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On the Inversion of the Classical Second Virial Coefficient

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For a large class of intermolecular potentials, the values of the second virial coefficient at a discrete set of temperature points in an arbitrarily small neighborhood of the origin determine the potential uniquely.

KEY WORDS: Second virial coefficient; intermolecular potential; the Laplace–Stieltjes integral.

1. INTRODUCTION

The inverse problem in statistical mechanics consists in finding an intermolecular interaction consistent with the known macroscopic properties of a system. A problem of recent interest has been to investigate to what extent the second virial coefficient $B(\beta)$ determines the pair potential $\phi(r)$.[1,2] In Ref. 1 it was shown that if $\phi(r)$ is reasonable and of a definite sign, then $B(\beta)$ determines $\phi(r)$ uniquely. In Ref. 2 the condition of definiteness of $\phi(r)$ was dropped but it was required to be analytic in a neighborhood of the positive real line R^+.

$B(\beta)$ is given by

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

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where $\beta = 1/kT$ and $\phi(r)$ is spherically symmetric and pairwise additive potential. $\phi(r)$ is also assumed to be bounded below, i.e., $\phi(r) \geqslant -b$, $b \geqslant 0$, and to decrease faster than r^{-3} as $r \to \infty$, so that the integral on the right side of (1) exists. By integrating by parts, one has that

$$\tau(\beta) = 3B(\beta)/2\pi\beta = -\int_0^\infty e^{-\beta\phi(r)} r^3 \, d\phi(r) \tag{2}$$

Let $\tilde{\phi}(r) = \phi(r) + b$. We have that $\tilde{\phi}(r) \geqslant 0$ and

$$\tilde{\tau}(\beta, b) = [\exp(-\beta b)]\tau(\beta) = -\int_0^\infty \{\exp[-\beta\tilde{\phi}(r)]\} r^3 \, d\tilde{\phi}(r) \tag{3}$$

In Ref. 2, $\tau(\beta)$ was reduced to the Laplace transform of a possibly unbounded and discontinuous function. In the present note we extend the work of Ref. 2 in that we show that $\tilde{\tau}(\beta, b)$ can be written as the Laplace–Stieltjes integral with a measure $\mu(s)$ of bounded variation on R^+. Some of the properties of the Laplace–Stieltjes integrals enable one to determine $\mu(s)$ at its points of continuity from the knowledge of $\tilde{\tau}(\beta, b)$ at a carefully chosen discrete set of points on the positive β line. This set turns out to be included in an arbitrarily small neighborhood of zero temperature. Further we show that $\mu(s)$ determines $\phi(s)$ uniquely with milder restrictions on the potential than those imposed in Refs. 1 and 2.

2. REDUCTION OF $\tilde{\tau}(\beta, b)$ TO A LAPLACE–STIELTJES INTEGRAL

Theorem 1. Let $\phi(r)$ be continuous and $\phi(+0) > \phi(r) \geqslant -b$ for each r in R^+. Also let $\phi(r)$ have a finite number of points of increase (decrease) in any finite right neighborhood of zero. Then $\tilde{\tau}(\beta, b)$ is given by

$$\tilde{\tau}(\beta, b) = -\int_0^b e^{-\lambda s} \, d\mu_1(s) + \int_b^\infty e^{-\lambda s} \, d\mu_2(s) \tag{4}$$

where $\lambda = \beta - \alpha$, $\alpha > 0$, and $\mu_1(s)$ and $\mu_2(s)$ are bounded, nondecreasing functions of s on their respective domains.

