Helmholtz Free-Energy Bounds from High-Temperature Series?*

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In theoretical equation-of-state investigations an important goal is to obtain the Helmholtz free energy, from which other thermodynamic properties can be obtained. The Helmholtz free energy is hard to calculate directly. A less ambitious goal is to relate the free energy for the system of interest to the properties of a simpler, well-understood system. The simplest example of such a "perturbation" calculation considers the effect on the free energy when attractive forces are added to a purely repulsive hard-sphere system.

This idea that attractive forces can be treated as a perturbation, with the distribution of particles being determined by short-range repulsive forces goes back to van der Waals and Boltzmann. Zwanzig[1] formulated the corresponding perturbation theory precisely, showing that the change in Helmholtz free energy caused by adding an attractive potential to a repulsive hard-core interaction could be expressed as a high-temperature series in $1/T$, where T is the temperature. Until recently it had been relatively unnoticed that the first term in Zwanzig's series provides a rigorous upper bound on the Helmholtz free energy:

$$A \leq A_o + \langle E - E_o \rangle. \tag{1}$$

The subscripts refer to reference-system properties and the averaging indicated by angle brackets in (1) is carried out using the distribution characterizing the unperturbed reference system. In the proof[2] of (1) we replace $(E - E_o)/kT$ by x:

$$\exp[-(A - A_o)/kT] = \langle e^{-x} \rangle = e^{-\langle x \rangle} \langle e^{-x + \langle x \rangle} \rangle$$

$$\geq e^{-\langle x \rangle} \langle 1 - x + \langle x \rangle \rangle = e^{-\langle x \rangle}. \tag{2}$$

Seventy years ago Gibbs[3] derived inequalities that closely resemble (1). Inequality (1) is attributed to Bogolyubov by Bazarov,[4] who first used this "Gibbs–Bogolyubov" inequality in numerical thermodynamic calculations.

The Gibbs–Bogolyubov inequality can be used to select the best value of any parameter on which the reference-system energy depends. Bazarov used a harmonic Einstein model, and minimized the free energy by varying the Einstein frequency. Bazarov's numerical melting-line results were only in semiquantitative agreement with rare-gas experiments because no liquid-phase properties were considered in his calculation.

Mansoori and Canfield[5] carried out a much more thorough variational calculation, in all three phases, using the Einstein-like Lennard-Jones–Devonshire cell model to describe the solid phase, and the Wertheim–Thiele[6] solution of the hard-sphere Percus–Yevick equation to describe the fluid phases. The results Mansoori and Canfield obtained[7] closely resemble those of the exact computer experiments.[8] Mansoori and Canfield's success in using just the one-term Gibbs–Bogolyubov inequality suggests that higher-order terms should lead to a quantitative theory of liquids. Mansoori and Canfield thought that higher-order inequalities could be obtained by truncating Zwanzig's $1/T$ series after terms other than the first. But their results from truncation of the series after the third term were disappointing.

To understand the failure of third-order truncation, we explored the higher-order terms. We found that such inequalities do not, in fact, exist![9] Although higher-order truncated series *may* provide extrema in free energy as the parameter characterizing the reference system is varied, there is no guarantee that the truncated free energy will bound the true free energy.

The simplest way to show this lack of general higher-order inequalities is to examine special cases for which the free energy is known and compare truncated series approximations with the known free energy. The case of a system with only three energy levels, $-\epsilon$, 0, and ϵ, is already complicated enough to illustrate the lack of inequalities convincingly. If the state of zero energy corresponds to the reference-system energy, and has degeneracy g in the system of interest, then the canonical partition function is $2\cosh(\epsilon/kT)+g$, from which the high-temperature expansion of the free energy difference, $(A-A_o)/kT$ can be calculated:

$$-(A-A_o)/kT = xy + (x^2y - 6x^2y^2)/12 + \cdots, \quad (3)$$

where x is $(\epsilon/kT)^2$ and y is $(2+g)^{-1}$. For g small $(0, 1, 2)$ and x equal to 1 the truncated free energy series predicts too low a free energy if truncated after the x or x^3 terms and too high a free energy if truncated after the x^2 term. These bounds are *all reversed* if g is 5.

These simple cases illustrate that at least through *seventh-order* terms in the high-temperature series only the Gibbs–Bogolyubov bound is generally valid. Even this simple example is fairly realistic. The perturbation energies could refer to energy states in a crystal, or in a gas, in which the particles spend most of the time in free flight $(E=0)$, and have occasional collisions with other particles (attraction, $E=-\epsilon$; followed by repulsion, $E=\epsilon$).

The lack of higher-order bounds on the free energy means that a fresh approach is needed to extend the Mansoori–Canfield theory.

[1] R. W. Zwanzig, J. Chem. Phys. 22, 1420 (1954).

[2] For additional references and applications see A. Isihara, J. Phys. A 1, 539 (1968).

[3] J. W. Gibbs, *Collected Works* (Yale U. P., New Haven, 1948), Vol. 2, p. 129.

[4] I. P. Bazarov, Dokl. Akad. Nauk SSSR 135, 1351 (1960) [Sov. Phys. Dokl. 5, 1293 (1961)].

[5] G. A. Mansoori and F. B. Canfield, J. Chem. Phys. 51, 4958, 4967 (1969). See also J. Rasaiah and G. Stell, Mol. Phys. 18, 249 (1970).

[6] M. S. Wertheim, Phys. Rev. Letters 8, 321 (1963); E. Thiele, J. Chem. Phys. 39, 474 (1963).

[7] For a similar, but more complex theory, see D. Henderson and J. A. Barker, J. Chem. Phys. 52, 2315 (1970).

[8] W. W. Wood, *Physics of Simple Liquids*, edited by H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke (Wiley, New York, 1968), Chap. 5.

[9] Mansoori and Canfield's higher-order inequalities are based on an incorrect version of the high-temperature expansion coefficients. Zwanzig's coefficients are correct. See the discussion on p. 541 of Ref. 2.