which $R_{ninj} = n^\mu n^\sigma\partial x^\nu/\partial\hat x^i\,\partial x^\rho/\partial\hat x^j\,R_{\mu\nu\sigma\rho}|_{\partial\mathcal{M}}$ and $R_{nn} = \hat g^{ij}R_{ninj}$. Also $\hat D_i$ is the induced covariant derivative acting on tensor fields on the boundary $\partial\mathcal{M}$ and $F_{ni} = n^\mu\,\partial x^\nu/\partial\hat x^i F_{\mu\nu}|_{\partial\mathcal{M}}$ where $F_{\mu\nu}$ is the field strength tensor associated with the vector gauge field A^μ defined by $F_{\mu\nu}=\partial_\mu A_\nu-\partial_\nu A_\mu+[A_\mu,A_\nu]$. The form of these results, derived from the heat content asymptotics $\mathcal{T}_\Delta$ with the use of the expansion

$$\Delta f|_{\partial\mathcal{M}} = (-n^\mu n^\nu\partial_\mu\partial_\nu+K\,n^\mu\partial_\mu-\hat D^i\hat D_i+X)f|_{\partial\mathcal{M}} \tag{36}$$

confirms the consistancy of the original expansion for $\mathcal{T}_\Delta$.

With this expansion for $\hat{\mathcal{T}}_\Delta$ it is now straightforward to derive an expansion for the free energy using equations (10) and (12). Specializing to dimension $d=3$, a flat manifold $\mathcal{M}$, and $\Delta=-\nabla^2$ one finds for Dirichlet boundary conditions as $\kappa\to\infty$

$$\begin{aligned}\mathcal{E}^D\sim\frac{\kappa}{2}\int_{\partial\mathcal{M}}\mathrm{d}S\Big\{&\Big(-1+\frac{1}{2\kappa}K+\frac{1}{4\kappa^2}(\tfrac12K^2-\hat R)\\&+\frac{1}{8\kappa^3}(K^3-2\hat RK+\hat\nabla^2K)\Big)\hat\varphi^2\\&-\frac{1}{2\kappa^2}\partial_i\hat\varphi\,\partial^i\hat\varphi-\frac{1}{2\kappa^3}K^{ij}\partial_i\hat\varphi\,\partial_j\hat\varphi\Big\}\end{aligned} \tag{37}$$

and correspondingly for Neumann boundary conditions with $\psi=0$

$$\begin{aligned}\mathcal{E}^N\sim\frac{1}{2\kappa}\int_{\partial\mathcal{M}}\mathrm{d}S\Big\{&\Big(1+\frac{1}{2\kappa}K+\frac{1}{4\kappa^2}\big(\tfrac32K^2-\hat R\big)\\&+\frac{1}{8\kappa^3}(3K^3-4\hat RK+\hat\nabla^2K)\Big)\hat\rho^2\\&-\frac{1}{2\kappa^2}\partial_i\hat\rho\,\partial^i\hat\rho-\frac{1}{2\kappa^3}(K^{ij}+\hat g^{ij}K)\partial_i\hat\rho\,\partial_j\hat\rho\Big\}\end{aligned} \tag{38}$$

where $\hat{R} = \hat{g}^{ij}\hat{R}_{ij}$ is the intrinsic scalar curvature of the boundary. In flat space $\hat{R} = K^2 - K_{ij}K^{ij}$ and $\hat{\nabla}^i\hat{\nabla}^j K_{ij} = \hat{\nabla}^2 K$ and for a two-dimensional boundary $\hat{R}_{ij} = \frac{1}{2}\hat{R}\hat{g}_{ij}$. If R_1 and R_2 are the two principle radii of curvature of the boundary then $K = 1/R_1 + 1/R_2$ and $\hat{R} = 2/R_1R_2$. The highest-order terms $O(\kappa^{-3})$ in the integrand of the above equations are new, while the other terms are in agreement with previous results [1,3].

Acknowledgments

I am grateful for helpful conversations with H Osborn and P Gilkey. I thank the Royal Commission for the Exhibition of 1851 for an overseas scholarship.

References

[1] Duplantier B 1990 *Physica* **168A** 179
Duplantier B, Goldstein R E, Romero-Rochin V and Pesci A 1990 *Phys. Rev. Lett.* **65** 508
[2] Goldstein R E, Pesci A and Romero-Rochin V 1990 *Phys. Rev.* A **41** 5504
Duplantier B 1991 *Phys. Rev. Lett.* **66** 1555
[3] McAvity D and Osborn H 1992 *J. Phys. A: Math. Gen.* **25** 3287
[4] van den Berg M and Gilkey P B *Preprint*
[5] Desjardins S and Gilkey P B *Preprint*
[6] van den Berg M, Desjardins S and Gilkey P B *Preprint*
[7] McAvity D 1992 *Class. Quantum Grav.* **9** 1983
[8] Phillips C G and Jansons K M 1990 *Proc. R. Soc.* A **428** 431