Proof. At first we assume that $\tilde{\phi}(r)$ is made of a finite number of semimonotonic pieces. Let $0 = r_0 < r_1 < \cdots r_{2n+2} = \infty$, where $\tilde{\phi}(r)$ is decreasing on (r_{2j}, r_{2j+1}) and nondecreasing on (r_{2j+1}, r_{2j+2}), $j = 0, 1, 2, \ldots, n$. From (3), $\tilde{\tau}(\beta, b)$ is given by

$$\begin{aligned}\tilde{\tau}(\beta, b) &= -\sum_{j=0}^{n} \left(\int_{r_{2j}}^{r_{2j+1}} \{\exp[-\beta\tilde{\phi}(r)]\} r^3 \, d\tilde{\phi}(r) \right. \\ &\qquad \left. + \int_{r_{2j+1}}^{r_{2j+2}} \{\exp[-\beta\tilde{\phi}(r)]\} r^3 \, d\tilde{\phi}(r) \right) \\ &= \sum_{j=0}^{n} \left[\int_{s_{2j+1}}^{s_{2j}} e^{-\beta s} F_{2j}(s) \, ds - \int_{s_{2j+1}}^{s_{2j+2}} e^{-\beta s} F_{2j+1}(s) \, ds \right]\end{aligned}$$

where $s_k = \tilde{\phi}(r_k)$, $F_k(s) = [\tilde{\phi}_k^{-1}(s)]^3$, $k = 1$ to $2n + 2$; $\tilde{\phi}_{2j}(r) = \tilde{\phi}(r)$, $r \in (r_{2j}, r_{2j+1})$ and $j = 0$ to n; $\tilde{\phi}_{2j+1}(r) = \tilde{\phi}(r)$ for $r \in I_{2j+1} \subseteq (r_{2j+1}, r_{2j+2})$ where $\tilde{\phi}(r)$ is increasing on I_{2j+1} and $j = 0$ to $n - 1$. The change in variable can be justified; e.g., by Theorem II.a. of Ref. 4.

Let $\{\xi_j\}$ be the subsequence of $\{s_j\}$ defined by

$$0 \leqslant \xi_0 \leqslant \xi_1 \leqslant \cdots \leqslant \xi_m = b = \xi_{m+1} \leqslant \cdots \leqslant \xi_{2n+2} = \phi(0)$$

where m is the number of turning points of ϕ in $[0, b)$. $\tilde{\tau}(\beta, b)$ can now be written as

$$\tilde{\tau}(\beta, b) = \sum_{k=0}^{m-1} \int_{\xi_k}^{\xi_{k+1}} e^{-\beta s} \psi_k^1(s)\, ds + \sum_{k=m+1}^{2n+1} \int_{\xi_k}^{\xi_{k+1}} e^{-\beta s} \psi_k^2(s)\, ds \tag{5}$$

where

$$\psi_k^1(s) = \sum_{i+1}^{n_k} [F_{2k_i}(s) - F_{2k_i+1}(s)] \tag{6a}$$

and

$$\begin{aligned}\psi_k^2(s) &= \sum_{i=1}^{n_k+1} F_{2k_i}(s) - \sum_{i=1}^{n_k} F_{2k_i+1}(s)\\ &= F_{2k_1}(s) + \sum_{i=1}^{n_k} [F_{2k_{i+1}}(s) - F_{2k_i+1}(s)]\end{aligned} \tag{6b}$$

where n_k is the number of increasing pieces of $\phi(r)$ in (ξ_k, ξ_{k+1}). Since $F_{2k_i}(s) < F_{2k_i+1}(s)$ and $F_{2k_{i+1}}(s) > F_{2k_i+1}(s)$ for each (k, i), from (6a) and (6b), it follows that $\psi_k^1(s) \leqslant 0$ and $\psi_k^2(s) \geqslant 0$ for each k.

