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# Inversion of the Classical Second Virial Coefficient

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It is shown that, on the basis of some weak assumptions regarding the nature of the intermolecular pair potential, the classical second virial coefficient determines the potential uniquely.

**KEY WORDS:** Inverse problem; intermolecular potential; second virial coefficient; Laplace transform in statistical mechanics; temperature dependence of second virial coefficient.

A problem of recent interest[1-3] has been that of determining the intermolecular potential from the second virial coefficient,

$$B(\beta) = -2\pi \int_0^\infty [e^{-\beta\varphi(r)} - 1]\, r^2\, dr \tag{1}$$

where $\beta = 1/kT$ and $\varphi(r)$ is the spherically symmetric and pairwise additive intermolecular potential. Keller and Zumino[1] stated that if $\varphi(r)$ is analytic, then $\varphi$ is uniquely determined by $B(\beta)$. In this note, we demonstrate the following theorem:

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**Theorem.** Let the following hold:

(a) $\varphi(r)$ is analytic (and real-valued) for $r > 0$;
(b) $\varphi(r) = O(r^{-3-\epsilon})$, $\epsilon > 0$, as $r \to \infty$;
(c) $\varphi(r) \uparrow \infty$ as $r \downarrow 0$.

Then $B(\beta)$ given by Eq. (1) determines $\varphi(r)$ uniquely [subject to (a)–(c)].

Proof. We note first that (b) and (c) ensure the existence of the integral in (1) "at both ends." Next, integration by parts gives

$$3B(\beta)/2\pi\beta = \int_0^\infty e^{-\beta\varphi(r)} r^3 \varphi'(r)\, dr \tag{2}$$

Now, let $0 = r_0 < r_1 < r_2 < \cdots \to \infty$, where $\varphi(r)$ is decreasing on $(r_{2j}, r_{2j+1})$ and increasing on $(r_{2j+1}, r_{2j+2})$, $j = 0, 1, 2,\ldots$. (The argument is essentially the same and even easier if there are only finitely many such $r_j$.) Then

$$3B(\beta)/2\pi\beta = \sum_{j=0}^{\infty} \int_{r_j}^{r_{j+1}} e^{-\beta\varphi(r)} r^3 \varphi'(r)\, dr$$

$$= \sum_{j=0}^{\infty} \int_{s_j}^{s_{j+1}} e^{-\beta s} [\varphi_j^{-1}(s)]^3\, ds$$

where $s_j = \varphi(r_j)$ and $\varphi_j^{-1}(s)$ is the function inverse to $\varphi(r)$ for $r_j < r < r_{j+1}$, $j = 0, 1, 2,\ldots$. It follows that

$$3B(\beta)/2\pi\beta = \int_{-\infty}^{\infty} e^{-\beta s} F(s)\, ds, \qquad \beta > 0 \tag{3}$$

where for any $s \neq 0$,

$$F(s) = -\sum_{s_{2j+1}<s<s_{2j}} [(\varphi_{2j}^{-1}(s)]^3 + \sum_{s_{2j+1}<s<s_{2j+2}} [\varphi_{2j+1}^{-1}(s)]^3 \tag{4}$$

[Note that since $s_j \to 0$ as $j \to \infty$, each $s \neq 0$ belongs to only finitely many intervals $(s_{2j+1}, s_{2j})$ or $(s_{2j+1}, s_{2j+2})$. Thus each of the two sums in (4) is a finite sum. Also if $s < \inf_{j\geqslant 0}(s_j)$, then both sums are vacuous and $F(s)$ is understood to equal 0. The values of $F(s)$ for $s = s_i$ ($j = 0, 1, 2,\ldots$) or $s = 0$ are of course irrelevant. Finally, the above interchange of summation and integration can be justified by an argument based upon (b) and Lebesgue's dominated convergence theorem.] If $s > \sup_{j\geqslant 1}(s_j)$, Eq. (4) reduces to

$$F(s) = -[\varphi_0^{-1}(s)]^3, \qquad (s > \sup_{j\geqslant 1} s_j) \tag{5}$$

Let us now suppose that $\varphi(r)$ can be replaced by another function $\psi(r)$ in (a)–(c) and Eq. (1). Then, by Eq. (3),

$$\int_{-\infty}^{\infty} e^{-\beta s} F(s)\, ds = \int_{-\infty}^{\infty} e^{-\beta s} G(s)\, ds \qquad (\beta > 0)$$

where $G(s)$ corresponds to $\psi(r)$ as $F(s)$ corresponds to $\varphi(r)$ in Eq. (4). By the uniqueness theorem for (bilateral) Laplace transforms, $F(s) = G(s)$ for almost all $s$ (and therefore for all $s$ where both functions are continuous). Therefore (5) implies that $\varphi_0^{-1}(s) = \psi_0^{-1}(s)$ for all $s$ in some neighborhood of $\infty$. Thus $\varphi(r) = \psi(r)$ for all $r$ in some right neighborhood of 0. By the analyticity assumption (a), we conclude that $\psi(r) = \varphi(r)$ for all $r > 0$, as required.

As an example of the inversion process, we treat a reduced Lennard-Jones $m$–$n$ potential

$$\varphi(r) = 4(r^{-m} - r^{-n}); \qquad m, n \geqslant 4, \quad m > n \tag{6}$$

for which

$$B_{m-n}(\beta) = -(3/m) \sum_{j=0}^{\infty} (4\beta)^{[(m-n)j+3]/n} \Gamma([jn - 3]/m)/j! \tag{7}$$

The Laplace inversion is carried out using the Hankel contour integral[4] formula, with the result

$$r^3(\varphi) = -(3/m) \sum_{j=0}^{\infty} (1/j!)(4/\varphi)^{[(m-n)j+3]/m} \times \Gamma([jn - 3]/m)/\Gamma(m - 3 - [m - n]\, jm) \tag{8}$$

An iterative solution of Eq. (6) for $r^3(\varphi)$ yields the same series expression.

## REFERENCES

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