Now, for an s in $(\xi_k, \xi_{k+1}) \subseteq (0, b)$, let $\mu_1^k(s) = -\int_{\xi_k}^s e^{-\alpha t} \psi_k^1(t)\, dt$ and for an s in $(\xi_k, \xi_{k+1}) \subseteq (b, \infty)$, let $\mu_2^k(s) = \int_{\xi_k}^s e^{-\alpha t} \psi_k^2(t)\, dt$ for some $\alpha > 0$. It follows that $\mu_1^k(s)$ and $\mu_2^k(s)$ are nondecreasing functions of s on their respective domains. They are also bounded since each term on the right side of (5) exists for each $\beta > 0$. From (5) one has that

$$\tilde{\tau}(\beta, b) = -\sum_{k=0}^{m-1} \int_{\xi_k}^{\xi_{k+1}} e^{-\lambda s}\, d\mu_1^k(s) + \sum_{k=m+1}^{2n+1} \int_{\xi_k}^{\xi_{k+1}} e^{-\lambda s}\, d\mu_2^k(s) \tag{7}$$

where $\lambda = \beta - \alpha$. Define further

$$\mu_1(s) = \sum_{k=0}^{l-1} [\mu_1^k(\xi_{k+1}) - \mu_1^k(\xi_k)] + \mu_1^l(s), \qquad s \in (\xi_l, \xi_{l+1}) \subseteq (0, b)$$

and

$$\mu_2(s) = \sum_{k=2n_b-1}^{l} [\mu_2^k(\xi_{k+1}) - \mu_2^k(\xi_k)] + \mu_2^l(s), \qquad s \in (\xi_l, \xi_{l+1}) \subseteq (b, \infty)$$

Since $\{\xi_k\}$ is included in a set of measure zero, $[\mu_i(\xi_k + 0) - \mu_i(\xi_k)] = 0$ for $i = 1$ or 2, and each k. Hence $\mu_1(s)$ and $\mu_2(s)$ are nondecreasing, bounded functions of s defined everywhere on $[0, b)$ and $[b, \infty)$, respectively. At the end points 0 and b they are defined by right continuity. Also $\mu_1(0) = \mu_2(b) = 0$. It is now obvious that the right side of (7) can be summed to yield the right side of (4).

Finally, the restriction of n being finite can be removed by observing that $d\tilde{\phi}(r)$ changes its sign only a finite number of times for r in $[0, R]$, $R < \infty$. Let

$$\tilde{\tau}_i(\beta, b) = -\int_0^{R_i} \{\exp[-\beta\tilde{\phi}(r)]\} r^3 \, d\tilde{\phi}(r), \qquad i = 1,2,..., \quad R_1 < R_2 < \cdots$$

where R_i are chosen such that the choice of the limits of summation in (5) is legitimate. For sufficiently large R_1, one has that $|\tilde{\tau}_i(\beta, b) - \tilde{\tau}(\beta, b)| < \varepsilon/2$ for any $\varepsilon > 0$ and each i. Hence $|\tilde{\tau}_i(\beta, b) - \tilde{\tau}_j(\beta, b)| < \varepsilon$. Consequently, $\{\tilde{\tau}_i(\beta, b)\}$ is a Cauchy sequence, and each of $\tilde{\tau}_i(\beta, b)$ can be written as the right side of (7). QED

The restriction $\phi(+0) > \phi(r)$ is unnecessary for the results which follow. If $\phi(+0) \leqslant \phi(r)$ for some r, the second integral on the right side of (4) can be written as a difference of two integrals:

$$\int_b^\infty e^{-\lambda s} \, d\mu_2(s) \rightarrow \int_b^c e^{-\lambda s} \, d\mu_2(s) - \int_c^\infty e^{-\lambda s} \, d\mu_3(s)$$

where $\mu_3(s)$ is also bounded and nondecreasing on $[c, \infty)$ and the following results can be seen to be true with slight modifications in the proofs.

Corollary 1. $\tilde{\tau}(\beta, b) = \int_0^\infty e^{-\lambda s} \, d\tilde{\mu}(s)$, $b \geqslant 0$, where $\tilde{\mu}(s)$ is of bounded variation.

Proof. Define $\tilde{\mu}(s) = -\mu_1(s)$ for s in $[0, b)$ and $\tilde{\mu}(s) = -\mu_1(b - 0) + \mu_2(s)$ for s in $[b, \infty)$. $\tilde{\mu}(s)$ is of bounded variation and the right side of (4) can be summed to yield the desired result. QED

Since $\tilde{\mu}(s)$ is decreasing only when s is in $[0, b)$, for positive potentials one has a stronger result:

Corollary 2. $\tilde{\tau}(\beta, 0) = \int_0^\infty e^{-\lambda s} \, d\mu(s)$, where $\mu(s)$ is bounded and nondecreasing.

Proof. The result follows by setting $b = 0$ in (4) and $\mu(s) = \mu_2(s)$ for each s. QED

3. DETERMINATION OF $\phi(r)$

Knowledge of $\tilde{\tau}(\lambda, b)$ for each $\lambda > 0$ enables one to determine $\tilde{\mu}(s)$ uniquely at all points of its continuity; i.e., on $\bigcup_{k=0}^{\infty} (\xi_k, \xi_{k+1})$. However, much less information is sufficient to determine $\tilde{\mu}(s)$.[2] Probably the strongest and, from the practical point of view, the most useful result can be stated as follows:

Lemma 1. Let $\phi(r)$ be as in Theorem 1. Then $\tilde{\tau}(\lambda_i, b)$, $i = 0, 1, 2,...$, where $\{\lambda_i\}$ is an unbounded, increasing sequence such that $\lambda_0 = 0$ and $\sum_{i=1}^{\infty} (1/\lambda_i) = \infty$, determines $\tilde{\mu}(s)$ uniquely on $\bigcup_{k=0}^{\infty} (\xi_k, \xi_{k+1})$.

Proof. From Theorem 1, $\tilde{\tau}(\beta, b)$ is a Laplace–Stieltjes integral with measure $\tilde{\mu}(s)$ being of bounded variation. Hence,[3] $\tilde{\tau}(\lambda_i, b)$, $i = 0, 1, 2,...$, determine $\tilde{\mu}(s)$ uniquely at all of its points of continuity; i.e., on $\bigcup_{k=0}^{\infty} (\xi_k, \xi_{k+1})$. QED

Let $\lambda_i = (1/kT_i) - \alpha$, or $T_i = 1/k(\alpha + \lambda_i)$, for an arbitrary $\alpha > 0$. $\{T_i\}$ is obviously a discrete set in $[0, 1/k\alpha]$. Thus the knowledge of the second virial coefficient at a discrete set of points, consistent with the hypothesis of Lemma 1, in an arbitrarily small right neighborhood of $T = 0$ determines $\tilde{\mu}(s)$ uniquely. Some of the inversion formulas approximate $\tilde{\mu}(s)$ by a series of step functions and hence $d\tilde{\mu}(s)/ds$ by a series of delta functions.[4] As we shall see, knowledge of $d\tilde{\mu}(s)/ds$ is necessary in determining $\phi(r)$. Hence, such formulas are not suitable for determining $\phi(r)$. However, there are formulas available which enable one to approximate $\tilde{\mu}(s)$ by a continuously differentiable sequence.[(6)] In the following we assume that $\rho(s) = d\tilde{\mu}(s)/ds$ has been determined by some such inversion formula on $\bigcup_{k=0}^{\infty} (\xi_k, \xi_{k+1})$, which also determines ξ_k, $k = 0, 1, 2,....$

Theorem 2. Let $\phi(r)$ be as in Theorem 1 and have a unique continuous inverse on $(\alpha_1, \alpha_2) \subseteq R^+$. Then $\{\tilde{\tau}(\lambda_i, b)\}$, as defined in Lemma 1, determines $\phi(r)$ uniquely on (α_1, α_2).

Proof. Under the hypothesis of the theorem, $\rho(s) = e^{-\alpha s} F_{2k}(s)$ with some k on some interval (β_1, β_2). From Lemma 1, $\rho(s)$ is uniquely determined, since it is continuous, on (β_1, β_2) by $\{\tilde{\tau}(\lambda_i, b)\}$. The $F_{2k}(s)$ is given by $F_{2k}(s) = e^{\alpha s}\rho(s)$. Let $f_{2k}(s) \equiv [f_{2k}(s)]^{1/3}$ (real value). $\phi(r)$ is given by $\phi(r) = f_{2k}^{-1}(s)$, s in (β_1, β_2), on $(f_{2k}^{-1}(\beta_1), f_{2k}^{-1}(\beta_2)) = (\alpha_1, \alpha_2)$. QED

From Theorem 2 follow the following useful corollaries.

[2] See, e.g., Ref. 4, Chapters VII and VIII, for various inversion formulas involving some other information on $\tilde{\tau}(\lambda, b)$ than $\tilde{\tau}(\lambda, b)$ itself.

[3] See, e.g., Ref. 4, pp. 100–105; Ref. 5, Vol. II, pp. 513–517.

[4] It should be mentioned here that $\tilde{\mu}(s)$ is differentiable on $\bigcup_{k=0}^{\infty} (\xi_k, \xi_{k+1})$.

Corollary 3. Let $\phi(r)$ be as in Theorem 1 and analytic in some neighborhood of $I \subseteq R^+$. Also let it have a single-valued, continuous inverse on some interval $(\alpha_1, \alpha_2) \subset I$. Then $\{\tilde{\tau}(\lambda_i, b)\}$ determines $\phi(r)$ uniquely on I.

Proof. From Theorem 2, $\{\tilde{\tau}(\lambda_i, b)\}$ determines $\phi(r)$ uniquely on (α_1, α_2). On I it is obtained by analytic continuation. QED

The result of Corollary 3 is clearly valid if $I = \bigcup_{i=1}^n I_i$, $I_i \subset R^+$, and the set $\bigcap_{i=1}^n I_i$ is of measure zero and I_i, for each i, contains an interval on which $\phi(r)$ has a single-valued, continuous inverse. On a set of measure zero, $\phi(r)$ is determined by continuity. The following corollary extends this result to the case when $\bigcap_{i=1}^n I_i$ is of nonzero measure. It suffices to consider the case of two intervals I_1, I_2.

Corollary 4. Let $\phi(r)$ be as in Theorem 1 and analytic in some neighborhoods of I_1 and I_2, have single-valued, continuous inverses on at least one interval in each one of I_i, $i = 1, 2$, and on the complement I_c of $I_1 \cup I_2$ in I. Then $\phi(r)$ is uniquely determined by $\{\tilde{\tau}(\lambda_i, b)\}$ on I.

Proof. From Corollary 3 it follows that $\phi(r)$ is uniquely determined by $\{\tilde{\tau}(\lambda_i, b)\}$ on I_1 and I_2. From Theorem 2 it is also uniquely determined on I_c. And since it is continuous on I, $\phi(r)$ is uniquely determined on I. QED

4. DISCUSSION

We require knowledge of $\{\tilde{\tau}(\lambda_i, b)\}$ to determine $\phi(r)$ uniquely. However, $\{\tilde{\tau}(\lambda_i, b)\}$ can be easily obtained from the second virial coefficient $B(T_i)$. Further, the inversion formulas involved yield an approximating sequence to $\rho(s)$, rather than $\rho(s)$ itself. It is clear from the analysis of Section 3 that this enables one to construct an approximating sequence tc $\phi(r)$. There is a fair amount of flexibility that can be exercised in choosing the set $\{\lambda_i\}$. The results of this paper are particularly useful for practical purposes, for experimentally, one only measures $B(T)$ at a finite number of temperature points. This knowledge can be used to construct an approximate $\rho(r)$ in a particular class directly, or one can compute theoretical values of $B(T)$ using a model potential and compare them with the experimental values.

We have avoided unnecessary generalizations to include pathological potentials. The class to which $\phi(r)$ is assumed to belong is sufficiently large to include most of the model potentials normally considered in physics and chemistry.

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